Diverse monogenetic volcanism across the main arc of the central Andes, northern Chile.

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University of Iowa

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DIVERSE MONOGENETIC VOLCANISM ACROSS THE MAIN ARC OF THE CENTRAL ANDES, NORTHERN CHILE.

by

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Geoscience in the Graduate College of The University of Iowa

May 2017

Thesis Supervisor:  Professor Ingrid A. Ukstins Peate
This is to certify that the Ph.D. thesis of

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the thesis requirement for the Doctor of Philosophy degree
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To my Dad, who introduced me to the beauty of the natural world.
To my Mom, who believed I could do anything.
And to ‘Grammy’ Edelman, who taught me to always hold on to a sense of wonder.
“Go climb a volcano.”

- Lassen Volcanic National Park
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Abstract

Instances of fault-controlled monogenetic volcanism across the subduction arc of the Central Andes at ~ 23°S illuminate the nature of different parental melts being delivered to the crust. Evidence of magmatic history is preserved in bulk rock geochemistry, the content of melt inclusions, and mineral compositions. Volcanism in this region is dominated by felsic and intermediates lavas as the thickened crust (55 – 65 km) and vast volumes (> 500,000 km³) of mid-crustal magma beneath the Altiplano-Puna high plateau region prevent mafic magmas from reaching the surface (Davidson & De Silva, 1991; Beck et al., 1996; Perkins et al., 2016). However, small volumes of relatively undifferentiated lava have been delivered from the lower crust to the surface along zones of crustal weakness without extensive processing by crustal assimilation and/or extended storage in sub-volcanic magma chambers. Monogenetic eruptions of less-differentiated lava provide important constraints on compositions normally obscured by crustal processing in the Central Andes.

Basaltic andesite sampled within the frontal arc (Cerro Overo maar) is a regional mafic end-member and approximates the composition of parental arc magmas derived from partially-molten lower crustal regions where mantle-derived magmas interact with the surrounding lithosphere and undergo density differentiation (MASH zones). Basaltic olivine-hosted melt inclusions from Cerro Overo provide a glimpse of less-evolved melt composition from this region and suggest mobilization of MASH magma by injection of basaltic melt. Basaltic andesite sampled from the eastern (back) margin of the frontal arc (Puntas Negras – El Laco) is another regional mafic endmember, representing a mantle-derived magma composition that is transitional between subduction arc magmatism and intraplate magmatism of the back-arc. The internal crystal architecture revealed by major and trace element zoning of olivine phenocrysts indicates Cerro Overo magma experienced continuous ascent, while Puntas Negras magma
experienced a brief period of stalling or storage near the brittle-ductile transition zone (~ 25 km). Aphyric intermediate monogenetic lavas sampled west of (before) the frontal arc display Adakite-like signatures (e.g. high Sr/Y and Sm/Yb) represent small amounts of melt generated with a significant contribution from direct melting of the metabasaltic slab or delaminated lithospheric root at high pressure. These three magmatic regimes sampled at monogenetic centers approximate different end-member compositions being delivered to the lower crust of the Central Andes from which the range of intermediate main arc volcanism in the Altiplano-Puna region is ultimately derived.
This work presents several small-volume eruptions of lava which provide new constraints on different compositions of mantle-derived magmas delivered to the base of the crust of the Andes. Melting is generated deep in the mantle beneath northern Chile as the tectonic Nazca plate beneath the Pacific Ocean sinks beneath the west coast of the South American continent. As this melt propagates upwards, it forms magmas of a wide range of compositions as separate batches experience variable amounts of crystallization, assimilation of surrounding rock, mixing with other magma(s), density fractionation, and/or prolonged storage in the crust of the Earth. The style and magnitude of volcanic eruptions at the surface is highly dependent on the composition(s) of the magma which are erupted as lava or ash. The thick (> 55 km) and complex lithosphere beneath the Andes of the Altiplano and Puna plateaus of northern Chile exerts a heavy influence on ascending mantle-derived magmas. Volcanism in the region dominantly erupts lava with compositions reflecting lithospheric alteration processes. The monogenetic (single eruption) volcanos presented in this study represent instances where fault systems reaching to the base of the crust have delivered magma to the surface with relatively minimal degrees of alteration since their genesis in the mantle. The origins of these volcanoes include melting of the mantle under the influence of fluids derived from the subducted Nazca plate, decompression melting of the mantle as it upwelled to fill space created at the base of the lithosphere by foundering of dense material, and melts derived directly from the lithospheric material sinking into the mantle.
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Preface

This work addresses several different minor eruptions of distinct lavas within the modern volcanic arc front of the central Andes (i.e., the ‘Spine of the Andes’). Fieldwork for this project in 2014 targeted minor volcanic centers of variable morphology, age, and composition identified as unique features by a combination of satellite imagery and a handful of suggestive publications (Google Earth, 2014; Zeil, 1964; Gardeweg & Ramirez, 1982; De Silva, 1989a; De Silva & Francis, 1991; Marrett & Emerman, 1992; González-Ferrán, 1995; Gonzalez et al., 2009; Uktins-Peate, pers. comm., 2012). The studied lavas are summarized here. Cerro Overo maar is a phreatomagmatic, Quaternary monogenetic eruption of olivine-phyric basaltic-andesite along an anticline within the modern arc. This lava represents the most mafic arc composition known in the Altiplano-Puna volcanic region (21 – 24°S; De Silva & Francis, 1991). La Albóndiga Grande is a dome of olivine-phyric basalt andesite located a few kilometers from Cerro Overo maar. The maar and dome are compositionally indistinguishable and thus assumed to be cogenetic. The Puntas Negras-El Laco lava flow, a small volume of young (< 1 Ma) olivine-clinopyroxene-bearing basaltic-andesite near the Chile-Argentina border, was erupted along a major regional lineament and represents a transitional lava between the arc front and back-arc, intraplate magmatism. El País lava flow is an erosional remnant of a pyroxene-rich andesitic flow, potentially from the Pliocene, which represents a transitional composition between the mafic rocks of Cerro Overo and intermediate rocks of the arc stratovolcanoes. The aphyric andesites of the Tilocálar Group are found west of the arc along compressive structural features (thrust faults and antiforms) at the southeast margin of the Salar de Atacama. The Tilocálar Group is composed of the Tilocálar Norte and Tilocálar Sur minor volcanoes and Cerro Tujle maar, all of which display distinct adakite-like geochemical signatures, suggesting these lavas were derived from small melt fractions of metabasaltic material at high pressure during the Mid-to Late-Pleistocene. In all, this survey of minor volcanism of the Andean Central Volcanic Zone (CVZ) arc describes lava compositions representing at least three distinct magmatic origins, contributing to our understanding of the Andean arc as a complex and diverse system.
Introduction

The Andean Central Volcanic Zone

The Andean Central Volcanic Zone (CVZ), or Central Andes, spans 14-28°S (Figure 1), and is home to 44 active stratovolcanoes and cones, over 18 minor centers and fields, and at least 6 potentially active major silicic centers (Stern, 2004). The oceanic Nazca plate (< 60 Ma) is being subducted beneath this segment of the Andes with a dip of 25-30° at a rate of 7-9 cm/yr to a depth ≥ 400 km (Chen et al., 2001). The northern end of the Central Volcanic Zone is bound by subduction of the Nazca Ridge at around 14°S. At the southern border of the CVZ, the slab shallows without breaking as the Andes transitions into the non-volcanic Pampean flat-slab region (Stern, 2004; Moreno & Gibbons, 2007). The boundary between the subducting Nazca Plate and South America is delineated by the Peru-Chile Trench (also known as the Atacama Trench in northern Chile). Volcanism in the Central Andes manifests inland 240-300 km east of the trench and some 120 km above the subducted slab and is dominated by intermediate arc andesites and felsic crust-derived ignimbrites (Figure 1) (Stern, 2004). The modern volcanic arc (the “spine of the Andes”) passes through Peru, Chile, Bolivia, and Argentina nearly continuously with a gap in active volcanism from 19-21°S. A double-thickened crust (50 – 80 km) underlies the subduction arc, and lava compositions reflect extensive interaction with the lithospheric mantle and continental crust due to deep stagnation, extensive differentiation in magma storage zones, and/or assimilation of crustal material (Figure 1) (Hildreth & Moorbath, 1988; Davidson et al., 1991; De Silva & Francis, 1991; Stern, 2004; Hora et al., 2007). For these reasons, mafic magmatism is rare in the central Andes and the nature of parental melts poorly constrained (De Silva & Francis, 1991; Davidson et al., 1991; Stern, 2004).

Regional transverse lineaments cut the crust at a NW-SE orientation, exerting a control on the locations of surface volcanism, including minor centers (Coira & Mahlburg Kay, 1993; Coira et al., 1993; Kay et al., 1994; Matteini et al., 2002; Norini et al., 2013). A distinct eastward bend in the arc away from the trench around the Salar de Atacama basin at 22-24° S is associated with a number of contractional structural features, which have also provided magmatic pathways for instances of minor volcanism (Reutter et al., 2006; Gonzalez et al., 2009) (Figure 2). Mafic lavas erupted along these structural features provide opportunities to study the nature of CVZ.
magnas before they experience the extensive processing common to the region. The large-scale transverse lineaments have been theorized to cut to the base of the crust or lithosphere (e.g. Matteini et al., 2002; Norini et al., 2013) and therefore have the potential to channel magma straight from the lower crust or lithospheric mantle to the surface. Thrust-faults only cut the brittle upper crust, with a potential to deliver magnas from the depth of the brittle-ductile transition (~ 15 – 20 km) (Zandt et al., 2003) or shallower.

The middle latitudes (21-24° S) of the CVZ host the Altiplano-Puna Volcanic Complex (APVC), a major silicic volcanic province defined by massive deposits of Miocene age ignimbrite volcanism (De Silva, 1989a). This volcanic and geomorphic region spans over 50,000 km² at the intersection between the Bolivian Altiplano and the Argentinian Puna high plateaus in the “spur” of northern Chile (Figure 3). Massive nested caldera complexes (e.g. La Pacana, Pastos Grandes, Vilama, and Guacha Caldera, all erupted with a VEI > 8) erupted approximately 70,000 km² of ignimbrite in pulses from ~10.4 to 2.9 Ma (e.g. Figure 4) (Gardeweg & Ramírez, 1987; deSilva, 1989a; Salisbury et al., 2011). The silicic magma supply originated by large-scale melting of the mid-crust due to compressive shortening and continual injections of mafic melt as the subduction angle steepened (Coira et al., 1993; Stern, 2004). A remnant of this ignimbrite era remains in the form of the Altiplano-Puna Magma Body, a massive (~500,000 km³) sill-like body at the rheological boundary between ductile lower crust and extended brittle upper crust (~ 20 km depth) (Figure 2) (Chmielowski et al., 1999; Zandt et al., 2003). Modeled as a partially molten, dacitic crystal mush, the Altiplano-Puna Magma Body has acted as a density filter for denser (i.e. more mafic than dacitic) magma since at least the mid Miocene (Zandt et al., 2003; Del Potro et al., 2013). The continued existence of crustal magma storage is also evident in uplift and geothermal activity in and around the Altiplano-Puna caldera complexes (De Silva, 1989a).

The central Andean region is also marked by major (100s of km) subparallel structural lineaments, which cut the crust and control the surface expression of volcanism (Figure 5) (Davidson & De Silva, 1992; Matteini et al., 2002; Norini et al., 2013). These include the Tupiza Lineament in Bolivia, which passes through the frontal arc at 19° S, and the Chile/Argentina Calama-Olcapato-El Toro and Archibarca transcurrent fault systems which pass through the arc at 23° S and 25° S, respectively (Davidson & De Silva, 1992; McLeod, 2012). The Calama-Olcapato-El Toro (COT) system passes through the Altiplano-Puna Volcanic Complex just north
of the Salar de Atacama (Figure 5). Around 23.5° S, 67.6° W, the COT lineament intersects compressive structural features related to the Salar de Atacama (Figure 5). East of the frontal arc, compositions of lava erupted along this lineament show evidence for variable contributions from dehydration-induced calc-alkaline subduction magmatism, silicic (ignimbritic) mid- to upper-crustal material, lower-crustal magma formed from asthenospheric upwelling mixed with material from the underthrust Brazilian shield, and behind-the-arc high-K (shoshonitic) basaltic melt related to episodes of delamination of the lithosphere and lowermost crust (Matteini et al., 2002; Kay et al., 2012). However, a general absence of lavas with primitive compositions, due to the thick crust and mid-crustal melt bodies, has made it difficult to identify the distinct contributions from different magmatic sources and their role in producing the observed geochemical variability within Andean volcanism (e.g. Davidson et al., 1991; Matteini et al., 2002).

The most mafic lavas currently recognized in the Altiplano-Puna region are the olivine-phyric basaltic andesites erupted at Cerro Overo maar (23.518 S, 67.662 W) and a lava flow in the Puntas Negras volcanic complex (23.743 S, 67.476 W), near Salar El Laco (Figure 6) (De Silva; 1989a; this study). Both volcanic centers are young (Pliocene or later), located along the Calama-Olacapato-Del Toro lineament, and geochemically affiliated with modern frontal arc volcanics (Figure 6). Cerro Overo maar is fully derived from an arc magma tapped by deep faulting, and the Puntas Negras-El Laco lava flow to the southeast appears to represent a transitional lava dominantly sourced from the arc but with an intraplate contribution (i.e. decompression-induced melting). Mafic volcanism found in the back-arc of the CVZ was produced by lithospheric delamination and has origins in intraplate melting and not production from the fluid-flux melting which has produced magmas of the main arc (Figure 5) (Kay et al., 1994). Structurally controlled minor volcanic centers such as Cerro Overo and Puntas Negras-El Laco, emplaced outside the current borders of the Altiplano-Puna Magma Body, provide a “view” around the thick crust of the central Andes and into the generation of primitive magma above the subducting Nazca slab. West of the frontal arc, at the southeastern margin of the Salar de Atacama, Tilocálar Norte, Tilocálar Sur, and the Cerro Tujle maar are eruptions of less-evolved, nearly aphyric andesite controlled by fold-and-thrust features (Figure 6). These minor volcanic centers have produced lavas with heavily fractionated rare earth elements and other compositional features suggesting they are at least partially derived from melting in the lower
crust. These young minor centers are west of the active arc, but still provide a view into magmatic activity at depth.

**Geologic History of the Central Andes**

Orogenic processes have been building the Andes, the longest continental mountain chain in the world, along the western margin of South America since at least the early Jurassic. Currently, subduction of the Nazca and Antarctic plates beneath South America manifests as four “volcanic zones” where subduction is steep (> 25°), the Northern (NVZ; 6° N – 3° S), Central (CVZ; 14° – 28° S), Southern (SVZ; 33° – 46° S), and Austral volcanic zones (AVZ; 49° – 55° S), and as non-volcanic “flat slab” regions where subduction is shallower (< 10°) (Stern, 2004) (Figure 1). Spread across these four volcanic segments are over 200 potentially active quaternary volcanoes, at least twelve massive silicic caldera systems, and innumerable minor centers (De Silva & Francis, 1991; Stern, 2004). The Andes are notable not only for their extent and vigorous volcanic activity, but also for regions of thickened crust (up to > 80 km) in the Central Volcanic Zone, also host to some of the most arid terrain on the planet (deSilva & Francis, 1991; McGlashan et al., 2008). Volcanism in the Andes is dominantly intermediate (thus “andesite”) with subordinate felsic and mafic components. Throughout the arc, subduction-generated magma broadly experiences differentiation of magmas in the lower crust by melting, assimilation, storage and homogenization (MASH processes), shallow crustal ponding of differentiated magmas, and mafic recharge leading to subsequent eruption (Stern, 2004; Reubi & Blundy, 2009).

The majority of Andean orogenesis is generally accepted as post-dating the opening of the Atlantic Ocean during the Mesozoic (e.g. Stern, 2004). Subduction-related magmatism initiated by 185 Ma at the latest, and the arc front has migrated eastward since the Jurassic due to long-lived subduction (Scheuber et al., 1994; Stern, 2004). The Andean basement mainly consists of Paleoproterozoic to early Mesozoic crystalline metamorphic terranes accreted to the western edge of the Brazilian craton starting from the late Paleozoic (Stern, 2004, and references therein). Basement exposure is poor, if at all present, and the exact nature and affinity of basement rocks beneath the modern arc is rarely well-constrained (e.g. McLeod et al., 2013). Isotopic domains of post-Miocene (Cenozoic) volcanism reflect the nature of basement terranes, indicating ongoing interaction between the sub-Andean terranes and contemporary
magmatism (Wörner et al., 1992; Aitcheson et al., 1995; Mamani et al., 2008, 2010). This interaction is also evident in rare basement xenoliths erupted with lava (McLeod, 2012).

The contemporary Central Volcanic Zone consists of a basement of Paleozoic metamorphic and igneous rocks overlain by calcalkaline volcanics of various ages and compositions. The Nazca plate currently subducts beneath the central Andes bearing east-northeast (79° ± 4) at a rate of 61 ± 3 mm per year (Isacks et al., 1982; Delacour et al., 2007). Subduction evolution, dominantly steepening and shallowing of the subducting slab, has caused the location of frontal arc and the arc-trench distance to vary over time (Moreno & Gibbons, 2007). In the Central Andes, the modern frontal arc is located eastward of and parallel to the paleoarc Cordillera Domeyko in Chile. Ignimbrite volcanism derived from crustal melting in the northern Puna plateau (~23° S) migrated westward during the late Miocene as the subducting slab steepened, from the eastern 6.7 Ma Coranzuli to the ~4.0 Ma Atana ignimbrite (Coira et al., 1993; Kay et al., 1999).

Volcanism on the Puna plateau of the Central Andes began in the late Oligocene and became widespread during the Miocene (~10 Ma), at which time spreading ceased along the Farallon-Nazca Ridge and initiated at the East Pacific ridge (de Silva, 1989; Matteini et al., 2002) (Figure 1). Compressional tectonics during this time, known as the Quechua deformational phase, caused extensive eastward thrusting and thickening of the crust in the Central Andes (Isacks, 1988; Matteini et al., 2002). Structural transcurrent fault lineaments cutting the crust show tectonic activity dating back to at least the Cretaceous, and activity is thought to have been particularly high ~10 Ma, during the Quechua phase (Allmendinger et al., 1983) (Figure 5). More recent arc and back-arc volcanism manifests along these lineaments, with stratovolcanoes and minor centers following the NW-SE trend of the faulting (Davidson & De Silva, 1992; Kay et al., 1994; Matteini et al., 2002; Norini et al., 2013). The pathways defined by these regional lineaments, along with localized extensional tectonics facilitates rapid transport of magma along faults with minimized crustal contamination (Matteini et al., 2002). The olivine-phyric basaltic andesite erupted at Cerro Overo maar represents subduction origin magma channeled from the MASH zone at the base of the crust to the surface without significant amounts of subsequent processing. The basaltic andesite Puntas Negras-El Laco lava flow is along situated along the COT lineament and represents a combination of fluid-flux subduction
zone and intraplate melting similarly directed to the surface without substantial assimilation of crust or magmatic differentiation in shallow magma storage zones.
### Table 1 - Summary of Neogene magmatism in the Central Andean Volcanic Zone.

<table>
<thead>
<tr>
<th>Setting</th>
<th>Time Period</th>
<th>Magmatic Petrogenesis</th>
<th>Volcanism</th>
<th>Geochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Frontal Arc (Western Cordillera)</strong></td>
<td>Miocene – Recent</td>
<td>Calc-alkaline subduction magmatism derived from asthenospheric melting due to dehydration of the downgoing Nazca plate.</td>
<td>Stratovolcanoes and monogenetic centers</td>
<td>Intermediate calc-alkaline subduction magmatism</td>
</tr>
<tr>
<td><strong>Trans-arc, along NW-SE trending lineaments</strong></td>
<td>Miocene – Recent</td>
<td>Variable mixing of lower-crustal magma formed from asthenospheric upwelling*, fluid-fluxed subduction related melt, &amp; melts from the underthrust Brazilian Shield (Matteini et al., 2002) *(± dehydration due to amphibolite-eclogite transition)</td>
<td>Stratovolcanoes, domes, and monogenetic centers</td>
<td>Transitional from arc-like compositions to intraplate and/or crustal magmatism (Matteini et al., 2002)</td>
</tr>
<tr>
<td><strong>Back-arc</strong></td>
<td>Mainly Pliocene – Quaternary (Davidson &amp; De Silva, 1992; Kay et al., 1994)</td>
<td>Delamination and/or convective removal of the lithosphere and lowermost crust, leading to upwelling of asthenospheric material. Melting caused by decompression and increased heat flux (Kay et al., 1994) Intraplate – high degree of partial melt over thin lithosphere CA – intermediate lithosphere, medium degree of melting; at the boundaries of seismic gap Shoshonitic – thick crust, small degree of melt.</td>
<td>Monogenetic fields in southern Bolivia at the northeast margin of the Puna (Davidson &amp; De Silva, 1992; Hoke &amp; Lamb, 2007) and at the eastern extent of the southern Puna in northwest Argentina (24° to 27° S) (Kay et al., 1994).</td>
<td>Back-arc calcalkaline (high-K with La/Ta &gt; 25), intraplate (high-K with La/Ta &lt; 25), and Shoshonitic (very high-K basalts) (Kay et al., 1994; Risse et al., 2013)</td>
</tr>
<tr>
<td><strong>Caldera</strong></td>
<td>Miocene</td>
<td>Ponded crustal melt (the Altiplano-Puna Magma Body) primed by mafic recharge, possibly a result of removal of the lithospheric root (De Silva et al., 2006; Kay &amp; Coira, 2009)</td>
<td>Nested caldera complexes producing ignimbrite sheets and domes.</td>
<td>Dacite - rhyolite</td>
</tr>
</tbody>
</table>
Volcanism in the Central Andes

The Central Andes is characterized by calcalkaline volcanics of various ages over a basement of mainly Paleozoic metamorphic and igneous rocks. Volcanism in the Central Andes since the Miocene consists of ignimbrite-producing caldera systems, effusive domes, cinder cone and flow complexes, monogenetic centers, and stratovolcanoes (Figure 2; Figure 5; Figure 7) (Gonzalez-Ferrán, 1995). The large stratovolcanoes are built on a base of 3000 – 4000 m above sea level and are the highest altitude active volcanoes in the world (Gonzalez-Ferrán, 1995). Volcanism has generally migrated eastward since the Jurassic due to long-lived subduction of the Nazca/Pacific plate beneath South America, and the paleoarc Cordillera Domeyko is still apparent in northern Chile (Scheuber et al., 1994). Stratovolcanoes are composed of dominantly andesitic lavas with minor pyroclastic deposits and may have dacitic to rhyolitic effusive domes or basaltic andesitic flank eruptions, as well (De Silva & Francis, 1991; Wörner et al., 1992; Mattioli et al., 2006; Moreno & Gibbons, 2007). Intraplate mafic – intermediate lava and high-K shoshonitic basalt have been erupted in the back-arc as a result of lithospheric delamination (Davidson & De Silva, 1992; Kay et al., 1994; Hoke & Lamb, 2007), but mafic rocks are rare within the arc, and the character of primary subduction magmatism is poorly understood (De Silva, 1989a; Davidson et al., 1991; De Silva & Francis, 1991; Stern, 2004; Quade et al., 2014). Less-evolved arc-related andesite and basalt are uncommonly erupted in small volumes at structurally-controlled complexes and monogenetic centers which provide valuable data on primitive composition(s) (De Silva, 1989a; this study). Conversely, highly silicic ignimbrite eruptions cover vast areas, sourced from the largest imaged magma reservoir on the planet, generated from roughly equal proportions of mantle and crustal melting, and erupted from massive, nested calderas (De Silva, 1989b; Coira et al., 1993; Salisbury et al., 2011; Ward et al., 2014).

The largest concentration of ignimbrites is located between 21-24°S, defining the Altiplano-Puna volcanic complex (DeSilva, 1989a). The massive, nested Miocene calderas (e.g. La Pacana is 60 x 30 km) which produced these eruptions are trench-parallel and located behind the main arc (Lindsay et al., 2001). The source of this silicic magmatism is extensive partial melting of the upper continental crust triggered by upwelling hot asthenosphere as the dip of the Nazca plate varied from shallow in the Early-Middle Miocene to steeper in the Late Miocene (Isacks, 1988; Coira et al., 1993). Melted crustal material has ponded extensively in the upper crust in the
form of a massive (∼500,000 km³) sill-like reservoir of partial melt at 10 – 20 km depth known
the Altiplano-Puna Magma Body (APMB) (Zandt et al., 2003; Ward et al., 2014; Perkins et al.,
2016). Delamination (or convective removal) of the lithospheric root centered beneath specific
calderas (i.e. Cerro Galan) may have also instigated widespread crustal melting via increased
magmatic flux to the crust (De Silva et al., 2006; Kay & Coira, 2009; Kay et al., 2012). Models of
removal of the lithospheric root and/or slab roll-back account for the dominant westward
migration of ignimbrite ages in the Altiplano-Puna region, but not the more erratic timing
further east along the Calama-Olacapato-El Toro Lineament, indicating an additional upper
crustal structural control (Matteini et al., 2002).

The crustal melt supply of the caldera systems in the Miocene persists today in the sill-like,
regionally pervasive Altiplano-Puna Magma Body at 10 – 20 km depth with the density of a
dacitic crustal mush (Zandt et al., 2003; Ward et al., 2014). Ward et al. have created 3-D seismic
images of the magma body based on joint inversion of Rayleigh-wave dispersion from ambient
seismic noise and P-wave receiver functions from broadband seismic stations in the region
(2014). Based on this data, the low-velocity zone appears to be an amalgamated plutonic
complex ~ 200 km in diameter and ~ 11 km thick, centered below the observed uplift at
Uturuncu stratovolcano (Ward et al., 2014). A dacitic crystal-mush source is also supported by
the composition of erupted ignimbrites, which tend to be relatively homogenous, crystal-rich,
and dacitic Figure 8) (De Silva & Francis, 1991). Zoning of ignimbrite and xenoliths indicate
magma mobilization by injections of mafic or (presumably secondary) rhyolitic melts into the
crystal mush storage zone (Schmidt et al., 2001; Lustrino, 2005; Perkins et al., 2016). No major
ignimbrites have been erupted in the region since the late Miocene. However, Holocene age
silicic lava domes and flows have been interpreted as “leaks” from the large magma storage
zone below the Altiplano-Puna region (De Silva, 1989 a; Chmielowski et al., 1999). Active
geothermal manifestations also indicate persistent crustal magmatism. The largest geothermal
fields of the region at Sol de Manana in Bolivia (22.38° S, 67.07° W) and El Tatio in Chile (22.33°
S, 68.02° W) are located along recent NW-SE trending normal faults along the boundaries of
large caldera complexes (Cortecci et al., 2005).

The composition of volcanic rocks ranges from basaltic andesite to rhyolite and is
dominantly medium-K calcalkaline in character (Figure 8). Andesite and dacite are the dominant
compositions, with more and less evolved lavas erupted as relatively minor components
Plagioclase is present as phenocrysts across nearly all compositions. Amphibole is common in andesites, biotite and two feldspars in dacite and rhyolite, and olivine and pyroxenes are present in basaltic andesites (Moreno & Gibbons, 2007). The majority of the arc rocks follow major element trends consistent with fractionation of plagioclase, pyroxenes, and Fe-Ti oxides, such as correlation of increasing SiO$_2$ with increasing K$_2$O and decreasing CaO, MnO, MgO, Al$_2$O$_3$, and FeO$^*$ (Figure 8) (GEOROC, accessed 2015). Both closed-system magmatic differentiation paths, where isotopic composition varies little with evolution (e.g. Lascar volcano, O’Callaghan & Francis, 1986), and open-system processes involving assimilation and crystal fractionation (AFC), where isotopic composition changes with magmatic evolution (e.g. Ollagüe stratovolcano, Mattioli et al., 2006), have been observed in the Central Volcanic Zone. Disequilibrium textures are common in Central Andean volcanic rocks and indicate that both assimilation and magma mixing processes are important in the region (Stern et al., 2004 and references therein).

Source region contamination is thought to play an important role in Central Volcanic Zone magma evolution, as well as intracrustal contamination and differentiation. Compared to the less-evolved lavas of the Southern Volcanic Zone, CVZ magmas have a higher $^{87}$Sr/$^{86}$Sr, lower $^{143}$Nd/$^{144}$Nd, and are enriched in incompatible elements (Stern, 2004). Additionally light-heavy rare earth element (LREE/HREE) fractionation decreases with decreasing HREE concentration, implicating contamination deep enough to be in the garnet stability field (Feeley & Davidson, 1984), as heavy rare earth elements are preferentially included in the garnet structure. This effect has variably been attributed to increased subduction erosion adding a crustal component to the mantle wedge and/or ponding and differentiation of magmas to a more buoyant basaltic andesite composition in the lower crust (Feeley & Davidson, 1994; Goss et al., 2013).

Mafic volcanism in the CVZ (i.e. less evolved than andesites) has mainly been erupted at behind-arc minor volcanic centers and in volcanic monogenetic fields (Figure 5; Figure 8) (Davidson & de Silva, 1995; Delacour et al., 2007; Hoke & Lamb, 2007). The majority of these behind-arc centers appear to have developed during Oligocene-Miocene and Pliocene-Pleistocene magmatic pulses from intraplate melting, generated from a slightly depleted MORB-like source modified by slab fluids (Kay et al., 1994; Hoke & Lamb, 2007). In the southern CVZ (24° to 27° S), Plio-Quaternary basaltic to high-Mg andesitic (42 – 65 wt % SiO$_2$) intraplate behind-arc volcanism was controlled by faulting related to a change in regional stress at 2-3 Ma
Crustal contamination, calculated at 20-25% crustal melt for most CVZ mafic lavas, is evident through chemical characteristics (Sr, Nd, and Pb isotopic ratios and Eu anomalies) and xenocrysts of quartz and feldspar with reaction rims (Kay et al., 1994). Kay et al. attributed the change in lithospheric stress and apparent spike in back-arc mafic volcanism to lithospheric delamination and subsequent influx of hot asthenosphere heating the subducting slab and melting at the base of the crust (1994).

The Altiplano-Puna Volcanic Complex

The Altiplano-Puna volcanic complex (APVC) of the central Andes is a physiographic province spanning latitudes 21-24° S characterized by large, nested calderas and associated silicic ignimbrite sheets and dacitic domes (Figure 2) (deSilva, 1989a). Subduction at these latitudes is steep and relatively uniform (~30°) and the subducted slab is 100-250 km below the surface (Cahill & Isacks, 1992). The crust beneath the region reaches maximum thicknesses of ~80 km, and intermediate – silicic magmas which reach the surface are highly evolved and/or heavily contaminated with crustal material as a result (Wörner et al., 1994; McGlashan et al., 2008). Additionally, a regionally-pervasive, sill-like body of dacitic crystal mush has limited mafic magmatism in the region at least since the mid-Miocene (Figure 2) (Zandt et al., 2003). The majority of the large-scale silicic volcanism occurred in pulses from ~8.4 to 2.9 Ma, throughout the Neogene, caused by melting of the middle crust due to injections of mafic melts, and/or a component of crustal shortening (deSilva, 1989a; Salisbury et al., 2011). Approximately 70,000 km² of ignimbrite have been erupted from a plutonic complex estimated to consist of ~500,000 km³ of dacitic partial (up to 25%) melt, based on 3-D seismic imaging. (Ward et al., 2014). With a base elevation of 4000 m above sea level, the Altiplano-Puna Volcanic Complex defines a regional highland second only to the Tibetan Plateau in regard to elevation, extent, and crustal thickness (deSilva, 1989b).

Ignimbrites erupted in the region are compositionally monotonous, dominantly calc-alkaline, high-K, crystal-rich dacites with a minor rhyolite component (Lindsay et al., 2001). Phenocryst phases are typically plagioclase, quartz, amphibole, Fe-Ti oxides, and biotite (up to 5mm) with accessory minerals zircon, apatite, and titanite (sphene) (Salisbury et al., 2011). Four massive calderas with dimensions greater than 45 km (La Pacana, Guacha, Vilama, and Pastos Grandes) have produced at least seven “supereruptions,” classified as M8 or higher on the
Volcanic Explosivity Index (Newhall & Self, 1982; Sparks et al., 2005). Many smaller dacitic ignimbrite shields and effusive dacitic and andesitic domes add to the major silicic province, unassociated with any major calderas (e.g. Salisbury et al., 2011). No major ignimbrite eruptions have occurred since the Pliocene. Holocene silicic magmatism has occurred as large lava domes and flows, interpreted as “leaks” from the regional mid-crustal magma storage zone (Chmielowski et al., 1999). Certain Puna ignimbrites (Tuzgle, Galan, and associated rocks) have “intraplate-like” Ba/Ta and La/Ta signatures, suggesting the involvement of a mantle component, while the larger Coranzuli, Panizos, and Atana ignimbrite sheets show more arc-like ratios, implicating a subduction-related endmember (Figure 9; Figure 10) (Coira et al., 1993 and references therein).

The source of silicic magmatism has been interpreted as large-scale crustal melting related to over 350 km of crustal shortening and associated thickening at approximately 12-10 Ma (De Silva, 1989a; Davidson et al., 1991; Zandt et al., 2003; Stern, 2004; Kay et al., 2012). Evidence includes isotopic and geochemical data indicating 50-80% crustal component involvement in ignimbrites, a dearth of mafic volcanism in the region, and the absence of mafic cumulates or xenoliths in the ignimbrites (De Silva, 1989a; Kley & Monaldi, 1998; Lindsay et al, 2001; Salisbury et al., 2011). In this sector of the Puna plateau, the subducting slab steepened during the late Miocene, and as the mantle wedge thickened, the increased asthenospheric heat caused partial crustal melting, producing vast amounts of highly silicic melt, erupted as ignimbrite sheets (Coira et al., 1993; Kay et al., 1999). Late Miocene ignimbritic volcanism migrated westward as subduction steepened, from the 6.7 Ma Coranzuli ignimbrite to the 4.5–3.8 Ma Atana ignimbrite (Coira et al., 1993). It is this ∼4 Ma Atana ignimbrite which immediately underlies much of the Quaternary Altiplano-Puna volcanism.

A negative density anomaly, low velocity zone exists at ∼20 km beneath the central Andes which has been interpreted as partially-molten, sill-like intrusion, dubbed the Altiplano-Puna magma body (APMB) (Schmitz et al., 1997; Chmielowski et al., 1999; Zandt et al., 2003). High heat-flow, decadal scale uplift and deformation, and low-level geothermal activity have been attributed to this magma body (Chmielowski et al., 1999; Henderson & Pritchard, 2013). The APMB, geophysically imaged as a Low Velocity Zone, has been interpreted to lie at a major rheological boundary between ductile lower crust and extended brittle upper crust and acts as a “density filter” to ascending mafic magma (Zandt et al., 2003). The top of the low velocity zone
is relatively well-constrained at 14-20 km depth (alt: 4 – 25 km below sea level), although thickness estimates have ranged from ~ 1 – 20 km (Chmielowski, 1999; Yuan et al., 2000). The most recent efforts in 3-D seismic imaging have identified the dimensions of the low velocity zone as ~ 200 km in diameter, ~ 11 km thick, and ~ 500,000 km³ by volume (Ward et al., 2014). This same seismic study has interpreted the Altiplano-Puna Magma Body as an amalgamated plutonic complex and the largest magma body imaged on Earth (Ward et al., 2014). The low seismic velocity, very high conductivity, and low density geophysical characteristics can be explained if the body is modelled as a dacitic crystal mush with 15-30 volume % interconnected melt (Del Potro, 2013). Gravity surveys have revealed what appears to be diapirically-ascending bodies of dacitic melt, and although 5 of the 6 imaged rising bodies are not correlated with surface volcanism, the center of the low velocity zone is directly beneath the uplift at composite volcano Uturuncu (22.22° S, 67.18° W) (Del Potro, 2013; Ward et al., 2014). It remains unclear how exactly magma travels from the mid-crust to the surface, although the APMB is generally accepted as the source of the differentiated magma which formed the vast ignimbrites of the Altiplano-Puna Volcanic Complex (Del Potro, 2013).

In addition to the extensive silicic volcanism in the region, active main-arc stratovolcanoes of the subduction arc pass through the APVC, including Lascar, Chiliques, Ollagüe, and San Pedro – San Pablo (Gonzalez-Ferrán, 1995). These composite volcanoes are currently active (Lascar is the most active volcano in the Andes) and erupt medium- to high-K calcalkaline basaltic andesitic – dacitic lavas which display typical arc-like trace element signatures (Figure 11; Figure 12; Figure 9) (deSilva & Francis, 1991; Mattioli et al., 2006). These arc volcanoes have experienced significant crustal (and/or trench sediment) participation and display relatively high $^{87}$Sr/$^{86}$Sr (largely > 0.7070), low $^{143}$Nd/$^{144}$Nd (< 0.51225), and Pb isotopic compositions which reflect contamination from the underlying crust (GEOROC, accessed 2/25/14; deSilva & Francis, 1991; Mattioli et al., 2006). As with the rest of the central Andes, it is unclear to what extent primary magmas generated in the asthenospheric wedge have experienced source region composition preceding Assimilation and Fractional Crystallization (AFC) differentiation processes, and the rarity of mafic magmas in the region has prevented in-depth characterization of primary composition(s).

*Note:* “AFC processes” describes the consumption of country rock by primitive magma, which adds crustal material to the magma, reducing its heat, causing partial crystallization.
Some of the more mafic APVC material is from flank eruptions at San Pedro and Ollagüe (La Porunita and SC2) volcanoes, which have respectively erupted high-K basaltic trachyandesite (56 wt% SiO₂, 4.85 wt % MgO) and trachyandesite (58.0 wt% SiO₂, 4.28 wt% MgO) (Mattioli et al., 2006). Young cinder cone and lava flow complexes at the southern edge of the APVC, such as El Negrillar, La Negrillar, and Cordon de Puntas Negras are correlated with regional faulting and have erupted less-evolved andesites than the stratovolcanoes, although little compositional data has been published (Figure 5) (deSilva & Francis, 1991). A small handful of fault-related, quaternary maar volcanoes have erupted less-evolved lava, although these monogenetic centers remain largely unstudied and, in some cases, unnamed (deSilva & Francis, 1991). The most mafic of these centers is Cerro Overo, a Plio-Pleistocene maar at the apex of an antiform which has erupted basaltic andesitic (54 wt % SiO₂, 7.85 wt % MgO) lava recognized in the whole of the APVC (deSilva & Francis, 1991; this study). Regional structural features, such as reverse faults at the eastern edge of the Salar de Atacama or the Calama-Olacapato-El Toro transcurrent fault system, host additional minor volcanic centers with less-evolved mafic products (this study; Matteini et al., 2002). Magmatic composition in the region frequently appears to be derived from the mixing of multiple endmembers, including a primary mafic component (Davidson et al., 1991; Matteini et al., 2002; Kay et al., 2012; Burns et al., 2015; Blum-Oeste & Wörner, 2016). A better understanding of primitive volcanism in the region will lead to a better understanding of the contributions of distinct sources and their role in developing the compositional differences seen in volcanism of the Central Andes.
Lithospheric and crustal architecture of the Central Andes

The crust is exceptionally thick below the Central Volcanic Zone (14° – 28° S), generally ~ 65 km but exceeding 80 km thick in places due to subduction-related shortening and magmatic underplating (De Silva & Francis, 1991; Beck et al., 1996; Zandt et al., 1996; Stern, 2004; Yuan et al., 2002; McGlashan et al., 2008; Mamani et al., 2010). Basement ages range from ~2 Ga in southern Peru, younging to late Precambrian-Paleozoic in the southern extent of the Central Andes (Stern, 2004). The rocks immediately underlying Holocene volcanoes are volcanic rocks of late Oligocene-Quaternary age, including well-preserved stratovolcanoes, ignimbrite sheets, and caldera systems (Gonzalez-Ferrán, 1995). Volcanism appears to have begun in the south and has generally migrated northward (De Silva & Francis, 1991). Directly west of the CVZ is the Peru-Chile trench, a destructive convergent margin with relatively low sediment input, which reaches a maximum depth of 8,055 m below sea level at 23° S (Thornburg & Kulm, 1987; De Silva & Francis, 1991; Stern, 2004). Delamination or foundering of the base of the lithosphere has cause upwelling of hot upper mantle, which in turn has produced areas of dynamic isostatic uplift and back-arc intraplate magmatism (Coira et al., 1993; Kay et al., 1994; Yuan et al., 2002; Risse et al., 2013).

Paleozoic History of the Western Margin of South America

Basement lithology of the central Andes is dominantly a series of metamorphic Proterozoic terranes which were accreted, some possibly rifted and re-accreted, along the western margin of Amazonian Archean cratons (Gondwanaland) during the Paleozoic to early Mesozoic, before the start of the Andean orogenic cycle (Bahlburg & Hervé, 1997, 2000; Stern, 2004). The basement of the southern Central Volcanic Zone, the eastern Northern Volcanic Zone, and the Southern and Austral Volcanic Zones consists of younger Paleozoic to Mesozoic rocks (Stern, 2004 and references therein). In the Neoproterozoic through Paleozoic, Proterozoic rocks were affected by a series of igneous and metamorphic events. The complex history forming the core of the Andes continues to influence modern magmatic genesis and evolution, evidenced mainly by xenoliths and isotopic evidence (e.g. Wörner et al., 1992; Aitcheson et al., 1995; Mamani et al., 2008; Mamani et al., 2010; McLeod et al., 2013). Faulting and other structural features are also controlled by the pre-existing Andean basement.
geometry, shaping magmatic pathways and emplacement within the magmatic domains of the subduction system (e.g. Matteini et al., 2002; Mamani et al., 2010; Lin et al., 2016).

Pre-Andean accretion and other margin-building events occurred at the active western margin of Gondwanaland, notably the Pampean orogeny in the Cambrian to Early Ordovician, Oclóyic orogeny in the Middle to Late Ordovician, Chanic orogeny in the Early to Middle Devonian, and Gondwanian orogenic cycle in the Late Paleozoic-Triassic (Bahlburg et al., 2000; Stern, 2004). During the Paleozoic, the tectonic setting of northern Chile and northwest Argentina sequentially evolved through collisional, foreland basin active margin, collisional, passive margin, and finally active subduction margin (Bahlburg & Hervé, 1997). Metamorphic events from the Pampean to Oclóyic events have contributed significantly to crustal basement of the central Andes. The Arequipa-Antofalla terrane which currently underlies the majority of the Altiplano-Puna plateau (Mamani et al., 2010) collided with Gondwanaland in the Cambrian to early Ordovician, but subsequently rifted away and re-accreted during the Oclóyic orogeny in the Middle to Late Ordovician (Bahlburg & Hervé, 1997; Keppie and Ramos, 1999).

Overprinting and contributions to future Andean basement rocks during accretion include multiple syndeformational intrusions by peraluminous granitoids, extensive folding and thrusting, different episodes of arc-related volcanism and calcalkaline granitoid intrusions, partial ophiolites with peridotites, gabbros, and serpentinite in tectonic thrust slices with MORB signatures, amalgamation of exotic terranes (Laurentian?) (Bahlburg & Hervé, 1997, 2000; Stern, 2004). Periods of localized extension and back-arc rifting contributed minor pillow basalts and mafic sills of within-plate geochemical affinity as well as felsic-to-intermediate intrusions (Bahlburg & Hervé, 1997; 2000). Sedimentary basin deposits since incorporated into the Andean core include sandstones and siliciclastics, volcanioclastics, turbidites, shales, and marine carbonates (Bahlburg & Hervé, 2000).

The immediate result of the complex tectonic history of pre-Andean rocks in the Paleozoic is the development of a highly diverse basement. Interactions between modern arc magmatism and crustal material have the potential to be lithologically, and thus geochemically, complicated. In addition, any melt fractions derived from the deep crust (i.e. the basement) can encompass a broad potential range of compositions. Different incorporated basement materials, be they melt or rock, will have significant variations in radiogenic isotopic composition, e.g. Pb, which will be reflected in the final volcanic product (Wörner et al., 1992;
Mamani et al., 2008). If included as xenoliths, this potentially allows for correlation of included rocks with basement units, although if fully assimilated, isotopic contributions could be obfuscated by a wide variety of incorporated material producing only an “average” composition. Changes in major oxides as indicators of evolution will not likely be affected by variable crustal input, but trace elements along with isotopic composition could vary within a magmatic batch due to smaller-scale heterogeneities at depth (Mamani et al., 2010). Additionally, the variable crust could make along-arc variations in melting and magmatism difficult to discern from varying along-arc crustal basement contributions. As the central Andes are believed to have experienced significant incorporation of crustal material into the sub-arc asthenospheric wedge, there is potentially large geochemical variability in the mantle source of primary melts itself.

Due to the numerous episodes of compression, thrusting, faulting, basin formation, orogeny, and accretion, the lower crust below the central Andes is undoubtedly structurally complex. Accommodation of modern stress and strain in the South American crust must be controlled, at least in part, by rheological differences in the deep crust. A clear example is the Salar de Atacama in the Central Volcanic Zone, which overlies a subsiding, exceptionally dense crustal block (Arriagada et al., 2006; Reutter et al., 2006). This sub-Andean basement feature acts as an indenter, focusing deformation at its margins and blocking asthenospheric flow at depth, causing the eastward bend in the central Andean subduction arc at around 23°S (Kuhn, 2002; Muñoz et al., 2002; Reutter et al., 2006; Lin et al., 2016). Young minor volcanism has manifested along contractional structural features created by the anomalous Salar de Atacama block as a clear example of the influence of ancient geology on the modern arc (Gonzalez et al., 2009). The broad, NW-SE trending lineaments which potentially cut the entire crust of the central Andes have also been theorized to be dominantly controlled by basement domains (Matteini et al., 2002; Norini et al., 2013). Faulting and structure in the mid- to upper-crust in the central Andes has repeatedly been implicated in exerting significant spatial control as to the emplacement of magmas and magma chambers (e.g. Davidson & De Silva, 1992; Matteini et al., 2002; Muñoz et al., 2002; Zandt et al., 2003; Stern, 2004; Hoke & Lamb, 2007; Del Potro et al., 2013; Lin et al., 2016). Monogenetic intermediate to mafic volcanism in general has largely been attributed to fault-controlled channeling of magmas to the surface, preventing significant crustal assimilation or magma stalling deeper in the crust (De Silva & Francis, 1991; Kay et al., 1994; Stern, 2004; Mattioli et al., 2006). Cerro Overo maar, a mafic maar surrounded by intermediate stratovolcanoes is an instance of structurally-controlled volcanism which has
escaped extensive differentiation and processing due to lineaments potentially controlled by the nature of the Central Volcanic Zone basement (De Silva & Francis, 1991; Gonzalez-Ferrán, 1995; this study).

As crustal material reaches depths where metamorphic phase changes occur, the rate of reaction and resultant metamorphic rock will reflect the heterogeneity of the protoliths. Lithospheric delamination is dependent on eclogitization of deep lithospheric material, leading to density inversion and removal of lithospheric root, and is believed to be an important process at the Andean margin, particularly below the central Andean plateaus (Kay et al., 1994; Lustrino, 2005; Hoke & Lamb, 2007; Kay et al., 2012). The distribution of basement terranes from Paleozoic events may exert significant influence on the location and propagation of lower lithospheric events, and thus control on topographic uplift and non-arc-related magmatism. Delamination related magmatism is found in the back-arc of the CVZ, where intraplate melting has produced magmas with distinct compositions from the main arc, largely erupted along structural features (Davidson & De Silva, 1992; Kay et al., 1994; Davidson & De Silva, 1995; Hoke & Lamb, 2007; Risse et al., 2013). As asthenosphere upwells and heats the lower crust, the ease of melting deep crustal materials of different lithologies may contribute to the creation and development of mid- to upper-crustal magmatic bodies, such as the Altiplano-Puna Magmatic Body (APMB). The AMPB is believed to be at least a partial magmatic source for the vast silicic ignimbrite sheets recently deposited at the surface of the central Andes and to act as a crustal filter to more primitive magmas (Zandt et al., 2003; Del Potro et al., 2013). The APMB is located north of where the most significant delamination has been seismically imaged, and delamination-related mafic magmatism is not present east of the APMB, although it is found in the back-arc to the north and south, at the margins of the Puna plateau (Davidson & De Silva, 1992; Kay et al., 1994).

The Contemporary Deep Crust and Lithosphere of the Central Andes

The lower crust and lithosphere below the Central Volcanic Zone is complex and variable, with a broad crust-mantle transition. Several geodynamic processes have been active in the region, such as magmatic underplating, lithospheric delamination, crustal flow, partial melting, and mantle hydration (Yuan et al., 2002; Moreno & Gibbons, 2007; McGlashan et al., 2008). Seismic velocity data implies the crust has a felsic composition down to 50-55 km depth,
transitioning into more mafic (dense) material below this (Yuan et al., 2002). Deviations in geophysical data from isostatic predictions are correlated with surficial manifestations of volcanism and imply large-scale active processes are occurring at depth, such as destruction/removal of lithosphere or coupling with the upper mantle (Cahill & Isaacks, 1992; Zandt et al., 2003; Reutter et al., 2006; Hoke & Lamb, 2007; McGlashan et al., 2008). Seismic reflection data suggests the depth to the Moho varies across a broad range from 57 to 82 km (McGlashan et al., 2008). In comparison, the surface elevation of the Central Andes only varies ~3.3-4.1 km above sea level (Stern, 2004). Large-scale variations in eclogitization of the lower crust are unlikely to be the source of Moho topography, as P-wave velocities are anomalously felsic down to the deep crust below the Altiplano-Puna (Beck & Zandt, 2002; McGlashan et al., 2008). Variable crustal thickness could also be the result of lower crustal flow through planar channels opened by gravitational pull from sinking lithospheric root. However, ponding under thinner crust and crustal blocks shifting toward isostatic equilibrium would eventually eliminate Moho topography in this scenario (McGlashan et al., 2008).

The most likely geodynamic processes affecting the Moho depth are lower crustal/lithospheric delamination, mantle-crustal lithospheric coupling, or a combination thereof (Kay et al., 1994; Schurr et al., 2006; McGlashan et al., 2008). Crustal delamination has been associated with lithospheric architecture and mafic magmatism with intraplate compositional features to the north and south of the Altiplano-Puna region (Figure 5) (Davidson & De Silva, 1992; Kay et al., 1994; Davidson & De Silva, 1995; Lustrino, 2005; Hoke & Lamb, 2007; Liang et al., 2014). Delamination can also explain why, despite an ~10 km thinner crust beneath the Puna (Yuan et al., 2002), the Puna region has a higher average elevation than the Altiplano to the north due to dynamic isostatic uplift caused by upwelling hot upper mantle (Risse et al., 2013). This upwelling mantle and increase in heat being delivered to the crust may have also been one of the major mechanisms in creating the massive mid-crustal magma bodies which fueled the large silicic caldera eruptions of ignimbrite in the Miocene (Kay et al., 1994).
Methods

This project is focused on the petrologic and compositional description of monogenetic, within-arc volcanism of the Altiplano-Puna region of the central Andes. Samples, volcano descriptions, and GPS coordinates were acquired over a series of field expeditions to northern Chile in 2007, 2008, and 2014. Subsequent petrographic descriptions and geochemical analyses took place in the United States. Rock sample processing took place at the Petrography and Clean Lab facilities at the University of Iowa. Whole-rock major and trace element analyses were conducted by inductively-coupled plasma mass spectrometry (ICP-MS) at the University of Iowa, supplementing a small, pre-existing dataset collected via X-ray fluorescence (XRF) and ICP-MS, respectively, by Ingrid Ukstins Peate at Washington State University in 2009. Also at this time, Dr. Ingrid Ukstins Peate analyzed major and trace element compositions of a set of rehomogenized olivine-hosted melt inclusions by laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS). Whole-rock radiogenic isotope ratios were collected at the University of Illinois, Champaign-Urbana (Sr) and at New Mexico State University (Sr, Nd, Pb) by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). Olivine-hosted melt inclusion Sr isotopic compositions were analyzed by thermal ionization mass spectrometry (TIMS) at New Mexico State University. Additional data on mineral, glass, and melt inclusion composition and X-ray maps were collected by electron probe microanalysis (EPMA) at the University of Iowa. Supplementary age data collection and calculations were by Dr. Bill McClelland at Arizona State University for zircon U-Pb crystallization ages and (U/Th)-He reheating ages, analyzed by magnetic sector high resolution ICP-MS with an Alphachron MkII He extraction/measurement system.

Fieldwork in the Atacama Desert, Chile

In October - November 2014, an expedition from the University of Iowa, consisting of Ingrid Ukstins Peate, Samuel Saltzman, and myself travelled to northern Chile to conduct fieldwork in the Atacama Desert. In Chile we were joined by Christian Tambley of Campoalto Operaciones, who functioned as a guide, logistician, administrator, and interpreter for us. This work was funded by the University of Iowa Office of the Vice President for Research and Economic Development (OVPRED) and generous grants from the University of Iowa’s Center for Global and Regional Environmental Research (CGRER). During fieldwork we camped at the
western edge of the Cordón Altos de Toro Blanco (23.508° S, 67.694° W), along the southern shore of hypersaline Laguna Lejía or stayed in the towns of Talabre (23.32° S, 67.89° W) and Socaire (23.59° S, 67.89° S). The primary target of fieldwork relating to this project was sampling and field observation of Cerro Overo maar (21.517° S, 67.662° W), previously recognized as the most mafic lava in the Altiplano-Puna region (21° - 24° S) of the central Andes (De Silva & Francis, 1991) and initially investigated by Dr. Ingrid Ukstins Peate in 2007 and 2008. During these earlier expeditions, Dr. Ukstins Peate had identified a previously undocumented dome of olivine-phyric basaltic andesite (21.526° S, 67.685° W), herein known as La Albóndiga Grande. Due to favorable expedition outcomes, we were able to investigate additional minor volcanic centers Dr. Ukstins Peate and I had located as points of interests using the volcanic maps of Gonzalez-Ferrán (1995), the tectonic maps of Gonzalez et al. (2009), Google Earth satellite imagery, and de-classified CIA aviation charts of northern Chile. Potential sampling targets were identified by their location (i.e. isolation), morphology, and relative color. When seen in satellite images, more mafic rocks stand out as dark brown rocks in contrast to the extensive pale tan to light brown ignimbrite sheets of the region. Fieldwork consisted of sampling, measurements, collection of GPS points, field observations, and extensive photography.

Samples

A total of 123 samples of varying lithology from eight localities were analyzed in the course of this study. Seventeen samples were initially collected during unrelated fieldwork by Ingrid Ukstins Peate in 2007 (7) and 2008 (10) from Cerro Overo maar and the associated Albóndiga dome. An additional 105 samples of lava, xenoliths, and ignimbrite were collected from volcanic centers in the Central Andes during fieldwork in 2014. One sample from the Cerro Chascón dacite dome (23.008° S, 67.692° W) was contributed by Dale H. Burns to help provide regional context. Sample locations are listed in Table 4. Sample collection criteria included targeting a full range of the available rock types, textures, and mineralogies present at each center and avoiding samples with extensive post-eruptive alteration (e.g. oxidation, caliche encrustation, or secondary vesicle mineralization). GPS coordinates were recorded for every collected sample (Appendix A). At the University of Iowa, portions of hand samples were crushed to ≤ 0.5 cm diameter pieces using a Braun Chipmunk™ jaw crusher. Aliquots of the crushed samples with minimal contamination (i.e. caliche, oxidation) were reduced to fine
powders for subsequent wet chemistry using a ball mill with alumina grinding components. The remaining crushed samples were passed through U.S. standard sieves of ≤ 2 mm, ≤ 1 mm, ≤ 0.500 mm, and ≤ 0.250 mm. Olivine crystals, where present, were handpicked from the sieved separates.

**Petrographic Thin Sections**

Initial processing of recovered rock samples was conducted at the UI Petrographic Laboratory facilities, including cutting of thick sections by myself and the production of five preliminary thin sections, polished to microprobe standards by Matthew Wortel to guide additional sample selection and targeting. Subsequently, (36) probe-polished slides were produced by National Petrographic Service, Inc. (NPS) from billets cut at UI. Observations of thin sections were made by petrographic microscope with plane- and crossed-polarized lights options and Scanning Electron Microscopy (SEM).

**Whole-Rock Major Elements by ICP-MS CCT**

Major element concentrations (TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MnO, MgO, CaO, Na$_2$O, K$_2$O, P$_2$O$_5$) were measured using Collision Cell Technology (CCT) in concert with the Thermo Scientific X-Series 2 ICP-MS at the University of Iowa. This method extracts sample ions under vacuum into a “collision cell” filled with non-reactive He gas positioned before the quadrupole analyzer. Collisions between the inert gas and the analyte prevent the spectrometers from being overloaded by the higher concentrations of the major elements, which can be measured at the same time as trace elements while CCT is in use. Basaltic standard W-2 was analyzed repeatedly at intervals to monitor drift and accuracy. Due to the use of HF acid in the dissolution chemistry employed in producing the input solution, SiO$_2$ cannot be directly measured accurately as silicone is partly carried off as silicon tetrafluoride (SiF$_4$), a gaseous byproduct of the dissolution \[4HF + SiO$_2$ \rightarrow SiF$_4$ + 2H$_2$O\] (also known as “Fluoro acid air”). The values for SiO$_2$ reported in this work are calculated by the difference from 100% for the 9 major elements measured and the several minor elements measured concurrently (Sc, V, Cr, Co, Ni, Cu, Zn, Sr, Y, Zr; generally < 0.2 % total). Published values for basaltic standard W-2 (SiO$_2$ = 52.57 ± 0.32 wt %) were reproducible with this method (SiO$_2$ = 52.38 ± 0.19 wt %, n = 4), although ultimately these
calculated values are still upper limits (standard values from GEOREM, accessed 2016). While the parental magmas may have carried a significant percentage of water, the solidified lavas and pyroclastic materials analyzed can reasonably be assumed to be volatile-free (i.e. degassed).

**Whole-Rock Trace Elements by ICP-MS**

Aliquots of sample whole-rock powders, along with a blank and several established mafic and felsic standard powders were weighed out and dissolved in high purity HNO₃, HF, and HCl. Digested samples were then spiked with known amounts of Re and In (functionally absent from geologic samples) to be measured relative to the unspiked unknown (i.e. the analyte concentration) to account for any matrix effects and monitor any deviations in analytical success during measurement. The spiked samples were then diluted by addition of 2% HNO₃ down to 1 part analyte per 4500 parts solution and 10 ppb spike concentration. Dilution is necessary to keep the mass spectrometer from being overwhelmed and to extend calibration bounds.

Samples were analyzed from solutions by the Thermo Scientific XSeries-2 ICP-MS at the University of Iowa under the direction of Dr. David Peate. Spectrometer measurements were acquired for 43 minor and trace elements (Li, Be, B, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, Th, U). Internal standards were monitored during analyses to correct for variations in the instrument response and to calculate the analyte concentrations of the unknown samples. A procedural blank and established natural standards were analyzed along with the unknowns. Standard samples covering the mafic to intermediate spectrum (45 – 59 wt % SiO₂) included BHVO-2, W-2, and BIR-2. Intermediate to felsic standards (60 – 75 wt % SiO₂) included in analyses were BCR-2, AGV-2, and JA-1. Standard basalt W-2 was analyzed repeatedly throughout runs to monitor drift and internal accuracy.

**Whole Rock Radiogenic Isotopes by Multicollector ICP-MS**

Radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios for igneous systems are often employed as an indicator of the level of crust versus mantle contribution to the resulting rock. As Rb is heavily partitioned into any melts formed due to its incompatibility, it is concentrated more in the crust
relative to the mantle. Radioactive decay of $^{87}$Rb produces $^{87}$Sr, thus driving up the $^{87}$Sr/$^{86}$Sr ratio for rocks with higher levels of crustal involvement.

An initial set of 18 samples from Cerro Overo maar was analyzed at the isotope lab of Craig Lundstrom at the University of Illinois in Champaign-Urbana. Strontium was first separated from acid digested whole-rock powders at the University of Iowa geochemistry clean lab. Each sample was passed through a pipette tip columns loaded with ~300 μL of Sr-spec™ resin and a frit at the column tip, trapping Sr ions in the resin. After flushing the resin with HNO$_3$ to remove unwanted ions, water was then passed through the column, taking the Sr with it, and collected. This collected solution is then dried down on a hotplate, has a small amount of concentrated HNO$_3$ added, and then is diluted for mass spectrometry. At the Lundstrom lab, we analyzed samples with a Nu Plasma HR Multicollector Inductively-Couple Mass Spectrometer (MC-ICP-MS), a mass spectrometer capable of measuring multiple isotopes concurrently. The sample set included a blank and accepted standards BCR-2, BHVO-2, BIR-1, and JB-2. Additionally, internal standards were checked repeatedly throughout the analyses. The average analytical value measured by MC-ICP-MS for Sr standard NBS-987 was 0.710250 ± 0.000009 and for an internal UIUC coral standard was 0.709179 ± 0.000018, well within error of the accepted values. The measured $^{87}$Sr/$^{86}$Sr values for basaltic andesite from Cerro Overo maar averaged 0.706285 ± 0.000091 for 13 samples, ranging from 0.706166 (sample CIUP 08-16) to 0.706445 (sample CIUP 07-41). The measured $^{87}$Sr/$^{86}$Sr for felsic xenoliths sampled from Cerro Overo maar averaged 0.709504 ± 0.00014 for 5 samples, ranging from 0.709326 (sample CIUP 08-14) to 0.709681 (sample CIUP 08-97).

<table>
<thead>
<tr>
<th>Standard</th>
<th>Accepted ratio*</th>
<th>+/-</th>
<th>Measured ratio</th>
<th>+/-</th>
</tr>
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<td>JB-2</td>
<td>0.703661</td>
<td>.000032</td>
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<td>.000007</td>
</tr>
</tbody>
</table>

*Values from GEOREM, accessed 2016 (Jochum et al., 2005)
Radiogenic Sr, Nd, and Pb isotopic ratios were measured for 21 additional samples encompassing all sampled volcanoes using a ThermoFinnigan™ Neptune Plus MC-ICP-MS at New Mexico State University. Approximately 0.200 g of powdered sample was first dissolved with ultrapure hydrofluoric (HF), nitric (HNO₃), and hydrochloric (HCl) acids in clean Teflon™ beakers. Samples were then centrifuged to remove any undissolved solids. The elements of interest were extracted from the dissolved samples by column chromatography, dried down in Teflon™ beakers on a hot plate, and re-dissolved with a small amount of 7N HNO₃ before MC-ICP-MS analysis.

**Column Chromatography**

For analysis of whole rock radiogenic isotope composition, the specific elements to be analyzed need to be extracted from the bulk dissolved sample. Aliquots of sample in solution are passed through high aspect ratio glass columns to purify (i.e. isolate) the selected elements. An analytical blank was included as an analyte, spike with 0.0621 g of low U/Pb spike, 0.1250 g of low Rb/Sr (0.03) spike solution diluted to 0.00273 times, and 0.0842 g of fixed Sm/Nd spike. First, strontium (Sr) was collected using ~ 5.0 mL of Bio-Rad AG® 1-X8 200 – 400 mesh size, chloride form, cation-exchange resin. The dissolved samples were loaded in ≤ 0.5 mL aliquots onto columns prepped with 2.5N HCl. The columns were then washed in sequence with varying amounts (0.5, 0.5, 2.0, 6.5, 3.0, 5.0 mL) of 2.5N HCl which was collected in 60 mL Teflon™ beakers for subsequent Lead (Pb) purification. Purified Sr was collected in Teflon™ beakers in the next 6.0 mL of HCl passed through the columns. Rare Earth Elements (REEs) were collected in a subsequent wash of 10 mL of 6N HCl, from which Neodymium (Nd) could be extracted. The Pb wash, purified Sr, and REE separates were dried down on a hotplate and re-dissolved in 7N HNO₃.

For Nd purification, REEs collected during Sr purification were re-dried and then re-dissolved in 0.5 mL 0.25N HCl to be loaded onto chromatography columns filled with ~ 5.0 mL of Tru-spec® resin prepped with 0.25N HCl. After the sample aliquots were pipetted onto the columns, the resin was successively washed with 0.5, 0.5, 1.0, and 4.0 mL of HCl (not collected) to remove undesired elements. Purified Nd was collected with the subsequent 6 mL wash of 0.25N HCl in Teflon™ beakers, dried down on a hotplate, and re-dissolved in 7N HNO₃ in preparation for analysis.
Sample Pb was isolated by column chromatography from the initial washes collected during Sr purification. Samples were first re-dried on a hotplate and re-dissolved in ~ 0.5 mL of distilled 1N hydrobromic acid (HBr). Chromatography columns loaded with 2.0 mL of Bio-Rad AG® 50W-X8 200 – 400 mesh size, hydrogen form, anion-exchange resin were prepped with two washes of 2.0 mL and 1.0 mL 1N HBr. Sample aliquots of ~ 0.5 mL were loaded onto the anion-exchange columns by pipette and washed with two consecutive rounds of 0.5 mL of HBr and four rounds of 3.0 mL of 1N HBr (not collected) to clean the resin of elements other than Pb. Purified Pb was collected in clean Teflon™ beakers in a subsequent wash of 1.0 mL de-ionized H₂O followed by two 3.0 mL rounds of 1N HNO₃. The isolated Pb aliquots were dried down on a hotplate and re-dissolved in 7N HNO₃ in preparation for MC-ICP-MS analysis.

**Multicollector ICP-MS analysis at NMSU**

Purified Sr, Nd, and Pb sample solutions were analyzed for isotopic composition on the ThermoFinnigan™ Neptune Plus MC-ICP-MS at New Mexico State University using 7 Faraday collectors. The measured Sr isotopic ratios were normalized to \(^{86}\text{Sr}/^{87}\text{Sr} = 0.1194\) to account for mass fractionation. Measured Nd isotope ratios were normalized to \(^{146}\text{Nd}/^{144}\text{Nd} = 0.7219\) and corrected for any Samarium (Sm) included in the analytical runs. For Pb analyses, the MC-ICP-MS was set in static mode with a \(^{208}\text{Pb}\) reading of approximately 6 volts. Samples were mixed with NBS997 thallium to produce a Pb/Tl ratio between 2 and 4 prior to analysis. Measured Pb isotope ratios were normalized to \(^{203}\text{Th}/^{205}\text{Th} = 0.4189\) to account for mass fractionation.

**Single-crystal Strontium isotopes**

Olivine crystals were targeted for additional \(^{87}\text{Sr}/^{86}\text{Sr}\) isotopic analysis by Thermal Ionization Mass Spectrometry (TIMS) at the New Mexico State University (NMSU) Analytical Geochemistry Research Laboratory. As Sr does not incorporate into the crystal lattice of olivine due to elemental size and charge considerations, the measured isotopic ratio can be assumed to represent that of the material contained within any inclusions in the targeted crystal. Olivine crystals were separated by hand from crushed and sieved separates of olivine-bearing samples using a Leica stereoscopic microscope. Crystals were dominantly concentrated in the 500 μm sieve separates for Cerro Overo and La Albóndiga samples, and in the 1000 μm (1 mm) separate for lava samples from The Puntas Negras-El Laco lava flow. Suitable target crystals for isotope work were individually selected for single, large inclusions (preferably glassy). The selected
crystals were then etched in 10% hydrofluoric acid (HF) to remove all adhering groundmass material (10 – 40 min), weighed, and photomicrographed through a Leica binocular microscope.

**Single crystal digestion**

At NMSU, the olivine crystals were dissolved in Teflon™ beakers with double-distilled (ultrapure) concentrated HF (0.5 mL) and 14N HNO₃ (0.5 mL) and HCl. Before digestion, crystals were spiked with a high-purity, low Rb/Sr spike with high levels of ⁸⁴Sr in all samples, including the blank, such that total analyte abundances could be determined and the blank contribution removed from final results. Samples were left on a hotplate in sealed beakers overnight and then dried down. The dry residue was then re-dissolved in 1 mL of ultrapure 6N HCL in sealed beakers overnight and then dried down once more. Samples were then dissolved one final time in 0.5 mL of 2.5N HCl. Teflon™ vessels used for chemistry were cleaned meticulously, including sitting on a hot plate filled with distilled aqua regia (HNO₃ + 3HCl) for over a week preceding use.

**Column chromatography**

Pure Sr and Rb were separated from dissolved samples by column chromatography, using cation-exchange resin. Strontium and Rubidium were isolated using 0.5 mL of Bio-Rad AG®1-X8 200 – 400 mesh size, chloride form, cation-exchange resin in high aspect ratio glass columns. To maintain low blank values, the resin was extensively pre-cleaned with 2.5N HCl and all acids used were fresh and doubly distilled at the NMSU Geological Sciences Clean Lab. Samples were pipetted onto the chromatography columns in ≤0.5 mL aliquots and washed through in a sequence of 0.05 mL, 0.05 mL, 0.1 mL, and 0.85 mL of 2.5N HCl. Rubidium was then collected in the next 0.5 mL of 2.5N HCl. After another wash of 0.2 mL of 2.5N HCl, strontium was collected in 0.7 mL of 2.5N HCl. Purified Sr and Rb extracts were collected in clean Teflon™ beakers and dried down on a hot plate. These procedures resulted in an analytical blank with only 0.186 ppb of Sr while the extracted volume of Sr per sample was estimated at 10–20 ng. Well-established basaltic standards BCR-2 and BHVO-2 were included to check reproducibility, as well as several of the whole-rock material from this project also measured by MC-ICP-MS (see previous subsection) to allow for internal comparison.

**Thermal Ionization Mass Spectrometry**

Single crystal Sr isotopes were measured using the VG Sector Thermal Ionization Mass Spectrometer (TIMS) at New Mexico State University under the guidance of Dr. Frank Ramos. TIMS involves accelerating a beam of ions generated from the sample across an electrical
potential gradient and directing components of this beam into collectors on the basis of mass-to-charge ratio. A minimum of only 1-3 ng of Sr is needed to produce highly precise isotopic ratios from TIMS analyses (Ramos & Tepley, 2008). Samples (here, the extracted Sr) are mixed with pure, Sr-free Ta2O5 (tantalum pentoxide) and dilute H3PO4 (phosphoric acid), then loaded onto a rhenium filament. The Ta solution is used to enhance the efficiency of Sr ionization, thus allowing very small amounts of analyte to be measured. Before being loaded with sample, Re filaments had been brought up to and held at temperatures exceeding the Sr ionization point within the machine, and the spectrometer is manually checked for Sr and Rb signals, so that it is completely clear there is no contamination. Once loaded, samples were dried by running 0.8 – 1.4 amps through the Re filaments. Samples were loaded into the TIMS machine on a 10-sample turret, including at least one sample of a known Sr standard.

High precision 87Sr/86Sr analyses of spiked sample aliquots were conducted on the VG Sector TIMS using a dynamic peak jumping routine using 5 Faraday cup collectors. The Faraday collectors were tuned to an 88Sr intensity of approximately 3.0 volts. All measured ratios were normalized to 86Sr/88Sr = 0.1194 to account for mass fractionation and 84Sr/86Sr was continually monitored during analyses. Long-term machine reproducibility at NMSU of standard sample NBS-987 is estimated at 0.00002. Measured Sr ratios were corrected with an isotopic mixing equation (Equation 1). Further details of methodology are found in Ramos and Tepley (2008) and references therein. Further description of methodology can be found in Ramos and Tepley’s Reviews in Mineralogy & Geochemistry article (2008): Inter- and Intracrystalline Isotopic Disequilibria: Techniques and Applications, and references therein.

\[
\frac{87}{86}Sr(\text{Blank Corrected}) = F \times C_A \times \frac{R_1}{C_N + (1 - F)} \times C_B \times \frac{R_2}{C_N}
\]

Equation 1 – Isotopic mixing equation used for blank correction where F is the weight percent fraction, \(C_A\) is the concentration, and \(R_1\) is the isotopic signature of the combined sample and blank. \(C_B\) is the concentration, and \(R_2\) is the isotopic composition of the analytical blank. \(C_N\) is the weight percent concentration of the total weight of the sample and blank combined with the analytical blank.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Accepted ratio</th>
<th>+/-</th>
<th>Measured ratio, TIMS</th>
<th>+/-</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-2</td>
<td>0.70492</td>
<td>.00055</td>
<td>0.705043</td>
<td>.000017</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>0.703478</td>
<td>.000034</td>
<td>0.703564</td>
<td>.000014</td>
</tr>
</tbody>
</table>

Table 3 – Accepted and measured values for known standards analyzed by TIMS with reported error bounds. Standard values from GeoRem (Jochum et al., 2005).
Crystal and Glass Chemistry by Electron Microprobe

The University of Iowa JEOL 8230 Superprobe microprobe was used for in-situ compositional analyses of olivine, Cr-Al spinel, Fe-Ti oxides, clino- and orthopyroxene, plagioclase feldspar, and glass in groundmass matrices and melt inclusions. The Superprobe is fitted with a tungsten (W) filament, and can measure characteristic X-rays by WDS with five concurrently operating spectrometers and by EDS for the entire spectrum with a single, solid-state semiconductor detector. Data includes spot analyses, transects, and element maps (WDS and EDS). Backscatter Electron (BSE) imagery could also be collected, which produces greyscale images where image brightness is directly related to sample density. All procedures were designed, standardized, and executed at the University of Iowa Electron Probe Microanalysis (EPMA) laboratory. Targeted thin sections were produced and polished by either the University of Iowa Petrographic Laboratory or National Petrographic Services. A 10-15 nm carbon coat was applied with a Cressington 208Carbon High Vacuum Carbon Coater equipped with a Cressington MTM-10 High Resolution Thickness Monitor, which exploits the piezoelectric nature of an oscillating quartz crystal to monitor the thickness of a deposited film with a 0.1 nm resolution.

Common first-order tests for the accuracy and success of an EPM analysis are whether analyses of well-known standards can reproduce their accepted values, and whether totals (the sum of wt % for each measured species) reasonably approaches 100%. Strictness of this latter test vary by the nature of the target and the acceptable total window size has been determined by reproducibility and literature review per analysis type. For example, the predictable, strong, and low-impurity crystalline lattice of olivine can be expected to be reasonably reproduced with 99-101% elemental analysis totals for accurate measurements. Targets with higher amounts of impurities, such as oxides or pyroxene, or a less-predictable crystal structure, such as glass, will have larger windows of acceptable totals. Some minerals, such as micas, can be so unpredictable that a review of the literature finds published totals as low as 65 %. Standard reference materials were analyzed as unknowns during each analytical run to monitor calibration accuracy and analytical reproducibility, both between and within analytical sessions.

Theory of Electron Probe Microanalysis

Electron probe microanalysis (EPMA) is a non-destructive method of producing characteristic X-rays from a target using a focused electron beam. EPMA can be performed on
any polished solid surface, such as a rock sample thin section, although carbon coating is usually required as preparation. The energy carried by the electron beam scatters bound electrons from the inner k, l, or m orbitals of the target atoms, creating unstable vacancies which must be filled by electrons from higher-order orbitals (or by low energy free or unbound electrons). The inner atomic orbitals have a lower binding energy than outer shells, and the excess energy produced by transfer of electrons is then emitted as a photon in the X-ray range of the electromagnetic spectrum. As every element has a unique orbital structure, characteristic X-rays are produced which can be identified either by wavelength (\(\lambda\)) or by energy (\(E\)). There is a direct relationship between Energy and Wavelength:

\[
E = \frac{hc}{\lambda}
\]

Where \(E\) is photonic energy, \(h\) is the Planck Constant, \(c\) is the speed of light (also constant) and \(\lambda\) is the photonic wavelength, so the two attributes are equally characteristic. Characteristic X-rays intensities can be measured by either by wavelength dispersive X-ray spectroscopy (WDS) or energy dispersive X-ray spectroscopy (EDS). WDS employs moveable crystals to focus a specific X-ray wavelength onto a proportional detector by Bragg diffraction. Bragg’s law is:

\[
n\lambda = 2d \sin \theta
\]

Where \(\lambda\) is the incident wavelength, \(n\) is a positive integer, \(d\) is the interplanar distance separating lattice planes in a crystalline solid, and \(\theta\) is the scattering angle used to direct the specified wavelength to the detector. Only one wavelength at a time can be analyzed by WDS per crystal (i.e. per spectrometer). EDS, on the other hand, collects all wavelengths of the spectrum at once and converts X-ray photons to electron-hole pairs with a semiconductor detector. The energy required to create an electron-hole pair is known and can be used to identify characteristic energy bands, and the number of electron-hole pairs can be used to determine intensity. While EDS measurements cover more elements and are generally much quicker, WDS analysis has superior X-ray peak resolution and higher peak-to-background ratio (i.e. signal-to-noise), resulting in lower detection limits and production of much more precise data (Reed, 2005).

The major parameters adjusted in designing an EPMA procedure, or “recipe,” are the accelerating voltage, beam current, beam diameter (“spot size”), peak and background
counting time, and standardization. The accelerating voltage, measured in kiloelectronvolts (keV), is the potential difference (i.e. voltage) which draws electrons from the filament source in an electron gun and accelerates them down the column toward the target. As accelerating voltage increases, so does the volume of interaction between the beam and the target. When designing a procedure, an accelerating voltage needs to be chosen which allows for the electron beam to interact with enough of the target to produce a measurable amount of characteristic X-rays, but not so high that the beam passes through the material of interest and generates additional X-rays from whatever substrate is present. Commonly, accelerating voltage is in the 15 – 30 keV range for most analyses.

The beam current, described in nanoamperes (nA), is the current applied across the electron source filament. A higher beam current cause more free electrons to be produced in the filament, per unit time, and also increases the beam diameter. Higher beam currents can be used to accurately measure elements in lower concentrations as the increase in electrons ultimately leads to an increase in the amount of characteristic X-rays produced. However, if the beam current is set too high, more X-rays may be produced than can be counted by the detectors, leading to an underestimation of concentration. Practically, the accelerating voltage can be thought of as the “velocity” of the beam particles, and the beam current can be imagined as the “particle density” of the beam.

Adjustments to the electron beam diameter alters the size of the spot to which the electromagnetic lenses of the probe focus the beam at the surface of the target. Larger beam diameters can be useful when analyzing, for example, minerals with micro-zonation when a relative average composition is desired, or if a sample may be damaged (ablated) by a concentrated electron beam. Migration of alkali elements (K, Na) away from the high energy of the beam is also an issue that can be counter-acted by use of a broad beam, reducing the concentration of electrons at a specific point. A smaller spot size is useful, on the other hand, when the target is relatively small (< 10 μm) and robust enough to handle a high electron concentration, such as with mineral inclusions of metallic oxides.

Counting time for WDS is the amount of time the probe focuses a spectrometer on counting a specific X-ray wavelength. An accurate analysis can only be obtained by accounting for the amount of background X-ray radiation detected, which is then later subtracted from the
X-ray counts at the characteristic wavelength to obtain the number of counts produced by
electron bombardment of the target. Spectrometers are programmed to count X-rays both at
the characteristic peak as well as to either side of this wavelength. A linear extrapolation
between a positive and negative (higher and lower wavelengths, respectively) background
measurement, carefully chosen to avoid any interference from other elemental peaks, is
sufficient to produce a removable background count profile, but needs to be measured for every
element and every analysis. As a result, the microprobe operator aims to choose the lowest
counting time needed to obtain accurate and reproducible results to avoid excessive beam time,
as, apart from monetary concerns, the electron beam is not infinitely stable. Counting time for
EDS analysis is, quite simply, the amount of time the full spectrum is collected.

Standardization is the process by which raw X-ray counts are converted into
concentration, traditionally reported as weight percent (wt %), by comparing measured counts
with the number of counts detected from an identical analysis of a standard with known
composition. Microprobe software calculates additional corrections for atomic number (Z),
absorption (A), and fluorescence (F). These ‘ZAF’ corrections account for electron
backscattering, electron penetration (stopping), loss of X-rays due to absorption by other atoms,
and production of excess X-rays due to secondary fluorescence. The corrected X-ray counts, or
intensities, are then used to calculate the concentration of an element in the unknown using the
First Approximation of Castaing:

\[
C_i^{\text{unk}} \approx \frac{I_i^{\text{unk}} ZAF_i^{\text{unk}}}{I_i^{\text{std}} ZAF_i^{\text{std}}} C_i^{\text{std}} = K_i C_i^{\text{std}}
\]

Where the superscripts std and unk represent unknown and standard values, respectively, per
analyzed element, subscript \(i\). \(C\) is concentration, \(I\) is X-ray intensities, \(ZAF\) is the correction
factor, and \(K\) is the reduced variable relating standard to unknown composition, known as the \(k\)-
ratio (Reed, 2005).

**Mineral Spot Analyses and Transects**

High-precision WDS spot analyses of olivine crystals were executed with an accelerating
voltage of 20 keV, a 200 nA current, and a beam diameter of 5 μm. Peak counting times were
30 seconds for major elements (Si, Fe, Mg), 60 seconds for minor elements (Ca, Mn, Ni, Na), and
120 seconds for trace elements (Al, Co, Cr). Background counting times were half as long. The
calibrated microprobe procedure was able to reproduce Smithsonian Microbeam Standards Springwater (Fo83) and San Carlos (Fo90) olivine within error throughout analytical runs. Only analyses with 99-101% elemental totals were accepted. Na content was analyzed in a sequence of short 10 s peak counting times, later interpolated, to avoid issues with alkali migration. However, counting rates show no difference in measured Na over time, indicating this precaution was unnecessary for a target with such a robust crystalline lattice.

High-precision WDS spot analyses of metallic oxide minerals, mainly targeting Cr-spinel, employed an accelerating voltage of 20 keV, a 200 nA current, and a beam diameter set at “spot mode,” encompassing ~100 nm (0.1 μm) at this high of a beam current. Peak counting times were 30 seconds for major elements (Cr, Fe, Mg), 60 seconds for minor elements (Al, Ni, Ti, Mn), and 120 seconds for trace elements (Ca, Si). Background counting times were half as long. The calibrated microprobe procedure was able to reproduce Smithsonian Microbeam Standards Tiebaghi Mine Chromite (CROM; NMNH 117075) and Ilmensky Mountains Ilmenite (ILMN; NMNH 96189) within error. Acceptable analyses fell within 98-102% for elemental totals. Values for wt % SiO2, FeO, and MgO clearly identified any spots which included partial analysis of micro-inclusions, the host olivine, or other surrounding materials, and any Fe-Ti oxides, which appear nearly identical in electron backscatter (BSE) imaging. This was extremely important for geothermometry, as Al partitioning between Cr-Al-Spinel and host olivine crystals has a well-calibrated temperature dependence (Wan et al., 2008), but Fe-Ti oxides, such as magnetite, do not.

Pyroxene WDS analyses were conducted with an accelerating voltage of 20 keV, a beam current of 30 nA, and a beam diameter of a 5 μm circular spot. Major (Si, Na, Mg, Al, Fe, Ca) and minor (Ti, Mn, Cr, K) elements were measured for groundmass crystals and, where present, phenocryst cores, rims, and different sector zonations, easily identified by variations in Al or Ca seen in either BSE grayscale or rapid WDS x-ray maps. Lava from Cerro Overo maar, La Albóndiga dome, and The Puntas Negras-El Laco lava flow contain only clinopyroxene, dominantly diopside or augite. The El País Lava Flow contained both clinopyroxene (augite) and orthopyroxene (magnesian enstatite). Analyses of established Smithsonian standards Kakanui Augite (KAUG; NMNH 122142) and Natural Bridge Diopside (NBDI; NMNH 117733) at the beginning, middle, and end of runs were checked against published values to monitor the
accuracy and consistency of each analytical run. The window of total values ranged 97 -101% for accepted pyroxene spot analyses.

**Spot Analyses of Melt Inclusions and Groundmass Glass**

Groundmass and melt inclusion glass WDS spot analyses were conducted with an accelerating voltage of 20 keV, a beam current of 30 nA, and a broad spot size of 30 μm. Smaller inclusions were analyzed with beam diameters of 20 μm, 10 μm, or 5 μm as needed. The area of analysis was expanded as much as possible to minimize alkali migration through the glass and reduce beam damage to the sample, both of which are of greater concern when the target lacks a crystalline structure. A large group of elements, including some volatile species, were measured (Si, Al, Na, Mg, Ca, Cl, S, P, Ni, Fe, Mn, Cr, Ti, K), allowing for the difference between measured totals and 100 % to be interpreted as the percentage of water, which cannot be measured directly by EPMA. However, in the majority of analyses, elemental totals nearly at 100 % indicated the target material was degassed. Smithsonian basaltic glass samples A-99 (Makaopuhi Lava Lake, HI) and VG-2 (Juan de Fuca Ridge) could be consistently reproduced within error by the glass analysis procedure.

**Elemental (X-ray) Maps**

Full thin section WDS and EDS x-ray intensity maps were acquired by EPMA with a 15 keV accelerating voltage and a 30 nA beam current, with a 2 ms dwell time for large 10 x 10 μm pixels. This set-up produced maps of entire 18 x 35 mm thin sections (1800 x 3500 pixels) in 5-6 hours. Data from major element WDS maps (Mg, Fe, Ca, Si, and K or Na) were combined (added or subtracted) to create maps of a single, isolated mineral phases. For example, starting with an olivine-pyroxene-plagioclase-glass sample, addition of X-ray intensity from the Fe and Mg maps and subtraction of Ca and alkali intensity values produces a map highlighting only olivine crystals. These resulting maps can then be used to extract data on mineral modal percentages, crystal morphology and distribution, crystal orientation, and other quantifications of petrographic data (e.g. Higgins, 2006).

High resolution WDS compositional maps of single olivine crystals for major (Mg, Fe, Si), minor (e.g. Mn, Ca, Ni), and trace (e.g. Cr, Co, Ti, Al, Na, P) elements were obtained at the UI microprobe facilities for samples where olivine is present (i.e. Cerro Overo, La Albóndiga, Puntas Negras-El Laco). Diffusion studies commonly focus on Fe and Mg concentrations in olivine, although the cations Mg$^{2+}$ and Fe$^{2+}$ rapidly diffuse through the crystalline lattice, erasing original
zonation (Milman-Barris et al., 2008 and references therein). Ni and Mn diffuse slightly slower, but early-formed zoning is likely to be reset by diffusion, as well (Costa et al., 2008). “Primary zoning,” representing the original growth sequence of the crystals, can be captured by the distribution of concentration of P and Al, although Al zoning is often weak or absent, (Milman-Barris et al., 2008; Welsch et al., 2013, 2014; Shea et al., 2015). Olivine were chosen for trace element mapping based on the selection criteria of Shea et al.: crystals with archetypal morphology, displaying clear skeletal growth, with some apparent Fe-Mg zoning, and with an orientation in the section close to crystal axes $a$, $b$, or $c$ (2015). X-ray intensity map analyses were collected for compatible (Fe, Mg, Mn, Ni, Co) and incompatible (Ca, Al, P, Na, Ti, Cr) elements in the olivine lattice using the JEOL Superprobe at the University of Iowa. Acquisition employed a 20 keV accelerating voltage, a 300 nA beam current, a resolution of 1.5 by 1.5 μm pixels, and 300 μs dwell time per pixel. While the first maps included the entire set of compatible and incompatible elements listed above, eventually only Fe, Mg, Ni, Mn, and P were mapped by Wavelength-Dispersive X-ray Spectroscopy (WDS), as all zoning trends were visible in these five elements. A larger set of elements (Na, Mg, Al, Fe, Ca, K, Si, O) were concurrently mapped by Energy-Dispersive X-ray Spectroscopy (EDS), a quicker but lower resolution and less quantitative method.

**Smithsonian Microbeam Standards**
Springwater Olivine (Fo$\text{_{83}}$; NMNH 2566)
San Carlos Olivine (Fo$\text{_{90}}$; NMNH 111312-44)
Tiebaghi Mine Chromite (CROM; NMNH 117075)
Kakanui Hornblende (KHOR; NMNH 143965)
Kakanui Augite (KAUG; NMNH 122142)
Kakanui Anorthoclase (KANO; NMNH 133868)
Durango Fluoro-Apatite (FLAP; NMNH 104021)
Natural Bridge Diopside (NBDI; NMNH 117733)
Glass, Basaltic, A-99, Makaopuhi Lava Lake, HI (NMNH 113498-1)
Glass, Basaltic, VG-2, Juan de Fuca Ridge (NMNH 111240-52)
Ilmenite, Ilmen Mnts., USSR (ILMN; NMNH 96189)
Magnetite, Minas Gerais, Brazil (NMNH 114887)
Microcline, location unknown (NMNH 143966)
Plagioclase (Labradorite) Lake County, OR (NMNH 115900)

**Astimex 53 Minerals Standard Mount MINM25-53**
Nickel Silicide (synthetic)
Melt Inclusions – EMPA and LA ICP-MS at UI

The compositions of olivine-hosted melt inclusions were analyzed initially by Ingrid Ukstins Peate at Washington State University using a New Wave Research UP-213 Laser Ablation System and Thermo Scientific X-Series 2 ICP-MS in 2009. Additional microprobe analyses were performed by myself at the University of Iowa on a JEOL Superprobe 8230 in 2016. For microprobe analyses, melt inclusion-bearing crystals of olivine were handpicked from the olivine phenocryst separates derived from crushed and sieved samples of basaltic andesite. Crystals were individually mounted in ~ half centimeter sections of ¼-inch aluminum tubing with Dentsply caulk orthodontic resin™ which can easily be melted with the lowest settings of a hotplate. The mounted crystal tubes were set in a 1-inch stainless steel electron microprobe mount with six positions for tube-mounts to allow for simultaneous polishing and analysis. The crystals were polished with an auto-polisher until a melt inclusion was exposed at the surface. Crystals with exposed inclusions were removed from the stainless steel mount and replaced with an un-polished crystal. Olivine ¼-inch tubes with exposed melt inclusions were then given a final polish with a fined-grained (6 μm followed by 1 μm) grit, cleaned with ethanol, set in round brass microprobe mounts, and carbon-coated for EPMA.

Olivine-hosted melt inclusions were heated in a gas-mixing furnace at ~ 1200 °C for 10-15 minutes and then rapidly quenched to re-homogenize the inclusions to a glass ostensibly representing the nature of the melt as it was trapped. This process re-melts the contents of inclusions without melting the host crystal, removing the compositional heterogeneity induced in inclusions from post-entrapment crystallization (e.g. Kent et al., 2008). To account for compositional changes caused by re-homogenization (e.g. Fe-Mg diffusion or re-crystallization of olivine along the inclusion rim), olivine was added or subtracted from the measured melt inclusion compositions until the melt was in equilibrium with the olivine host (Danyushevsky et al. 2000, 2002; Kent et al., 2008). A Microsoft Excel spreadsheet freely distributed by Danyushevsky et al. (2000) takes raw inclusion and host olivine compositional data (in weight %) and calculates olivine stoichiometry, and the forsterite content (Fo) of both olivine and inclusions. The spreadsheet can then be used to add or subtracts olivine from the melt inclusion until equilibrium is established, as indicated by matching Fo composition between inclusion and host. These corrected compositions are reported.
Geothermometer and Barometer Models

Temperature and pressure estimates were modelled for different mineral phases and/or whole-rock compositions for each of the investigated volcanic centers using data from ICP-MS and EPMA. Since some of the thermometers and barometers include a dependency on H₂O content, this was also estimated by iterative calculations. Geothermometers and barometers apply the basic principles of thermodynamics to natural geologic materials, linking experimental and/or theoretical work to quantify the pressure- or temperature-dependent partitioning of elements between phases. Calculating temperature and pressure for different geologic processes is dependent on recognizing chemical equilibria which have significant differences in entropy (thermometers) or volume (barometers) between products and reactants (Putirka, 2008). Volcanic systems are difficult to work with as they are highly dynamic, generally have fewer crystalline phases, and often carry a compressible liquid phase which has no stoichiometric constraints on composition (Helz & Thornber, 1987; Putirka, 2008). Models have been developed and calibrated for volcanic systems, however, dealing with elemental partitioning between two concurrently growing minerals, between a mineral and the source “liquid” from which the crystal is forming, or simply from the major element chemistry of the whole-rock.

Many of the experimentally-established and well-calibrated thermometers and barometers for volcanic systems use equilibrium partitioning between crystalline phases and liquid (Putirka et al., 2008). While it is easy to establish what represents a crystalline phase (i.e. minerals), determining the correct composition for the liquid in which the crystal grew is not entirely straightforward. Bulk rock may represent the overall magmatic system, and thus the hypothetical liquid composition, but as phases are crystallizing, the liquid composition is changing. Addition of xenocrysts, antecrysts, and country rock will also skew bulk rock away from “real” liquid composition. Groundmass-only measurements are likely more reliable if they can be reasonably argued to have not been affected by post-crystallization assimilation of xenolithic material. While thermometers and barometers based only on crystalline phases maybe more complicated to use, they likely present better constraints.

First-order approximations for magmatic conditions come from stable phases observed in the rocks. Olivine, the dominant phenocryst in Cerro Overo, crystallizes with variable distribution of Mg and Fe between different systems, and Olivine is generally more magnesian
and less ferrous than the coexisting melt. Partitioning between liquid and crystal depends on both the availability of the two cations in the bulk composition and temperature of the system during crystallization. If equilibrium between phases (here liquid and olivine) can be established, meaningful temperature information can be extracted from this system based on equilibrium partition coefficients. Olivine is relatively simple to approach as Fe/Mg exchange occurs at a relatively constant ratio with little variation due to temperature or composition.

A critical first step in thermometry and barometry calculations is ensuring the input data exactly matches the form with which each model has been calibrated; a model employing cation fractions will not produce valid results with input data in mole fraction or wt% form (Putirka, 2008). For this work the first step was the creation of MATLAB code which automatically parsed microprobe data by component (i.e. measured oxide) and recalculated all data into the various schemes used in calculations (cation and mole proportion and fraction, Mg#, Cr#, and FeO\text{total}). Starting with data in spreadsheet format, this code produced data structures of the style TYPE.field, where ‘field’ was dynamically allocated based on the available analyses. The entire parsed and configured dataset could be then easily passed into additional functions, written specifically for this project, which calculate P and T from a variety of different thermometers and barometers, producing a range of values.

Additional Calculations were based on the methods described by Putirka (2008), many of which have been consolidated in Microsoft Excel spreadsheets freely distributed on his website (www.fresnostate.edu/csm/ees/faculty-staff/putirka.html). These spreadsheets are designed to take mineral or melt (i.e. whole-rock or glass) compositions and rapidly compute both the modelled temperatures and pressures as well as auxiliary information, such as partition coefficients. Excel can be forced to perform iterative calculations to solve for two variables at a time, allowing temperature, pressure, and H2O content to all be resolved if at least one value is known, estimated, or not required for a specific model.

**Geochronology: U/Pb & U/Th-He Dating of Zircon**

Data for zircon (ZrSiO₄) crystallization and re-heating from felsic xenoliths found at Cerro Overo maar was generated by Dr. Bill McClelland. Crystallization age was determined from U and Pb isotopic measurements conducted by magnetic sector high resolution inductively-coupled plasma mass spectrometry (HR-ICP-MS) and U/Th-He reheating ages were determined from U and Th isotopic measurements by HR-ICP-MS and He measurements analyzed with an
Alphachron MkII He extraction/measurement system. The crystallization ages represent the formation of igneous zircon and thus represent the eruption of the original ignimbrite. Re-heating age of Zircon represents the age at which the crystal was last brought above its helium closure temperature (175–193 °C) (Reiners, 2005), and is determined from subsequent accumulation of He created from the radioactive decay of U and Th.
Chapter 1: Structural control of mafic monogenetic volcanism within the arc of the 21°- 24° S large silicic province of the Altiplano-Puna region of the central Andes.
Abstract

Volcanism in the Central Andes is dominated by calc-alkaline intermediate composition lava erupted at stratovolcanoes of the arc front and caldera-sourced eruptions of felsic ignimbrites (Stern, 2004; Blum-Oeste & Wörner, 2016). Lavas with compositions outside of this limited bimodal distribution are mainly restricted to the back-arc, where multiple melting and tectonic regimes overlap (Kay et al., 1994; Matteini et al., 2002; Kay et al., 2009; Hoke & Lamb, 2007; Norini et al., 2013). Within the arc front itself, however, small volumes of uncommon lava compositions (for the Central Andes) are erupted along faults and zones of crustal weakness. While volumetrically insignificant in the context of the Andean arc front, such lavas provide important information about central Andean magmatism which is usually obscured by the dominant bimodal compositions. For example, the nature of the parental melts delivered to the crust which are eventually erupted as intermediate arc lavas is poorly constrained as mafic lavas are nearly absent from the region (e.g. De Silva, 1989a; Stern, 2004). A network of lithosphere-scale orogen-oblique transverse faults and middle- to upper-crustal orogen-parallel thrust faults have provided magmatic pathways through the Andean crust at ~23° S and a small number of monogenetic volcanoes have delivered uncommon lavas to the surface which provide important constraints on melting and crustal processing in the Central Andes.

This chapter describes several instances of minor volcanism which have erupted lava compositions uncommon in the central Andean arc front. The composition, volcanology, or tectonic setting of these minor volcanoes have not been previously reported in significant detail (Zeil, 1964; Gardeweg & Ramirez, 1982; De Silva, 1989a; González et al., 2009). Cerro Overo is a solitary maar which erupted olivine-phyric basaltic-andesite in the Quaternary at the intersection of different fault systems and represents the most mafic arc magmatism within the main arc of the Central Andes. An eruption of olivine- and clinopyroxene-bearing basaltic andesite lava within the Cordón de Puntas Negras along a transverse fault lineament at the eastern margin of the arc represents hybrid mafic arc/back-arc magmatism. Aphyric andesites erupted along thrust-faults at the SE margin of the Salar de Atacama define the Tilocálar Group, a series of loosely-related, adakite-like minor volcanoes west of the arc front. These three instances of minor volcanism producing uncommon composition lava are all associated with significant structural features and provide evidence for a central Andean magmatic system with a much greater diversity of melt origins and compositions than has been observed at the surface.
Introduction

The structure of the tectonic Altiplano-Puna high plateau region in the Central Volcanic Zone (CVZ) of the Andes is characterized by activity along both orogen-parallel thrust faults and orogen-oblique transverse lineaments accommodating crustal shortening of double-thickened crust. In three dimensional models of the Puna crust, the main fault planes of these two systems intersect at depth and are considered as different parts of the same tectonic system (Norini et al., 2013; Zhou et al., 2013), which control magmatic pathways and the emplacement of volcanoes. Instances of Quaternary mafic to intermediate monogenetic volcanism across the subduction arc of the Central Andes at ~23° S are the result of magmas delivered directly from the lower crust to the surface along this interconnected fault system. These lavas are end-member compositions not normally seen at the surface of the Altiplano-Puna high plateau region in northern Chile. Expansive caldera-erupted ignimbrite sheets distinguish this area as a unique volcano-tectonic subregion (21° - 24° S) known as the Altiplano-Puna Volcanic Complex (De Silva, 1989a; De Silva & Francis, 1991). The seven sampled locations are all monogenetic volcanoes located along regional structural features (i.e. crustal lineaments, reverse faults, and antiforms), which interact with the subduction arc of the Andes in the Altiplano-Puna region.

The Altiplano-Puna region is dominated by bimodal, felsic - intermediate volcanism and notoriously lacks a mafic volcanic component to shed light on the nature of parental magma(s) being delivered to the crust, which eventually evolve to form the ubiquitous arc andesites and crustal ignimbrite volcanism (De Silva & Francis, 1991; Coira et al., 1993; Salisbury et al., 2011). Primary melts of the central Andes are thought to first undergo differentiation at the base of the crust (MASH zone) before being subjected to either storage in a series subvolcanic magma chambers (AFC processes) or are injected into the 10 – 20 km deep, sill-like Altiplano-Puna Magma Body, the magma chamber that supplies the massive rhyo-dacitic caldera complexes of the region (De Silva, 1989b; Chmielowski et al., 1999; Zandt et al., 2003; Prezzi et al., 2009; Kay et al., 2010; Ward et al., 2014; Perkins et al., 2016). Back-arc volcanism of the Altiplano-Puna region ranges from basaltic to rhyolitic and displays compositional features of an intraplate origin distinct from a fluid-flux melting genesis (Kay et al., 1994; Davidson & De Silva, 1992). Magmatism in the back-arc has been attributed to removal of the eclogitized lithospheric root and slab roll-back accompanied by upwelling of hot asthenosphere, and surface volcanism displays a strong association with structural lineaments and upper crustal faulting (Davidson &
Cerro Overo maar and associated La Albóndiga dome (Figure 14) result from Quaternary eruptions of olivine-phyric basaltic andesite, which represent a regional mafic end-member for the arc (e.g., De Silva & Francis, 1991). The two lavas were erupted along an orogen-parallel antiformal feature, the Cordón Altos de Toro Blanco, which we propose is a splay of the larger Miscanti thrust fault some 10-12 km to the west (e.g., Lin et al., 2016). Cerro Overo maar and La Albóndiga dome are also located along the extrapolated path of the orogen-oblique Calama-Olacapato-El Toro (COT) fault lineament as it passes through the arc. The COT lineament is one of seven major NW-SE trending transverse fault zones accommodating stress in the modern Central Andes and has been associated with arc and back-arc emplacement of calderas, monogenetic centers, and stratovolcanoes (Riller et al., 2001; Matteini et al., 2002; Petrinovic et al., 2006; Acocella et al., 2011; Norini et al., 2013). Magmas along the COT are derived from the continental subduction arc, crustal melting, and/or adiabatic melting of upwelling asthenosphere following delamination of the lithospheric root of the Puna (Matteini et al., 2002; Acocella et al., 2011). East of Cerro Overo, at the back margin of the central Andean arc, a previously un-described olivine- and clinopyroxene-phyric basaltic andesite was erupted within the Cordón de Puntas Negras volcanic complex, which also follows the COT fault lineament. The Puntas Negras mafic lava represents another regional mafic endmember although it is compositionally associated with arc/intraplate transitional magmatism.

Basaltic andesite lava (54 wt % SiO₂, 7.4 wt % MgO) from Cerro Overo maar (23.52° S, -67.66° W), which represents the least-differentiated volcanism in the region (De Silva & Francis, 1991), avoided the full extent of (AFC) magmatic processing in middle-crustal storage zones or long-lived sub-volcanic plumbing systems. Crustal contamination has occurred, as indicated by silicic xenoliths and the isotopic nature of the lava, modeled as an estimated 10 – 15 % crustal melt combined with mantle-derived material (Rosner et al., 2003). The olivine- and pyroxene-phyric basaltic andesitic (53 wt % SiO₂, 6.7 wt % MgO) lava flow from the Puntas Negras volcanic complex (23.75° S, 67.47° W) is similar, although petrographic, isotopic, and compositional characteristics suggest the Puntas Negras magma experienced less crustal contamination and more extensive fractional crystallization than Cerro Overo magma. Regardless, both of these
basaltic andesites are the least-differentiated magmas ascended to the surface along faults of the Central Volcanic Zone.

Immediately west of (i.e. in front of) the frontal arc at ~ 23.8° S, small volumes of aphyric intermediate lava have been erupted along contractional features at the southeast margin of the Salar de Atacama (Table 7). Focused deformation occurs in this area of the Altiplano-Puna, the Lomas de Tilocálar, as an anomalously dense, subsiding lithospheric block beneath the Salar de Atacama acts as an indenter causing counter-clockwise motion (Kuhn, 2002; Lin et al., 2016). Monogenetic volcanism manifested along the hinge zones of fault propagation folds generated Cerro Tujle maar (23.83° S, 67.95° W), the polygenetic volcano Tilocálar Sur (23.98° S, 68.13° W), and the lava flows of Tilocálar Norte (23.95° S, 68.11° W). Magmas at these centers are high temperature, calc-alkaline andesite and dacite (59 – 63 wt % SiO₂, 2.4 – 3.6 wt % MgO) derived from high-pressure melting of metabasaltic lower crust, potentially delivered to the upper mantle by forearc subduction erosion or foundering of the lithospheric root. These lavas display an adakite-like signature reflecting their derivation from a mafic (as opposed to ultramafic) source with an intermediate composition primary melt (e.g., Martin et al., 2005). Radiogenic Sr isotopic ratios indicate a crustal source, and not derivation from the basaltic slab. For such an origin, the andesitic-dacitic composition is relatively undifferentiated magma. Both the Calama-Olacapato-El Toro lineament and its southern sister, the Archibarca lineament, are ~ 30 km from the west-of-the-arc Tilocálar Group monogenetic volcanic features. The eruptions of less-differentiated lavas at Tilocálar and Cerro Tujle along N-S trending contractional features at a distance from the deep-cutting transverse lineaments are further evidence the two fault systems are connected. Thrust features cut the upper (< 20 km) crust, and localized zones of extension provide vertical weakness that focus volcanism along these features (Gonzalez et al., 2009; Lin et al., 2016). Transverse lineaments cutting to the lower crust or even the base of the lithosphere provide pathways for magmas to reach the upper crust without experiencing the widespread, extensive differentiation by assimilation or storage that defines the CVZ (e.g., Matteini et al., 2002; Norini et al., 2013).
Table 4 - list of sample localities (lat/long) with brief lithology descriptions

<table>
<thead>
<tr>
<th>Location</th>
<th>Volcano Type</th>
<th>Rock Type</th>
<th>Mineralogy*</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo</td>
<td>Maar</td>
<td>Basaltic Andesite (54 wt % SiO₂)</td>
<td>olv', (sp, cpx, plg, ± qtz)</td>
<td>-23.5178</td>
<td>-67.6623</td>
</tr>
<tr>
<td>Cerro Overo</td>
<td>Xenoliths</td>
<td>Rhyo-dacite (65-75 wt % SiO₂)</td>
<td>± qtz, plg, ox, bt, amph, olv</td>
<td>-23.5266</td>
<td>-67.6851</td>
</tr>
<tr>
<td>Atana</td>
<td>Ignimbrite</td>
<td>Rhyo-dacite (63-72 wt % SiO₂)</td>
<td>qtz, ox ± plg, bt, hbl</td>
<td>-23.8358</td>
<td>-67.9519</td>
</tr>
<tr>
<td>La Albóndiga</td>
<td>Dome</td>
<td>Basaltic Andesite (56 wt % SiO₂)</td>
<td>olv', (sp, cpx, plg)</td>
<td>-23.5266</td>
<td>-67.6851</td>
</tr>
<tr>
<td>Punta Negras</td>
<td>Flow complex</td>
<td>Basaltic Andesite (53 wt % SiO₂)</td>
<td>olv', cpx', (sp, plg)</td>
<td>-23.7431</td>
<td>-67.4760</td>
</tr>
<tr>
<td>El País Lava</td>
<td>Flow</td>
<td>Basaltic Andesite (56 wt % SiO₂)</td>
<td>cpx', opx', plg'</td>
<td>-23.7972</td>
<td>-67.9619</td>
</tr>
<tr>
<td>Cerro Tujle</td>
<td>Maar</td>
<td>(trachy)andesite (59 wt % SiO₂)</td>
<td>olv' - rare (plg, ox)</td>
<td>-23.8358</td>
<td>-67.9519</td>
</tr>
<tr>
<td>Tilocálar Norte</td>
<td>Stratovolcano</td>
<td>Andesite/Dacite (64 wt % SiO₂)</td>
<td>aphyric (plg, ox)</td>
<td>-23.9503</td>
<td>-68.1071</td>
</tr>
<tr>
<td>Tilocálar Sur</td>
<td>Stratovolcano</td>
<td>Andesite (59 wt % SiO₂)</td>
<td>olv' - rare (plg, ox)</td>
<td>-23.9770</td>
<td>-68.1297</td>
</tr>
<tr>
<td>Cerro Chascón</td>
<td>Dome</td>
<td>Dacite – Basaltic Andesite mix (59 wt % SiO₂)</td>
<td>plg', cpx', olv', qtz', (ox)</td>
<td>-23.0182</td>
<td>-67.6882</td>
</tr>
</tbody>
</table>

*olv = olivine, sp = spinel, cpx = clinopyroxene, plg = plagioclase, qtz = quartz, bt = biotite, ox = oxides.

' - indicates phenocryst. (x) – indicates microlites.

Table 5 - Summary of chemistry and age of sampled volcanoes.

<table>
<thead>
<tr>
<th>Location</th>
<th>SiO₂ (wt%)</th>
<th>MgO (wt%)</th>
<th>K₂O + Na₂O</th>
<th>La/Yb</th>
<th>⁸⁷Sr/⁸⁶Sr</th>
<th>Age (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo</td>
<td>54.6</td>
<td>7.35</td>
<td>4.49</td>
<td>9.3</td>
<td>0.70621</td>
<td>77.4¹</td>
</tr>
<tr>
<td>La Albóndiga</td>
<td>56.2</td>
<td>7.32</td>
<td>4.36</td>
<td>8.7</td>
<td>0.70620</td>
<td>~75⁶</td>
</tr>
<tr>
<td>Punta Negras</td>
<td>52.8</td>
<td>6.71</td>
<td>4.71</td>
<td>14.3</td>
<td>0.70590</td>
<td>~75⁶</td>
</tr>
<tr>
<td>El País Lava</td>
<td>56.3</td>
<td>5.62</td>
<td>4.61</td>
<td>13.2</td>
<td>0.70679</td>
<td>~75⁶</td>
</tr>
<tr>
<td>Cerro Tujle</td>
<td>58.8</td>
<td>3.45</td>
<td>6.24</td>
<td>36.8</td>
<td>0.70647</td>
<td>~500⁶</td>
</tr>
<tr>
<td>Tilocálar Norte</td>
<td>63.4</td>
<td>2.44</td>
<td>6.98</td>
<td>60.3</td>
<td>0.70686</td>
<td>~500⁶</td>
</tr>
<tr>
<td>Tilocálar Sur</td>
<td>58.7</td>
<td>3.56</td>
<td>6.16</td>
<td>46.5</td>
<td>0.70695</td>
<td>460-730²</td>
</tr>
<tr>
<td>Cerro Chascón</td>
<td>58.5</td>
<td>3.42</td>
<td>5.27</td>
<td>7.6</td>
<td>0.70634</td>
<td>85³</td>
</tr>
<tr>
<td>C. Overo Xenolith</td>
<td>67.9</td>
<td>1.20</td>
<td>6.98</td>
<td>20.3</td>
<td>0.70950</td>
<td>4000⁵</td>
</tr>
<tr>
<td>Atana Ignimbrite</td>
<td>63.1 – 72.3</td>
<td>0.5 – 1.6</td>
<td>7.66</td>
<td>21.9</td>
<td>.7094-0.7097</td>
<td>4000⁴,5</td>
</tr>
</tbody>
</table>

¹Xenolith zircon U-Th/He Helioplot ages of 77.4 ± 5.4 ka (n=5). Uktins Peate, personal comm., 2012.
²Matrix glass ³⁹Ar – ⁴⁰Ar dates, western flank 730 ± 50 ka and center 460 ± 50 ka, Gonzalez et al., 2009.
³Sanidine ³⁹Ar – ⁴⁰Ar ages, reported as ~ 85 ka, Watts et al., 1999.
⁴K-Ar biotite ages for the Atana Ignimbrite are 3.8 ± 0.3 to 4.1 ± 0.4 Ma, Gardeweg & Ramirez, 1987.
⁵Zircon ²⁰⁶Pb/²³⁸U weighted mean age of 4.0 +/- 0.1 Ma (n = 17) McClelland, personal comm., 2013.
⁶Age approximated from degree of weathering relative to centers with known ages.
Geologic Background

To a first order, volcano locations across the Central Volcanic Zone of the Andes indicates a close association between structural features and trends of emplacement for all types of Neogene volcanism (Thorpe et al., 1984; De Silva, 1989a; Davidson et al., 1991; De Silva & Francis, 1991; Davidson & De Silva, 1992; Marret & Emmerman, 1992; Coira et al., 1993; Kay et al., 1994; Davidson & De Silva, 1995; Gonzalez-Ferrán, 1995; Kuhn, 2002; Jordan et al., 2002; Matteini et al., 2002; Richards & Villeneuve, 2002; Mattioli et al., 2006; Reutter et al., 2006; Petrinovic et al., 2006; Hoke & Lamb, 2007; Aron et al., 2008; Mamani et al., 2008; Gonzalez et al., 2009; Montero Lopez et al., 2010; Acocella et al., 2011; Del Potro et al., 2013; Burns et al., 2015). Major orogen-oblique, NW-SE trending transverse lineaments exert the most prominent control over magmatism across the arc and into the back-arc (Salfity, 1985; Riller et al., 2001; Richards and Villeneuve, 2002; Ramelow et al., 2006; Petrinovic et al., 2006; Acocella et al., 2011; Norini et al., 2013). These primary fault features show predominantly left-lateral motion (Allmendinger et al., 1983; Davidson & De Silva, 1992) and petrologic evidence suggests they cut to at least lower crustal depths (> 30 km) and potentially to the base of the lithosphere (50 – 65 km) (e.g., Matteini et al., 2002; Trumbull et al., 2006; Norini et al., 2013). Major instances of NW-SE aligned volcanism are collectively known as transverse magmatic belts (Salfity, 1985; Norini et al., 2013).

In the upper crust, compressive deformation in the Altiplano-Puna is generally distributed (Kley, 1996). A significant exception is where the anomalous, rheologically-strong Salar de Atacama lithospheric block acts as an indenter and focuses deformation at its margins as it is compressed eastward into the arc with some counterclockwise motion (Kuhn, 2002; Schurr & Rietbrock, 2004; Reutter et al., 2006). Here, N-S trending compressive features are prolific and connected by smaller lateral faults acting to transfer stress (Kuhn, 2002). Low-angle thrust faults and anticlinal folds associated with the Salar de Atacama are subjected to a degree of rotation, resulting in highly localized extension, which provides vertical pathways of weakness and focus small amounts of magmatism along compressive features (Kuhn, 2002; Aron et al., 2008; Gonzalez et al., 2009; Lin et al., 2016).

Arc volcanoes, caldera systems, back-arc volcanic centers, magma storage zones, and trans-arc minor volcanic centers show an association with one (or both) of these structural features and there is a clear genetic relationship between crustal deformation and magmatic
activity in the central Andes (De Silva & Francis, 1991; Davidson & De Silva, 1992; Kay & Kay, 1993; Kay et al., 1994; Matteini et al., 2002; Richards & Villeneuve, 2002; Gonzalez et al., 2009; Acocella et al., 2011; Norini et al., 2013). Delamination of the lithospheric root was associated with a change in the stress regime of the Altiplano-Puna region in the Plio-Pleistocene from NW-SE to E-W shortening and uplift (vertical extension) into a more complex regime involving both compression and extension (Kay et al., 1994; Allmendinger et al., 1997). This change in regional stress provided many structural weaknesses, including along reactivated fault features from pre-Andean orogeny (e.g., the basement structure) (Stern, 2004; Lin et al., 2016). Such faults and lineaments provide the pathways necessary for magmatic ascent from the deep crust or lithosphere to the surface without experiencing the extensive magmatic processing common to the central Andean arc (Davidson et al., 1991; Davidson & De Silva, 1992; Kay et al., 1994; Matteini et al., 2002; Richards & Villeneuve, 2002; Aron et al., 2008; Acocella et al., 2011; this study). Depth and connectivity of these systems dictate which magmas are delivered to the surface and their location dictates which part of the arc system is accessed. The complex faulting and structural controls that span the entire breadth of the CVZ arc provide several opportunities for fault-controlled magmatism to produce eruptions of lava compositions not commonly seen above the double-thickened lithosphere of the Altiplano-Puna region.

Major NW-SE Trending Structural Lineaments

Magma ascent in the central Andes, as in most arc settings, is dominantly controlled by density contrasts between melt and country rock, which in most cases requires mafic magmas to be extensively differentiated (i.e. evolve) during storage or stalling by assimilation, fractionation, and/or mixing (e.g., Thorpe et al., 1984; Davidson et al., 1991; Kay et al., 2010). For magma to ascend through 70 km of mainly felsic crust, low density melt must develop through extensive differentiation of magmas in sub-arc magma chambers via crustal assimilation, fractionation, and crystallization (AFC) (Davidson et al., 1991; Stern, 2004; Brown, 2007). Lineaments of crustal weakness provide opportunities for magma to rise more easily to the surface without undergoing the extensive differentiation common to the central Andean arc (e.g., Davidson & De Silva, 1992; Mattioli et al., 2006). Small batches of magma ascending along such structural controls may avoid extensive interaction with silicic country rock or stalling in upper crustal magma chambers, permitting the opportunity to study the nature of magmas
delivered to deeper portions of the CVZ arc and preceding the development of a composition dominated by crustal contamination and differentiation (e.g., Figure 15). For example, in the back-arc of the Bolivian Altiplano near the Salar de Uyuni (~ 20° S) fields of minor volcanic centers have erupted mafic lavas in a consistent NW-SE trend, reflecting the spatial control exerted by the regional crustal structural fabric (Figure 5) (Davidson & De Silva, 1992; Hoke & Lamb, 2007). Similar fault-controlled monogenetic volcanic fields are seen in the southern Puna in northwest Argentina where intraplate basalts and andesites are erupted in the back-arc, concentrated along lineaments (Kay et al., 1994; Norini et al., 2013). Frontal arc magmatism is also, in some instances, directed along these lineaments (Kuhn, 2002; Richards & Villeneuve, 2001; Matteini et al., 2002).

Several evenly-spaced major transcurrent fault lineaments cut through the Central Andes (Figure 5), in roughly parallel NW-SE orientation (Allmendinger et al., 1983; Salfity, 1985; Norini et al., 2013). In the Altiplano-Puna tectono-volcanic region, the Calama-Olacapato-El Toro (COT) fault system is the most significant structural feature passing through the frontal arc (Allmendinger et al., 1983; De Silva, 1989a). The COT lineament (Figure 2) is a left-lateral transcurrent (i.e., wrench) fault system oriented NW-SE and stretches ~ 600 km from the Chilean coast in the west to the Eastern Cordillera in northern Argentina to the east (Allmendinger et al., 1983; Matteini et al., 2002; Google Earth, 2016). One of several lineaments of similar scale in the Central Andes, the COT has controlled emplacement of post-Miocene volcanism in the Altiplano-Puna including that which generated stratovolcanoes deviating from the main arc axis, back-arc volcanic fields, and Quaternary monogenetic centers across the arc (Coira et al., 1993; Davidson & De Silva, 1992; Kay et al., 1994; Matteini et al., 2002; Accocella, 2011; Norini et al., 2013; this study). Miocene to recent deformation in the Puna plateau has been partially accommodated by orogen-oblique lineaments (e.g., the COT), along with orogen-normal shortening and crustal thickening (Isacks, 1988; Jordan et al., 1983; Allmendinger et al., 1997; Riller et al., 2001). Tectonic activity along the COT fault lineament dates back to at least the Cretaceous and is thought to have been particularly high at ~10 Ma during the Quechua deformational phase (Allmendinger et al., 1983). During this period, the Central Andes were under a compressional tectonic regime and experienced extensive crustal thickening due to eastward thrusting (Isacks, 1988; Marret et al., 1994). From 10 - 5 Ma, the Altiplano-Puna region was dominated by thickening of ductile lower crust and thinning of the lithosphere
Matteini et al., 2002). In the late Miocene, the Puna plateau experienced additional Basin and Range type tectonics with WNW-ESE shortening and ENE-WSW extension (Isacks, 1988).

Local extensional and transtensional tectonics may play a role in permitting magmatic ascent along the COT lineament, facilitating rapid magma transport along upper-crustal faults with relatively reduced crustal contamination. Compositions of lava erupted at the Tul Tul, Del Medio, and Pocitos composite volcanoes (24.15° S, 67.15° W) are more primitive than expected and likely a result of this fault system channeling melt generated from asthenospheric upwelling (Matteini et al., 2002). The COT lineament has also been implicated in emplacement of intraplate-affinity, shoshonitic back-arc basalts, which are some of the most primitive rocks (~48 wt % SiO₂) in all the Central Andes (Kay et al., 1994; Matteini et al., 2002). Further east, involvement of continental basement once again obscures the character of primary melts. Where major structural lineaments intersect the main arc, subduction magmas generated from dehydration of the Nazca Plate have an increased likelihood of reaching the surface without extensive contamination or evolution (e.g., Davidson & De Silva, 1992). The Cordon de Puntas Negras Volcanic Complex (23.6° S) consists mainly of concentrated arc volcanism directed eastward along the COT lineament, although the majority of eruptive centers within the complex remain unstudied (Figure 16) (Gardeweg & Ramirez, 1987; Matteini et al., 2002). Minor eruptions of olivine-phyric basaltic andesite along the COT lineament within the Cordon de Puntas Negras complex (23.74° S, 67.47° W) and within the arc near the base of Lascar stratovolcano at Cerro Overo Maar (23.51° S, 67.66° W) have been recognized as the most mafic eruptions of subduction magmatism in the Altiplano-Puna Volcanic Complex (De Silva, 1989a; this study).

The Salar de Atacama Anomalous Lithospheric Block

In the modern central Andes around 23° - 24° S, the main arc of the Altiplano-Puna and eastward (Figure 5) is characterized by basement blocks forming morphological highs and lows in loosely N-S trends (Matteini et al., 2002; Reutter et al., 2006). Local depressions have also been formed as pull-apart basins developed in large-scale strike-slip fault systems (Matteini et al., 2002). Salars (salt flats) form in the low regions partially infilled with recent sediment. Bracketing the Altiplano-Puna arc segment on the west (trench-ward) is the Salar de Atacama, an internally-drained basin presiding over an anomalously dense, 67 km thick lithospheric block, which forms a substantial topographic low (Figure 6; Figure 17) (Schurr & Rietbrock, 2004;
Arriagada et al., 2006; Reutter et al., 2006). Seismic data indicate a strong, dense underlying crustal block without a clear Moho and gravitational anomalies caused by dense bodies of unknown origin at 10-15 km and 4-6 km (Reutter et al., 2006 and references therein). Studies indicate the seismic properties of crust and mantle beneath the Salar de Atacama basin differ strongly (high $Q_p$ and $v_p$) from the surrounding lithosphere (Schurr & Rietbrock, 2004). Some (e.g., Yuan et al., 2002; Arriagada et al., 2006) have suggested the block is cold and dynamically subsiding, possibly in coordination with subduction of the Nazca plate. Eastward migration and counter-clockwise rotation of the Atacama block has created extensive faulting at the boundary of the basin (Figure 6), with associated minor volcanism (e.g., Cerro Tolonchar, Cerro Tujle, Tilocálar Norte and Sur) (Gonzalez et al., 2009; Lin et al., 2016).

The volcanic arc curves eastward around the Salar de Atacama basin, suggesting the Atacama basement irregularity extends deep enough to exert an influence on subduction-initiated volcanism, which originates in the upper asthenosphere. Mechanical coupling with the subducting slab has been inferred beneath the Salar de Atacama from tomographic data (Figure 18; Figure 4) (Yuan et al., 2002; Schurr & Rietbrock, 2004; Prezzi et al., 2009). In this way, the subsiding, exceptionally dense lithosphere blocks asthenospheric flow above the slab, deflecting subduction-related magmatism eastward in the Altiplano-Puna region around 23 °S (Yuan et al., 2002; Arriagada et al., 2006; Reutter et al., 2006). The thick, rheologically strong crust also acts as a resistant block, which concentrates compressional stresses at its boundaries by indenter-driven deformation (Kuhn, 2002; Muñoz et al., 2002; Arriagada et al., 2006; Aron et al., 2008; Lin et al., 2016). Indenter-driven deformatonal features are prolific at the eastern margin of the Atacama lithospheric block (Figure 6; Figure 19), particularly in the southeast where N-S trending pressure ridges, low-angle reverse faults, and strike-slip faults are numerous (e.g., Kuhn, 2002; Schurr & Rietbrock, 2004; Reutter et al., 2006; Aron et al., 2008; Gonzalez et al., 2009; Lin et al., 2016).

Thrust faulting at the margin of the Salar de Atacama likely cuts the entirety (~ 15 – 20 km) of the upper-crustal brittle zone (Lin et al., 2016), providing pathways for magma to reach the surface without interacting with upper-crustal magma storage areas where extensive assimilation, fractionation, and crystallization (AFC) processes occur (Davidson et al., 1991; Chmielowski et al., 1999; Zandt et al., 2003). The extent to which these features exert control over the location and/or composition of volcanism has not been thoroughly investigated,
although an association between contractional features and minor volcanism at the southeastern margin of the Salar de Atacama has been noted (Gardeweg & Ramirez, 1982; Gonzalez-Ferrán, 1995; Kuhn, 2002; Aron et al., 2008; Gonzalez et al., 2009; this study). In this compressional domain, at times labeled as the Lomas de Tilocálar, sigmoidal belts of linearly-arranged N-S pressure ridges and east vergent fold-and-thrust structures indicate sinistral transpression and localized clockwise block rotations (Kuhn, 2002; Lin et al., 2016). This concentration of tectonic features is due to deformation from the Atacama indenter guided by pre-existing basement structures. Complexities of compression with rotational aspects have produced highly localized extension and vertical weak zones formed parallel to fold axes (Aron et al., 2010). The occurrence of minor volcanism at the hinge zones of the Tilocálar, Tilomonte, and Tolonchar ridges in this region (Figure 19) indicates these weak zones offer pathways for magma to move through the upper crust to the surface (Figure 20). Where magmatic plumbing interacts with this deformation, the possibility arises of tapping into magmas not usually seen at front-arc volcanoes, such as at the highly fractionated andesites erupted at the small Tilocálar Norte and Sur volcanoes and Cerro Tujle maar.

The Tilocálar, Tilomonte, and Tolonchar Ridges

The Tilocálar Ridges and Tilomonte Ridges are a series of subparallel, north-south trending, eastward-verging anticlinal and thrust-fault features at the southeastern margin of the Salar de Atacama, in the Lomas de Tilocálar depression (Figure 19). Plio-Pleistocene compression and reactivation of older faults has created predominantly N-S striking, east-vergent thrust faults (Kuhn, 2002). The narrow Lomas de Tilocálar basin is (structurally) dominated by these ridges and bounded by the Cordón de Lila basement uplift to the west and the western slope of the Western Cordillera (i.e., the modern volcanic arc) to the east. The Tilocálar, Tilomonte, and Tolonchar ridges are formed from folded Pliocene ignimbrite sheets, dominantly the massive ~ 3.1 Ma Tucúcaro-Patao ignimbrite, and range from 50 to 400 m in height (Ramirez & Gardeweg, 1982; Gonzalez et al., 2009). The Lomas de Tilocálar deformation belt is the surficial expression of the eastward motion and counter-clockwise rotation of the crustal block beneath the Salar de Atacama (i.e., indenter-driven deformation), and hosts structurally-controlled minor volcanism (Kuhn, 2002; Gonzalez et al., 2009).

The crystalline Cordón de Lila basement uplift is acting as a local indenter inducing compression of the Tilocálar region (Kuhn, 2002) while the dense Atacama crustal block is acting
as an indenter on the larger scale of the Altiplano-Puna region (Arriagada et al., 2006). Lin et al.
(2016) suggest the Tilocálar and Tilomonte ridges formed as a result of pure-shear fault-bend
folding (i.e., a fault-related fold of a blind reverse fault) with a major décollement at about 2.5
km depth, and have been interpreted as splay thrusts of a larger fault (Kuhn, 2002). Minor
volcanism occurs at areas of localized extension along the hinge zones of these ridges (Gonzalez
et al., 2009; Lin et al., 2016). To the east, a prominent fault-propagation fold, the Tolonchar
Ridge (Also known as the Cordón de Tujle), is part of the same compressional system with
significant clockwise rotation and is also associated with volcanism in its hinge zone (Figure 19).
Deformation style in this region is strongly influenced by pre-existing basement structure and is
largely transpressive with strike-slip, wrench faults, and thrust fault splays connecting sigmoidal
and segmented ridges (Kuhn, 2002; Lin et al., 2016). This structure and the corresponding
basement have been interpreted as pre-Andean zones of structural weakness upon which post-
Miocene volcanism has been superimposed (Kuhn, 2002 and references therein).

Two Pleistocene-Holocene minor volcanoes at the hinge zone of the Tilomonte Ridges
and along the eastern (steeper) limb are, respectively, the geographically eponymous Tilocálar
Sur (-23.98, -68.13) and Tilocálar Norte (-23.95, -68.11), referred to jointly in this work as “the
Tilocálar” or “the Tilocálar volcanoes” (Figure 19; Figure 22; Figure 23). To the east, at the
northern end of Tolonchar Ridge (also known as the Cordón de Tujle), Cerro Tujle maar is the
result of an eruption of lava compositionally and petrographically similar to that of the
Tilocálar, emplaced along the hinge zone of the ridge. Structurally, Tolonchar ridge has been
inferred to have formed in a similar manner to the Tilocálar and Tilomonte ridges and the
structural mechanisms influencing minor volcanism (i.e., vertical pathways of weakened upper
crust) can be reasonably assumed to be comparable across the ridges of the Lomas de Tilocálar
basin (Kuhn, 2002; Aron, 2008; Gonzalez et al., 2009; Lin et al., 2016). The degree of weathering
and erosion at the Tilocálar and Cerro Tujle is practically identical, indicating all three are likely
of similar Quaternary age (Gardeweg & Ramirez, 1982; De Silva & Francis, 1991; Gonzalez et al.,
2009).

Young, andesitic volcanism correlated with structural features was originally recognized
in the Lomas de Tilocálar sub-region by Gardeweg & Ramirez (1982, in Spanish) and then by De
volcanism occurred during arc-perpendicular (E-W) compression with the listric and/or ramp-flat
thrust fault planes acting as magma channels, supported by the tectonic analyses of Kuhn (2002). The most in-depth study of the tectonic structure of the ridges (Lin et al., 2016) simply states “the topography [of the ridge] ... is complicated by young deposits of volcanic lava flows.” The regional tectonic regime has shifted and even inverted from extension to compression during growth of the Andes and the Altiplano and Puna high plateaus with compression dominating both during the Cenozoic and Miocene-recent (De Silva, 1989a; Kuhn, 2002; Stern, 2004; Reutter et al., 2006). The maximum compressional stress axis has been oriented consistently east-west over the last 28 Myr, and deformation has gradually migrated eastward (Jordan et al., 2002; Reutter et al., 2006; Aron et al., 2008). The ages of the 3.2–3.1 Ma Tucúcaro-Patao ignimbrite and the 800 ka and younger lava from Tilocálar Sur (Gardeweg & Ramirez, 1982) indicate that local structure is related to most recent tectonics. Neotectonic studies indicate the contemporary system has been active from at least the Pleistocene and is currently active (Gonzalez et al., 2009).

Reverse-faulting beneath the Salar has been active since at least 5.0 Ma, temporally overlapping with the later stages of large-volume, silicic ignimbrite eruptions (Jordan et al., 2002; de Silva, 1989 b). A history of episodic compressional deformation has been preserved at high resolution in the folding and faulting of halite deposits beneath the Salar de Atacama and investigated via deep oil-exploration boreholes and reflection seismic lines, confirming ~900 m of net reverse offset occurring during the Pliocene (700 m) and the Quaternary (200 m) (Jordan et al., 2002). Gonzalez et al. (2009) estimated fault motion of approximately 400 m over the last 3.0 Myr. The majority of features in this compressional system are blind with the topography hidden beneath evaporite deposits but an east-vergent, thin-skinned fold and thrust belt is surficially visible in volcanic rocks at the far southeast of the indenter-driven deformation zone (Jordan et al., 2002; Kuhn, 2002). The furthest eastward expression of this compressional belt is an 80-100 km long, 400 m high structure along the Miscanti Fault at the western limit of the active arc (Aron et al., 2008; Aron et al., 2010).

The western limit of the Tilocálar area is the north-plunging Cordón de Lila anticline composed of Paleozoic rocks (uplifted basement) that protrudes as a “peninsula” into the evaporite deposits of the Salar de Atacama and helps to define the southern extent of the salar basin (Kuhn, 2002). East of this large anticline is the Tilocálar Valley (Lomas de Tilocálar), a low area of Miocene-and-later ignimbrite sheets that slope upward to the south toward the El
Negrillar monogenetic volcanic complex and the Negro de Aras volcanic field (Gonzalez et al., 2009). Note this area was formerly referred to as the “Graben of Callejon de Tilocálar” (Gardeweg & Ramirez, 1982) before subsequent investigations determined the area as a thin-skin fold-and-thrust belt (e.g., Kuhn, 1997; 2002). Moderate to high-angle, north to north-northwest striking reverse faults with Quaternary offsets cut through both the Cordón de Lila peninsula and the Tilocálar Valley (Gardeweg & Ramirez, 1982; Niemeyer, 1984; Kuhn, 1997; Jordan et al., 2002). Fault scarps in the Tilocálar Valley cut 3.2 Ma ignimbrite and display tens of meters up to 200 m of offset (Jordan et al., 2002). The southern extents of the Tilocálar and Tilomonte Ridges are covered by the El Negrillar and Negro de Aras volcanic fields (Figure 19), where reverse faults have cut nearly 30 m high scarps in andesitic to basaltic Pleistocene lavas (Gonzalez et al., 2009). Although it is clear reverse faulting was active during at least the early stages of the volcanic field, the eight main vents of El Negrillar are not obviously aligned with local structure and further study is needed to determine this volcano-tectonic relationship.

The Miscanti Fault, with its 400 m of vertical relief, represents a first-order fault, with a modeled detachment level at approximately 8 km depth, while the Tilocálar and Tolonchar ridges are part of a shallower, second-order system (Aron et al., 2008). This shallower fault system is estimated to reach detachment levels at approximately 2-3 km depth, but are subordinate features (i.e., splays) of the listric thrust faults whose detachment levels reach ~ 8 km depth, at least (Arriagada et al., 2006; Aron et al., 2008). Beneath the Salar de Atacama, seismic reflection data indicate a major fault traverses a minimum of the 1500 m total evaporite thickness at the center of the Salar (Jordan et al., 2002). Related, and possibly coupled, faults to the west of the Salar de Atacama (e.g., in the Cordillera de la Sal, the Llano de la Paciencia, and the Cordillera Domeyko) show significant offset during the Miocene and Pliocene (Jordan et al., 2002; Muñoz et al., 2002), but fault-associated volcanism has not been reported in these areas. The Cordillera Domeyko is a range of siliceous volcanic rocks and granitoids of the Permo-Triassic magmatic belt overlain by Triassic marine sediments interbedded with basaltic and andesitic volcanics (Coira et al., 1982). Volcanism directed along the fault systems in the Lomas de Tilocálar area is undoubtedly generated at greater depths than the thrust faults cut and is less evolved than the felsic rocks of the brittle upper crust (15 – 20 km) (Chmielowski et al., 1999; Zandt et al., 2003). However, the compositions of the Tilocálers and Cerro Tujle indicate upper crustal structural features allow magma to circumvent the mid- to upper-crust magma.
storage zones wherein most Central Volcanic Zone arc lavas experience extensive (AFC) processing (e.g. Davidson et al., 1991; Mamani et al., 2010).

Lascar stratovolcano to the northeast lies within the main arc along-strike of the Miscanti fault and has been suggested to be spatially and temporally linked to the same Pliocene-recent fault system beneath the Tilocálar Ridges (Aron et al., 2008; Cembrano et al., 2008). Just southeast of Lascar stratovolcano, the mafic maar Cerro Overo and associate dome La Albándiga sit at the hinge and the base of a limb, respectively, of the Cordón de Toro Blanco anticline which runs parallel to the Miscanti Fault. Considering the listric geometry of fault systems in the area, fault-controlled volcanism will have tapped magma chambers west of the eventual eruptive site. In this way, Cerro Overo maar could result from eastward deflection of the same magma system feeding Lascar stratovolcano by upper-crustal thrust faulting splaying off of the Miscanti Fault to the west.

<table>
<thead>
<tr>
<th>Location</th>
<th>Vertical offset (m)</th>
<th>Age of offset surface layer (Ma)</th>
<th>Vertical offset rate (mm/yr)</th>
<th>Fault dipping angle</th>
<th>Long-term slip rate of the fault (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Southern Tilocálar Hills</td>
<td>250</td>
<td>3.0–3.2</td>
<td>0.078–0.083</td>
<td>25°±2°</td>
<td>0.17–0.21</td>
</tr>
</tbody>
</table>

Table 6 – Details of Quaternary tectonic motion within the subregion of the Tilocálar volcanoes as reported by Gonzalez et al. (2009). The surface layer in the area consists of the 3.1 ± 0.2 Ma Patao and 3.2 ± 0.7 Ma Tucúcaro ignimbrites (Gardeweg & Ramirez, 1982; Gonzalez-Ferrán, 1994).

**Monogenetic & Minor Volcanism**

The technical definition of the term “monogenetic” is quite literally “of a single origin.” In the context of volcanism, this can be interpreted as a volcanic center defined by a single eruptive event. In practice, however, the term “monogenetic volcanism” generally refers to volcanism which is low-volume and not long-lived or recurrent (e.g., White & Ross, 2011). This alternative use of the term includes single eruption events and also multiple flows/deposits from single or continual eruptions occurring on short time scales (years to decades), but not associated with a well-established magmatic plumbing system. Typically, monogenetic
volcanism occurs in groups or fields of tens to hundreds of maars, tuff rings, cinder cones, domes, and lava flows (Walker, 2000). These fields develop where magmatism is diffuse and often associated with relatively low magma supply. This is in contrast to volcanism that builds polygenetic stratovolcano or caldera systems, which have reliable, continuous, and focused magma supplies, which in turn lead to the formation of a well-established magmatic plumbing systems with discrete surface expressions (Walker, 2000; White & Ross, 2011). Pressure from a volcanic edifice can also inhibit magmatic ascent, even over thickened crust such as in the CVZ, where edifice loading is < 5 % with respect to total thickness (Hora et al., 2007). For this reason, mafic volcanic products are more likely to be found at monogenetic centers, representing ephemeral magmatic pathways through the upper crust, than at stratovolcanoes that result from long-lived episodic volcanism focused along the same magmatic plumbing system.

In the central Andes, monogenetic volcanic fields manifest in the back-arc of the system (i.e., to the east of the active subduction arc), following structural lineaments and zones of crustal weakness (e.g., Davidson & De Silva, 1992; Kay et al., 1994; Davidson & De Silva, 1995; Matteini et al., 2002; Hoke & Lamb, 2007; Norini et al., 2013). These monogenetic fields consist of collections of small-volume cinder cone, maar, and lava flow eruptions in close spatial and temporal relationships. Typically, these fields can also be broadly defined by a limited range in composition (e.g., Davidson & De Silva, 1992; Kay et al., 1994) and are correlated with broad magma generation events such as slab-rollback and delamination mechanisms associated with the central Andes (Coira et al., 1993; Kay et al., 1994; Hoke & Lamb, 2007; Risse et al., 2013). Part of what makes the volcanoes of this study particularly unique is they are isolated instances of minor volcanism which are not associated with monogenetic fields or groupings representative of major magmatic events, nor are they flank eruptions derived from the magmatic plumbing system of adjacent polygenetic volcanoes (e.g., as in Mattioli et al., 2006). Some of these volcanoes, such as the Tilocálar, perhaps result from multiple small-batch eruptions in one location (Gonzalez et al., 2009), but they are not well-established volcanic centers with well-defined edifices and long-lived, recurrent activity. Rather, volcanism addressed in this study results from singular occurrences of volcanic activity associated with irregular magmatic ascent related to structural features. More such volcanism than is recognized in this work is almost certain to have occurred and may be hidden or buried by the high-volume volcanic output of the calderas and the active arc along with, quite simply, the vastness and inaccessibility of the Atacama Desert.
The Substrate of the Arc: Ignimbrites, Calderas, and Complexes

The eruptive environment (i.e., substrate) of relatively low-volume and short-lived volcanism, such as that addressed in this study, exerts significant control over eruptive styles and the type of volcanic edifice formed (e.g., Ross et al., 2010). The Altiplano-Puna region (21° - 24° S) of the central Andes is defined by extensive ignimbrite sheets produced by a collection of caldera complexes during the late Miocene to Pleistocene (De Silva, 1989a). Ignimbrites in this region cover approximately 70,000 km² and have a combined volume of around 30,000 km³ (Lindsay et al., 2001b). All post-Miocene volcanism in the region, including the entirety of our study area, rests atop a base of massive silicic ignimbrite deposits. These deposits, along with forming the substrate for the studied eruptions, also are composed of the most evolved volcanic rocks of the Altiplano-Puna region (De Silva & Francis, 1991). As such, these ignimbrites represent the compositional antipode to the basaltic andesite of Cerro Overo, defining the full range of CVZ arc volcanism. Additionally, the massive calderas of the region tap a rhyo-dacitic magma storage zone in the middle to upper crust (e.g., Del Potro et al., 2013; Perkins et al., 2016), a significant density filter and potential supplier of crustal contaminant. The majority of Altiplano-Puna ignimbrites are monotonous, fine-grained, extremely crystal-rich, usually pumice-poor, and lack associated fall deposits (Gardeweg & Ramirez, 1987; De Silva, 1989b; Lindsay et al., 2001b). Petrologic evidence indicates these ignimbrites typically also had low volatile contents and high viscosities, requiring an external driving force for eruption (Lindsay et al., 2001a). The collapse and foundering of the magma chamber “roof” along marginal normal faults is most commonly implicated in the production of the large calderas and their associated eruptions (Ort, 1993; De Silva, 1998; Lindsay et al., 2001b).

Partially-welded volcanoclastic materials comprise a relatively weak or “soft” eruptive environment that can exert control on eruptive style for small-volume volcanoes. Maars, for example, when emplaced in softer environments tend to have shallower crater walls, cut less deeply into the substrate, and have shallower diatremes (Ross et al., 2010). The “softer” nature of the substrate rocks promotes rapid expansion of volatiles where the volcaniclastics are less-compacted (i.e., shallower), and groundwater is more likely to be diffusively distributed rather than concentrated along faults. Horizontal sills are also more likely to form than vertical dikes in softer substrates. Additionally, a more-destructible substrate promotes inclusion of
disaggregated pebbles or individual crystals from country rock instead of angular rock fragments in the erupted material (Ross et al., 2010). In a region as dry as the Atacama Desert, differences between a soft pyroclastic substrate (e.g., ignimbrite beneath Cerro Overo) and more coherent lava piles (e.g., stratovolcano flanks beneath Puntas Negras – El Laco) may dictate the difference between an explosive, maar-forming eruption and an effusive, cone- or flow-forming one. Also, the ease of destruction of the underlying country rock will also have an influence on the amount and coherence of upper-crustal xenoliths included in the erupted lava.
**Table 7 - Grouping of volcanic centers by petrography & geochemistry. Colors correspond to location. Green is volcanism within, and related to, the main arc. Blue is volcanism west of the main arc, at the southeast margin of the Salar de Atacama. Orange (Cerro Chascón) is near the northern of the Altiplano-Puna Volcanic Complex, in the marginal back-arc.**

<table>
<thead>
<tr>
<th>Eruptive Center</th>
<th>Group</th>
<th>Type</th>
<th>Age†</th>
<th>Mineralogy*</th>
<th>MgO wt%</th>
<th>La/Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo</td>
<td>1</td>
<td>Maar</td>
<td>77 ka</td>
<td>olv-crsp</td>
<td>7.3</td>
<td>9.2</td>
</tr>
<tr>
<td>Puntas Negras</td>
<td>1</td>
<td>Flow Complex</td>
<td>&lt; 1 Ma</td>
<td>olv-crsp-cpx</td>
<td>6.7</td>
<td>14.3</td>
</tr>
<tr>
<td>LP Lava Flow</td>
<td>1</td>
<td>Flow</td>
<td>&lt; 1 Ma</td>
<td>opx-cpx</td>
<td>5.6</td>
<td>13.2</td>
</tr>
<tr>
<td>Cerro Tujle</td>
<td>2</td>
<td>Maar</td>
<td>&lt; 1 Ma</td>
<td>aphyric</td>
<td>3.5</td>
<td>36.8</td>
</tr>
<tr>
<td>Tilocálar Norte</td>
<td>2</td>
<td>Shield/Flow</td>
<td>&lt; 1 Ma</td>
<td>aphyric</td>
<td>2.4</td>
<td>60.3</td>
</tr>
<tr>
<td>Tilocálar Sur</td>
<td>2</td>
<td>Shield/Flow</td>
<td>730-460 ka</td>
<td>aphyric</td>
<td>3.6</td>
<td>46.5</td>
</tr>
<tr>
<td>Cerro Chascón</td>
<td>3</td>
<td>Dome</td>
<td>unknown</td>
<td>fspr-qtz-olv</td>
<td>3.4</td>
<td>7.6</td>
</tr>
</tbody>
</table>

†“< 1 Ma” ages are based on morphology. Overo age is from U-Th/He. Tilo. Sur age is from (Gonzalez, 2009)
*olv=olivine, crsp=Cr-spinel, cpx=clinopyroxene, opx=orthopyroxene, fspr=feldspar, qtz=quartz

**The Atana Ignimbrite**

The Pliocene-age *La Pacana* caldera produced the rhyo-dacitic *Atana* Ignimbrite, which underlies much of the Altiplano-Puna Volcanic Complex, including *Cerro Overo* maar and *La Albóndiga* lava dome (Figure 24). *La Pacana* caldera is approximately 60 x 35 km and located at the eastern margin of the main arc front (caldera center at 23.17° S, 67.42° W) (Gardeweg & Ramirez, 1987). Outflow ignimbrite extends west, south, and east of the caldera with an estimated volume exceeding 2,500 km³ for the Atana ignimbrite and includes intracaldera facies rocks (Lindsay et al., 2001b). Ages from K-Ar dating of pumice glass and biotite grains from the Atana range from 3.8 ± 0.1 Ma to 4.2 ± 0.1 Ma (Gardeweg & Ramirez, 1987; Lindsay et al., 2001b). Field evidence indicates the ignimbrite is composed of multiple sub-units erupted in rapid succession (Gardeweg & Ramirez, 1987). Compositionally, the Atana is mainly dacitic although it ranges from nearly andesitic (63.1 wt %SiO₂) to rhyolitic (71.9 wt % SiO₂), of which the more silicic deposits are interpreted as representing the erupted highly-evolved “cap” of the magma chamber (Gardeweg & Ramirez, 1987; Lindsay et al., 2001a). The dominantly crustal origin of the ignimbrite is reflected in its enriched isotopic content ($^{87}$Sr/$^{86}$Sr = 0.7094–0.7131; $^{143}$Nd/$^{144}$Nd = 0.5122–0.5123) (Figure 25 - Figure 31).
Cerro Overo Maar

(23.5178° S, 67.6623° W)
Elevation: 4575 m ASL
Dimensions: 485 m x 600 m, 50 – 80 m deep
Area: ~ 914,203 m² = 0.914 km²
Crater volume (assuming ½ ideal ellipsoid) = 4.84x10⁷ m³ = 0.0484 km³
Surface area (½ ellipsoid) = 967,856 m² = 0.968 km²
60 samples collected:
23 samples of ejecta/lava, 13 xenoliths, 7 samples of local ignimbrite from 2014 field work.
17 samples from 2007 & 2008 expeditions (Ukstins-Peate).

Cerro Overo (23.5178° S, 67.6623° W) is a maar generated from an eruption of basaltic andesite at the foot of Chiliques stratovolcano. This explosion crater cuts into the surrounding country rock and is surrounded by a ring of ejecta (White & Ross, 2011). The Cerro Overo maar explosion was likely phreatomagmatic (i.e., produced by a subsurface interaction between magma and water, at which the water flashed to steam, leading to rapid expansion and uplift), and accompanied by catastrophic degassing of the magma itself (e.g. White & Ross, 2011). However, a lack of fine-grained deposits or palagonite indicates a minimal amount of water was involved. The crater is elliptical, approximately 480 - 600 m across and 60 - 80 m deep. A thin ejecta blanket surrounding the crater is partially-eroded, with an estimated original extent of 1-3 km from the eruption site and dominated by smaller (1 – 40 cm) lava clasts. Whether these clasts are truly juvenile (i.e., formed directly from cooling lava) or created from explosive fracturing of a semi-solidified cap on the rising magma is not entirely clear. Thicker (up to 5 m), discontinuous and disparate deposits of lava are restricted to the crater rim (Figure 33). Field and petrologic relationships indicate the nearby lava dome, La Albóndiga Grande (Figure 34), is affiliated with Cerro Overo, and may have formed from the same batch of ascending magma (see Chapter 2).

Thicker lava deposits at the crater rim ubiquitously display surface flow textures (e.g., pahoehoe “ropes”), cooling fractures, and oriented vesicles (Figure 35; Figure 36) - evidence the lava remained molten for some time after eruption and experienced minimal pre-eruptive cooling during ascent (White & Ross, 2011). Flow banding is prevalent at the near-surface of thicker deposits. Microphenocryst plagioclase lathes and elongated vesicles display strong flow
orientation in the banded regions of samples. Dominantly, lapilli and bombs are aerodynamically shaped from flight in a (partially) fluid state although the larger bombs have since broken into blocky forms. Exteriors of thicker lava deposits show banding in vesicularity (visible at the macro scale), and flow-alignment in crystals on the microscopic scale, particularly among microcrystalline plagioclase lathes (Figure 38 - Figure 41). Several rim deposits consist of accumulations of 1-10 cm thick layers of lava, forming thick piles of lava (Figure 45). Agglutinate and spatter textures indicate semi-molten, dynamic emplacement, and partially-welded scoria and lava fragments have formed cohesive, meter-scale masses. The outer surfaces of the lava conglomerate portions of outcrops display textures indicative of spattering, flowing lava, and/or directional cracks and gashes formed from contraction during cooling indicating emplacement while in an at least partially molten state. Occasional discrete bomb beds are found scattered 70 – 500 m from the crater rim and consist of 0.5 – 3 m scale fractured masses of glassy lava forming distinct ejecta piles 5 – 10 m across otherwise surrounded my cm-scale ejecta (Figure 46; Figure 47; Figure 48). These discrete bomb beds are only found S-SW of the maar crater, indicating the explosive direction of the maar-forming eruption. More distal ejecta is sparse, small (<3 cm), and displays aerodynamic morphologies indicative of juvenile nature (Figure 48). Isolated sub-rounded clasts (<2cm) of Cerro Overo basaltic andesite are found up to 3 km from the crater rim.

Country Rock Interaction

The country rock component of the ejecta from Cerro Overo maar is subordinate (<5%) and generally restricted to within the crater itself, likely due to the relative weakness of the underlying ignimbrite, sub-portions of which can be easily crushed in-hand. The exception is the few 1-2 m blocks of the underlying Atana ignimbrite that have been thrown some 80 – 100 m from the crater wall (Figure 33; Figure 49). The buff-to-white ignimbrite does, however, appear within the crater in a discontinuous ring of 5 – 30 m outcrops that show little evidence for interaction with the erupted lava (Figure 49). Hand samples and petrography confirm that none of the non-juvenile clasts found in and around the maar crater are from the Toconao ignimbrite (Figure 50; Figure 51), indicating the maar explosion did not reach a depth greater than the thickness of the Atana ignimbrite (reported to be 50 – 100m in this area; Lindsay et al., 2001 b). In the upper portion of the crater, ignimbrite outcrops nearer to the southwestern rim and
shows evidence of having been baked (i.e., heated) to various degrees (Figure 52). In the more affected portions, pumice clasts have been altered to a nearly homogenous, black obsidian-like glass. This evidence, along with the lack of mineralization or other signs of hydrothermal alteration indicates these rocks were “cooked” at high heat with low moisture. Interestingly, the altered ignimbrite sector is oriented near perfectly to point toward the Albón diga Grande lava dome, some 2.3 km to the southwest of the maar (Figure 14; Figure 34). Immediately east of the dome is a highly-localized, dike-like outcrop of highly-welded, slightly altered dacitic rock. This relationship may be indicative of the geometry of a shallow dike feature that fed the two volcanic features, which is oriented at ~ 65° from north. Additional evidence for the orientation of the eruption includes the uneven distribution of ignimbrite xenolith-bearing lava concentrated to the western and southern rim, and the distribution of discrete lava piles (bomb beds) away from the rim and found only to the south-southwest of the crater.

Another very minor (< 1 %), non-juvenile component of the Cerro Overo eruption are breccias containing clasts (< 0.5 cm – 3 cm) of country rock and fluidal blebs of basaltic material in a fine-grained matrix. These welded breccias are probably sourced from the diatreme, the sub-crater pipe-like structure connecting the surficial crater with the dike that fed the eruption. At the base of the diatreme, where it transitions to the feeder dike, contact breccias variably formed from volcanic components and brecciated country rock are produced by the violent interaction between hot magma and cool wall-rock during devolatilization,. These contact breccias include sections consisting of country rock-derived debris with bodies of coherent igneous rock incorporated while partially molten (White & Ross, 2011). However, these rocks are rare around Cerro Overo and have been included as semi-juvenile components of the ejecta, thus their origin cannot be decisively placed within the maar-diatreme system.

**Crater Morphology**

Assuming an ideal half-ellipsoid, the Cerro Overo crater has excavated approximately 48.4x10^6 m^3 of material (Equation 2). As the bottom of the crater is irregularly filled with drifts of aeolian sediment, this calculation offers a minimum estimate for the amount of material removed in the crater-forming explosion. Not only can we easily deduce that the Cerro Overo crater has been partially filled in since its original formation via wind, but maars are known to fill in from re-capture of their own ejecta, country rock clasts, and collapse and retreat of the crater.
walls and/or the ejecta ring. Unlike most maars, Cerro Overo is free from any signs of lacustrine sedimentation. Whether due to the maar never having hosted a lake or the deposits being buried beneath subsequent wind-blown sediment, we cannot be sure. However, the location of Cerro Overo on a local highpoint and the incredibly dry environment of the Atacama Desert, as indicated by the rapidly-shrinking adjacent hypersaline lake Laguna Lejía, makes it likely the maar never hosted any significant body of water. There is also no evidence Cerro Overo ever began transitioning from an explosive (phreatomagmatic) eruption to a cone- or flow-building magmatic eruption, which would invariably re-fill some of the excavated explosion crater. Generally, the switch from an explosive to a cone- or flow-forming eruptive style is associated with the groundwater supply of a maar becoming exhausted (Ross et al., 2010). Subsidence and diagenetic compaction are capable of expanding the volume of a post-eruptive crater, but we can assume these effects are negligible at Cerro Overo, especially considering the youth of the maar (White & Ross, 2011). Compilation studies have found the freshest maar craters have diameter:depth ratios between 3:1 and 7:1, and the ratio of the Cerro Overo crater is just above 7:1, as would be expected from the aeolian infilling it has experienced (Ross et al., 2010). Buried beneath the maar and its root zone is undoubtedly a magmatic source in the form of a dike or a sill. Given the location of the maar at the apex of an antiform, possibly a fault propagation fold, magma likely rose vertically as a dike until the near surface. Softer substrate, such as the partially-welded volcaniclastic country-rock material, promotes sills at shallow depths (Ross et al., 2010).

\[ V_{\text{Half Ellipsoid}} = \frac{1}{2} \left( \frac{4\pi}{3} \cdot a \cdot b \cdot c \right) \]

*Equation 2 – The equation for the volume of half an ideal ellipsoid where a is the long axis, b is the short axis, and c is the vertical axis, or “depth.” For Cerro Overo the axes are approximately \( a = 595 \text{ m} \), \( b = 485 \text{ m} \), \( c = 80 \text{ m} \).*

The planform of Cerro Overo crater is an ellipse with the major axis (~ 595 m) oriented nearly perfectly E-W and the minor axis (~ 485 m) oriented N-S. The crater rim is regular along the circumference of this ellipse, lacking any significant deviation from the shape. A line drawn through the ignimbrite exposures within the maar also delineates a regular ellipse with an E-W major axis (~ 430 m) and a N-S minor axis (~ 300 m). The elevation profile is E-W: 20° on west
slope, 27° on East. Reaches a minimum slope of ~14° at the NW and a maximum of 35°+ at the SE portion. This slight asymmetry in the Cerro Overo crater results from a slightly asymmetric explosive eruption. The simplest explanations for such an eruption rely on an imperfectly vertical delivery of magma or the influence of irregular substrate beneath the maar. The Atana ignimbrite has been observed to have significant internal variations (e.g., Gardeweg & Ramirez, 1987), although it appears horizontally homogenous where exposed in the maar crater. The heightened steepness of the southwestern slope, along with the concentration of upper crustal xenoliths and discrete lava bomb accumulations provide additional evidence for an oriented explosion “tilted” to the northeast, or at least concentrated near the southwestern part of the crater.

Table 8 - Summarized morphology of the rim of Cerro Overo crater and the ring of ignimbrite country rock outcropping approximately halfway down the crater walls.

<table>
<thead>
<tr>
<th></th>
<th>Major Axis (m)</th>
<th>Minor Axis (m)</th>
<th>Ellipticity</th>
<th>Eccentricity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo Crater</td>
<td>595</td>
<td>485</td>
<td>0.18</td>
<td>0.58</td>
</tr>
<tr>
<td>Ignimbrite Ring</td>
<td>461</td>
<td>323</td>
<td>0.30</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Ellipticity: \( e_p = (1 - \frac{\text{minor axis}}{\text{major axis}}) \)

Equation 3 - Dominantly used for classification of galaxy shapes, ellipticity is a measure of how ‘squashed’ an ellipse is, ranging from \( e_p = 0 \) for a circle (least squashed) to \( e_p = 1 \) for a line (most squashed).

Eccentricity: \( e_c = \sqrt{1 - (1 - \text{ellipticity})^2} \)

Equation 4 – Eccentricity describes the “regularity” of an elliptical shape. Defined for conic sections where \( e_c = 0 \) for a circle, \( 0 < e_c < 1 \) for an ellipse, and \( e_c = 1 \) is a parabola. Shapes derived from conic sections can be defined as geometrically similar (i.e. the same shape, although possibly scaled, rotated, reflected, or translated) if and only if they have equal eccentricities.

**Interpretation**

Rapid decompression and release of volatiles remains the most likely reason for producing the decompression wave needed to excavate such a large crater as Cerro Overo.
maar. The desiccated Atacama Desert provides less ambient groundwater than is usually required for such eruptions. Another maar in the region, Cerro Tujle, also lacks fine-grained pyroclastic deposits and produced similar, although less glassy lava deposits as Cerro Overo, indicating the dry environment may be a factor broadly controlling deposits of maar-diатreme volcanism in the region. Also markedly absent from both maars is a well-stratified ejecta ring. Normally interpreted as representing multiple eruptive episodes or stages (e.g., Ross et al., 2011; White & Ross, 2011), the lack of clear stratification at Cerro Overo indicates the eruption may have been a single, isolated event. Some degree of stratification between scoriaceous and thick lava layers is present in isolated sections along the crater rim (Figure 45), possibly representing an eruption with distinct scoria- and lava-producing stages.

The majority of ejecta surrounding the maar is no more than a few centimeters thick (the size of the clasts), with the exception of 1 – 5 m thick accumulations of volcanic bombs, scoria, and glassy lava at the immediate rim of the crater (Figure 53). Juvenile mafic material is well-preserved and shows no alteration to palagonite or clays. Notably, no fine-grained pyroclastic deposits (tuff, ash) are present, as is common around maars globally (White & Ross, 2011). Localized concentrations of scoriaceous clasts (up to 70% of the smaller ejecta) accompany some of the thicker lava deposits, although not in continuous distributions. Highly-vesiculated (> 20 % vesicles) scoria is relatively rare (< 10%) in the ejecta blanket beyond the rim (Figure 48). The lack of fine volcaniclastic material is notable as most maars are ringed with tephra, dominantly ash (< 2 mm) with subordinate lapilli grain-size (2 – 64 mm) which is usually transported and deposited by base surges (dilute pyroclastic density currents) and identifiable by conspicuous duneform deposits in the ejecta blanket (White & Ross, 2011). At Cerro Overo, the dominant juvenile ejecta is glassy lapilli with a subordinate bomb (> 64 mm) population. This absence of fine-grained deposits, even where wind-protected, casts doubt on the idea of a phreatomagmatic eruption, as explosive thermohydraulic reactions caused by fuel-coolant (i.e., magma-water) interactions have been observed in both laboratory and natural settings to cause extensive fracturing and shattering of lava, resulting in the generation of fine-grained material ubiquitously associated with maar-diатreme volcanism (White & Ross, 2011; Ross et al., 2011; Palladino et al., 2015; Valentine et al., 2015). There is also a complete lack of water-induced alteration products (e.g., palagonite) or deposits indicative of moisture in the eruption column (e.g., accretionary lapilli). Regardless, the presence of a deep crater at Cerro Overo indicates an event of intense rock-breaking and excavation generated by rising magma.
The extreme glassiness and low vesicularity (Figure 53) of much juvenile ejecta indicates the magma was fluid and partially degassed by the time it reached the surface (White & Ross, 2011). Bands and surfaces of the thicker lava deposits show sections of high vesicularity resulting from escape channels and de-volatilization of semi-molten lava, some undoubtedly post-eruptive. Welded-spatter zones, indicative of some eruptive periods with volatiles, consist of decimeter-size dense to moderately vesicular juvenile bombs in a scoriaceous matrix (Figure 54). The blocky-to-fluidal shape of much of the juvenile pyroclasts (Figure 47) results from fragmentation of poorly-vesiculated material, which indicates either a low volatile content in the hot material or quenching of the magma prior to substantial exsolution of volatiles (Houghton & Wilson, 1989; White & Ross, 2011). There is extensive textural evidence in the welded and flow-textured deposits of the maar indicating heat-retention, and geothermometry calculations generally range from 1090 to 1200 °C for eruptive temperatures, indicating a relatively low-volatile magma was involved. Microprobe analyses of volcanic glass indicate < 0.01 wt % volatiles (i.e., H₂O, CO₂), calculated by difference, although the lava can be assumed to have been degassed preceding or during the eruption, based on the morphology of the juvenile clasts. Plagioclase-liquid hygrometry modeling based on element exchange between the melt composition of the maar and groundmass plagioclase lathes (Putirka, 2008 and references therein) indicates an H₂O content of approximately 2.5 wt %. As the measured plagioclase was grown during or immediately preceding eruption, as indicated by their small size and flow-alignment, this value presumably represents a reasonable estimate of magmatic H₂O content at the time of eruption.

Cerro Overo has experienced crustal interaction, as evidenced by abundant silicic xenoliths (65-67 wt % SiO₂) entrained in the erupted lava (Figure 55 - Figure 59). Incorporated material ranges in size from xenocrysts of partially resorbed quartz and feldspar to partially re-melted, ductile stringers of glassy, vesicular quartz- and plagioclase - bearing silicic pods up to 3 m long. The xenolithic material is interpreted to have been derived almost entirely from the upper 20 – 40 m of crust and to have not been significantly assimilated. Xenoliths are not homogenously distributed and concentrated (almost entirely) on the less-steep, more-excavated western to southern portions of the crater. The source of the xenoliths appears be the immediately-underlying Atana ignimbrite, judging by similar mineralogy and compositional features. Both the Atana ignimbrite and the majority of xenoliths show a dominantly dacitic composition with a minor rhyolitic component. U-Pb dating of zircons from xenoliths also place
them within the age range determined for the Atana (Lindsay et al, 2001). Commonly the contact between xenoliths and mafic lava is sharp with little mixing apparent at either hand sample or microscopic scales. In many instances, there is an intermingling of basaltic and dacitic materials with either material trailing off into the other in stringers of melt plus crystals or as isolated pods. For the most part, however, even when there is significant mingling, the boundaries remain sharp at the microscopic scale and microbeam (EPMA) transects reflect minimal diffusion (Figure 37). Thin chill rims (< 500 μm – 5 mm) surround some felsic xenoliths, wherein the mafic material is exceptionally glassy with fewer microcrysts than the bulk groundmass. Olivine phenocrysts in these margins show an increased level of skeletal overgrowth and/or resorption, indicative of the high degree of undercooling imposed on the mafic lava from prolonged contact with cold wall-rock (Figure 40). This relationship supports a crystal growth model with addition of skeletal overgrowth on pre-existing olivine cores at or near the time of eruption.

**Etymology**

The word “Overo” most commonly refers to a specific sort of splotchy, irregular pinto coloration in horses (see the American Paint Horse Association’s Guide to Color Coat Genetics). However, the origin of this usage (in both Spanish and English) is from archaic Spanish meaning “egg-like.” In this way, Cerro Overo can be potentially translated to “Egg-like Hill,” which makes rather a lot of sense considering its appearance in planform (Figure 46).

It also bears noting that in some literature, the name “Cerro Overo” is applied to a stratovolcano near the Chile-Argentina border, adjacent to Cerro Grande volcano (23.77° S, 67.41° W). This nomenclature does not appear on all maps and it is unclear whether this larger composite cone truly shares a name with the maar of this study or rather, if this is a naming error founded in less-precise reporting of coordinates. Regardless, any instances referring to the stratovolcano near the international border will be written as “the Cerro Overo Stratovolcano,” while references to the maar will either be written as “Cerro Overo maar” or simply “Cerro Overo.”

The locality surrounding Cerro Overo is known by some as *El Paso de Vacas Muertas* due to the large number of cattle who died in this pass due to ill-fated attempts in bovine ranching
during the early twentieth century (Tambley, 2014, pers. comm.). The name is suitable, given
the ubiquity of desiccated skulls, bones, and hooves (some still shod) found around and in the
maar. However, I will omit this nomenclature to avoid confusion with the other Paso de Vacas
Muertas and the Quebrada Vaca Muerta of the Chilean Puna further south, the Cordón de la
Vaca Muerta in Argentina, the Cerro Vaca Muerta in Peru, and the many other dead-cow
themed geographic features in South America. Rather, the name Cordón Altos de Toro Blanco
(“White Bull Ridge”) will be used for the rise upon which the maar sits, a name I suspect also has
origins in the many bleached steer skulls and bones.

Table 9 – Features indicative of eruptive processes for maar-diatreme volcanoes, from White & Ross (2011).

<table>
<thead>
<tr>
<th>Feature</th>
<th>Site</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary current bedding, many layers</td>
<td>Ejecta ring, megablocks</td>
<td>Multiple, small pyroclastic currents produced during the maar-forming eruption; can continue after morphological crater has stabilized near end of eruption.</td>
</tr>
<tr>
<td>Country rock fragments</td>
<td>Ejecta ring, diatreme, root zone</td>
<td>Pyroclastic deposits of maar-diatreme volcanoes have variable but generally substantial contents of country rock fragments, particularly enriched in the root zone; one or more processes of fragmenting the volcanoes’ host rock are required. Shallow entrainment of loose conduit wall material is not restricted to maar-diatermes.</td>
</tr>
<tr>
<td>Fresh country rock fragments; low-temperature alteration.</td>
<td>Diatreme</td>
<td>Country rock fragments in diatremes are not commonly thermally metamorphosed (except where contained in juvenile fragments): alteration is generally hydrous. Structural and contact/metasomatic effects associated with diatreme formation are remarkably few.</td>
</tr>
<tr>
<td>Unwelded pyroclastic deposits.</td>
<td>Ejecta ring, diatreme</td>
<td>Unwelded deposits indicate that juvenile fragments were cooled during fragmentation, or during transport to depositional sites; rare large juvenile bombs may land while still deformable.</td>
</tr>
<tr>
<td>Welded deposits or clastogenic coherent rocks.</td>
<td>Root zone, intra-diatreme fragmentation zones</td>
<td>Welded deposits indicate local emplacement of still-hot fragments, indicating heat retention and minimal pre-deposition cooling.</td>
</tr>
<tr>
<td>Variably, but generally weakly vesicular juvenile pyroclasts.</td>
<td>Ejecta ring, diatreme, ± root zone</td>
<td>Pyroclast vesicularity is typically high for products of magmatic eruptions unless the magma has been degassed.</td>
</tr>
<tr>
<td>Blocky to fluidal pyroclast shapes.</td>
<td>Ejecta ring, diatreme, ± root zone</td>
<td>Shape of juvenile pyroclasts indicates fragmentation of magmas that are generally not highly vesicular, either because volatiles were lost prior to fragmentation, or because fragmentation quenched the magma prior to substantial exsolution of volatiles from the melt.</td>
</tr>
</tbody>
</table>
La Albóniga Grande Lava Dome

(23.5266° S, 67.6851° W)
Elevation: 4445 m ASL
Dimensions: ~ 60 m tall by 200 m across

La Albóniga Grande basaltic andesite dome (23.5266° S, 67.6851° W) is at the edge of the western limb of the Cordón Altos de Toro Blanco ridge, along the boundary of a small, oblong depression (~ 1000 m N-S by 500 m E-W) (Figure 34). La Albóniga partially spills over the topographic high on the northern margin of the depression, continuing down the steep slope (20° to nearly vertical) to the south until it meets the floor of the depression, where it forms a talus apron at the base of the dome structure (Figure 60; Figure 61). The immediately underlying stratigraphic unit is the same Atana ignimbrite cropping out along the crater walls of Cerro Overo maar. The Cordón Altos de Toro Blanco ridge is an anticline which extends North-South (~12°) between stratovolcanoes Chiliques and Aguas Calientes along which Cerro Overo maar is located at the hinge zone. The depression is isolated, unnamed, dominantly filled with fine aeolian sediment, and of unknown origin although it is potentially a small pull-apart basin resulting from subparallel transverse lineaments in the region (e.g. Mattioli et al., 2002). Ignimbrite outcrops along the eastern edge of this basin are fractured and show signs of hydrothermal interaction such as fracture planes filled with 1-2 mm crystals of euhedral magnetite, breakdown or alteration of biotite and amphibole phenocrysts, and displays general discoloration of the ignimbrite groundmass. The Atana ignimbrite is also exposed along the northern rim of the basin, immediately underneath the tongue of lava extending from the eastern shoulder of the dome.

The dome itself is approximately 60 m high on its southern side with only the upper 20-30 m exposed on the northern face (Figure 62). The southern face of La Albóniga is steep and crumbling into the adjacent topographic depression. The south slope consists of large lava boulders and blocks (1 – 5 m) lying on a bed of fractured lava (1 – 30 cm). It is 150 m across NE-SW (short axis) and some 215 m across NW-SE (long axis). At the southwest of La Albóniga, a secondary lobe some 15 m high and up to 130 m across extends ~ 80 m into the basin. The outer surface of the apex of the dome and the northern face of the dome is a coherent surface layer, which contrasts with the disaggregating boulders coming off the southern and western faces. The outer portion of the surface layer is generally more vesiculated (20-30 %) than lava from the interior of the dome (average 15 %). At the northeast of the dome, this surface layer
extends eastward up to 80m in a tongue, which appears to be the combination of a thin lava flow (1 – 3 m) and accumulated clasts of scoriaceous material in an apron (Figure 61). The surface of this flow is mostly covered in clasts, but where visible it displays an a’-a’ type texture. No vent or other obvious point-source is discernable. However, large crease structures are present near the edge of the dome, just west of its apex (Figure 61). These parallel, interconnected creases are large enough to climb through (1 – 5 m across) and lava in and around these features displays an increased level of vesicularity compared to rocks from the rest of the dome (Figure 62). These features developed as the outermost lava cooled more quickly than the interior, which created large cracks in the exterior as the more plastic interior lava continued to flow. Increased lava vesicularity within the crease structures may result from (gas) extrusion focused along these corridors of failure (Fink and Anderson, 2000). Lava sampled from the outermost portion of the dome also appears slightly more evolved than lava sampled from the glassier, less vesicular dome interior (Figure 63). Additional features of lava domes that are indicative of a more complex eruption, such as explosion pits or pressure ridges, are not observed. Overall, La Albón diga Grande dome appears to have been a relatively simple extrusion of olivine-phyric basaltic andesite that occurred along a zone of weakness at the margin of a small depression. The outer portion of the dome experienced the highest level of interaction with the surrounding rock and degassing and any assimilation was focused at this outer layer. A complete absence of the upper crustal xenoliths abundant at Cerro Overo maar is evidence for the relatively non-violent ascent of the magma. Also, if one accepts the compositionally and petrographically similar lavas originate from the same magma batch, this offers additional evidence that Cerro Overo lava acquired the vast majority of its xenoliths during crater excavation (i.e., eruption).
The Puntas Negras – El Laco Mafic Lava Flow

(23.7431° S, 67.4760° W) to (23.8091° S, 67.4172° W)
Elevation: 4750 m to 4270 m above sea level.
Surface area: ~ 10.3 km

Located in a mountain pass through the Cordón de Puntas Negras, near the Chile-Argentina border (23.74°S, 67.47° W), the Puntas Negras-El Laco Lava is a series of mafic flows originating from a single vent at 4770 m (15650’) elevation that flow ~10 km to the S-SE (167-120°, overall ~138°; Figure 64). The lava appears to originate from a single point source although no edifice or clear vent is visible, and travels approximately 10 km to the south – southeast, covering approximately 10.5 km² in total. Puntas Negras mafic lava flows are continuous, partially eroded, buried in recent aeolian sediment, and generally oxidized at the surface (Figure 65). Major mineralogy consists of phenocrysts and/or glomerocrysts of olivine (Fo83, 0.5 – 4 mm), clinopyroxene (diopside, 0.25 – 5 mm), and variable amounts of plagioclase (An60) in a groundmass of plagioclase (< 0.5 mm; 20-60 %; An60), clinopyroxene (< 0.25 mm; < 5 %; diopside-augite), and opaque oxide (< 0.1 mm; < 2 %) microphenocrysts in a mafic glass (20-50 %). Xenoliths are absent or extremely rare. The lavas are broadly divisible into two subsections – an Upper Flow nearer to the supposed vent and a more distal Lower Flow (Figure 64). Lava from the lower flow has more plagioclase phenocrysts and contains less olivine, clinopyroxene, and vesicles. The Upper flow is more crystalline in general. The two subdivisions are continuous with each other, although the flows further from the vent appear to be stratigraphically lower (older) than the lavas near the vent (Figure 64).

Overall, both Puntas Negras – El Laco flow subdivisions are physically similar on the macro scale. The lava flows show a coherent, less-vesiculated core (partially buried in recent Aeolian sediment) with a few lava tubes in flank sections. The base of the flow, where visible, follows pre-existing topography. Different flow layers, if present, are mostly fused together to the point of being indistinguishable. The lava surface is blocky and fractured with very little persistent evidence for flow textures such as pahoehoe, channeling, or a’a’ textures (Figure 65). The uppermost lava is the most vesiculated portion of both the Upper and Lower flows although Upper lavas display a significantly greater degree of vesiculation, particularly near the surface. Exterior surfaces are significantly oxidized (Figure 65). In some portions nearly all olivine and pyroxene phenocrysts are weathered out at the surface. The most oxidized material was generally avoided during sampling and further selected against during sample processing to
avoid any weathering effects on composition. The location of the vent source of the lava is not entirely clear and a projected location is marked at a high point from which all flows appear to radiate outward (Figure 64). A larger, reddened cinder cone adjacent to the flows was considered as a potential volcanological companion, but geometric relationships do not implicate the two. The cinder cone was not sampled. A dacitic lava dome adjacent to the flows was investigated, as well, but it also displays no relationship to the mafic lava (Figure 64).

We recovered 14 samples, including an adjacent intermediate dome.

**El País Lava Flow**
__Sampled at (-23.7972, -67.9619). Vent to the east.  
Elevation: 3164 m ASL__

El País is an isolated lava flow of unclear origin, and possibly an erosional remnant, in a basin to the north of the Cordon de Tujle anticline and bounded by antiforms related to East-verging thrust-faults (Figure 19). The lava bears glomerocrysts of green clinopyroxene (augite) and yellow-brown, mildly pleochroic orthopyroxene (enstatite) and phenocrysts of plagioclase (Figure 66). This flow has not previously appeared on any maps, geologic or otherwise. However, it may be a remnant distal lobe of lava related to the **Corral Negro** to the east, a poorly-studied complex of pyroxene-bearing andesites, basalts, and basaltic andesites described as corresponding to an eroded stratovolcano immediately southwest of Laguna Miscanti (Ramirez & Gardeweg, 1982; González-Ferrán, 1995). El País is among the most mafic andesite compositions of the arc front, spanning the compositional gap between the basaltic andesite of endmember Cerro Overo maar and the less-evolved lavas of the intermediate arc stratovolcanoes. One flow from **Corral Negro** was dated using K-Ar to 4.6 ± 2.3 Ma (Ramirez & Gardeweg, 1982). The Miscanti Fault separates these pyroxene-bearing lavas from the modern stratovolcanoes to the east. West of this fault (and the arc) is an open area at the southeast corner of the Salar de Atacama defined by thrust-faulting, east-verging anticlines, and strike-slip transfer faults. In this area, near the small settlement of Tilomonte, small roads and inways have been built in an area previously only accessed by foot and beast paths to provide access to powerline towers and copper deposits. Following these dirt roads and nascent tracks, we managed to access and sample fault-controlled volcanism at the Tolonchar and Tilocálar Ridges. The Corral Negro flows propagate westward from the topographic lineament of the fault.
although their eroded origin may have been east of the lineament. Due to the eroded nature of both Corral Negro and El País, it is unclear if these were fault-emplaced lavas. El País is unrelated to nearby Cerro Tujle, located less than 5 km to the south, both compositionally and structurally.

We recovered one sample.

**Tilocálar Norte Volcano**

*Vent at (-23.9503, -68.1071)*

*Elevation: 3026 m ASL*

*Tilocálar Norte (-23.9503, -68.1071) is a complex of aphyric andesitic and dacitic flows at the easternmost of the Tilomonte ridges, located approximately 3.5 km NE of Tilocálar Sur (Figure 19; Figure 23). Between Tilocálars Norte and Sur, the Tilomonte Ridges merge into a single ramp fold. Overall, the Tilocálar Norte flows extend 4.25 km north-south at approximately 1.0 km width and are clearly controlled by pre-existing topography. The majority of Tilocálar Norte lava emanated from a central vent and first travelled east (72.4°) down a scarp before either heading north (357°) for around 3.9 km or south (181°) for another 1.1 km. The andesitic lava (64 wt % SiO₂, 2.4 wt % MgO) is slightly weathered with an oxidized brown exterior and dark grey fresh interior, and is nearly aphyric with groundmass lathes of plagioclase and minor pyroxene. Portions of the flow, particularly near the southern lobe terminus, show secondary mineralization in pore spaces. The age of this volcano is unknown, although it is scarcely eroded and the lava appears fresh, particularly near the center of the flow. It is likely within the same age range as the eruptions of its sister, Tilocálar Sur, which has been dated as late Pleistocene (450 – 700 ka) by Gonzalez et al. (2009).*

The Tilocálar Norte “cone” formed entirely of lava emanating from a single vent location, with a surface area of approximately 3.5 km² and a volume of approximately 160x10⁶ m³ (González-Ferrán, 1995). The lava can be divided into three flows. The stratigraphically lowest directly overlies the Pliocene Tucúcaro ignimbrite and is exposed mainly as a small westward extension of the lava near the vent (Gardeweg & Ramirez, 1982). The second flow is a lobular effusion reaching some 800 m south of the vent. The third and most recent flow is the most extensive and is associated with a volcanic neck at the vent site and forms a lava tongue
which has traveled 3.8 km to the north. The substrate, Tucúcaro ignimbrite, is a welded dacite with a $^{40}$K/$^{40}$Ar age of 3.2 ± 0.3 Ma (Ramírez and Gardeweg, 1982).

~18 km south of Tilomonte, ~13 km west of Tolonchar, ~21 km SW of c. Tujle, 68 km SW of c. Overo

We collected 3 samples from different flow lobes

**Tilocálar Sur Volcano**

*Main vent at (-23.9770, -68.1297), explosion crater at (-23.9866, -68.1335)*

*Elevation: 3087 m; crater floor at 3053 m (360 m across, ~25m deep)*

Tilocálar Sur is a small polygenetic volcano with an edifice comprised mainly of less-evolved andesitic lava flows (58 wt% SiO$_2$, 3.6 wt% MgO) with minor pyroclastic deposits and andesitic breccias covering approximately 7.5 km$^2$ in total. The Tilocálar Sur edifice is a roughly circular and shield-like. It is located ~3.5 km southeast of Tilocálar Norte and centered at the hinge zone of the Tilomonte Ridge and abutted against the western edge of Tilocálar Ridge (Figure 67). The Tilomonte Ridges merge into a single lineament just north of Tilocálar Sur at a junction of complex structure. There are three Tilocálar Sur craters aligned along a graben structure cutting the volcano with the same NE-SW orientation as the underlying hinge zone of the ridge. The graben is approximately 1,700 m long and 250 m wide (Gonzalez-Ferrán, 1995). The southernmost crater is a roughly heart-shaped explosion crater, which has been previously misidentified as a meteor impact structure (Ferrando, 1977). The vent for Tilocálar Norte is also located along this NE-SW trend, to the northeast where the Tilomonte Ridges are split again. During fieldwork in 2014, we collected 5 samples from Tilocálar Sur: two from near the explosion crater and three from the flow lobes.

In total, Tilocálar Sur has erupted approximately 0.24 km$^3$ of andesitic to basaltic-andesitic breccias and lava, and pyroclastic deposits covering approximately 3.3 km$^2$ (Gardeweg & Ramirez, 1982). The lowest pyroclastic unit is comprised of blocks of andesite in a matrix of scoria and ash, evenly distributed in a roughly circular deposit centered on the main vent. Gardeweg and Ramirez (1982) observed larger lava blocks that appear fractured *in situ*, indicative of deposition at high temperatures, and fragments of brown sandstone, quartziferous
sandstone, and conglomerate recognized from the Tambores formation, which is exposed at nearby fault scarps. The western flank of Tilocálar Sur is then covered by a 10-20 m thick avalanche of basaltic andesite, which we sampled (Figure 67). This flow emanates from a central vent, forming a 1.5 km lobe flowing roughly E-W (heading 90.7°). The youngest Tilocálar Sur lava flow(s) emanates from the same central vent as a minimum of two overlapping flows (1.75 km and 1.38 km) directed SE-NW (heading 315°). The semi-circular crater (400 m across, 40 m deep) on the southern flank of the volcano (Figure 22) was probably caused by an explosion of volcanic gases or water vapor and cuts the pyroclastic deposits of Tilocálar Sur as well as the underlying Tucúcaro ignimbrite and sedimentary Tambores formation. Gardeweg and Ramirez (1982) proposed that this explosion was caused when the volcanic duct became blocked during the final stages of lava extrusion and led to an accumulation of gaseous components which escaped laterally and catastrophically. Pyroclastic material (scoria) produced in this explosion is relatively scarce and mixed in with the basal pyroclastic deposits, but are recognizable by their relative “freshness.” Tilocálar Sur is also accompanied by andesitic dike swarms striking NW-SE, parts of which are attached to the hanging wall of the thrust (Kuhn, 2002).

Cerro Tujle Maar
(-23.8358, -67.9519)
3570 m
335 m x 270 m, ~ 60 m deep
Area = ~ 284,000 m² = 0.284 km²
Volume (assuming ½ ideal ellipsoid) = 11,366,282 m³ = 0.0114 km³
Surface area (½ ellipsoid) = 311,078 m² = 0.311 km²

Lava erupted at the isolated Cerro Tujle maar (also written as Tucle or Tugle) is dark, glassy, and aphyric andesite (58.8 wt % SiO₂, 3.45 wt % MgO) distributed in a thin (1.5 m thick or less) ring of juvenile ejecta reaching up to 350 m from the crater rim to the southeast. Lava deposits are dominantly comprised of cm-scale scoriaceous materials and sub-angular lava blocks up to 3 m, which are restricted to the immediate 10 m around the rim (Figure 69). The ejecta blanket is asymmetric as the steeper slopes to the west and north of the maar have been subjected to enhanced erosion in these directions. The maar crater of Cerro Tujle is
approximately 60 m deep and elliptical, ~335 m across E-W and ~270 m across, north to south. The crater walls are particularly steep and, while some outcrops of the underlying ignimbrite are visible, is mostly filled with sands and the plants who love them. Weathering has turned portions of the ejecta a reddish-brown, but the lava is homogeneous in appearance and aphyric texture. Rare minor dacitic xenoliths (0.5 - 2 cm) are occasionally found in bands and groups in the lava and are irregularly distributed around the crater with the highest concentration at the northwestern portion of the ejecta deposit. Compilation studies have found the freshest maar craters have diameter:depth ratios between 3:1 and 7:1, and the crater ratio of Cerro Tujle is 4.5 – 5.6:1, indicative of its relative youth and pristine condition (Ross et al., 2010). Cerro Tujle maar is located 21 km to the northeast of the Tilocálar volcanoes, along the hinge zone of the Cordón de Tujle anticline (Figure 19), one of the N-S trending features related to contractional deformation at the southeast margin of the Salar de Atacama. This east-vergent anticline is also known as the Tolonchar Ridge after the small stratovolcano Cerro Tolonchar and is another instance of hinge zone volcanism approximately 11 km south of Cerro Tujle.

Due to the isolation of the peak from civilization and the rest of the Andean arc, Cerro Tolonchar has been considered as a construction site for the ground-based Giant Magellan Telescope, the European Extremely Large Telescope, and the Thirty Meter Telescope program. The stratovolcano has been ultimately rejected for all these astronomy projects due to its proximity to the high-powered lighting of lithium mines in the Salar de Atacama. However, an established vehicle track leads to the summit. Evidence in the form of concentrations of flakes and chipped rock at the crater rim suggests Tujle lava has been used by humans in construction of stone tools (Figure 70). Any additional assessment or conjecture on the archaeological significance of the maar is outside the scope of this paper.

Collected 3 samples from the maar in 2014
Petrography & Geochemistry

The Atana Ignimbrite

Outcrops of the Atana ignimbrite at the western margin of La Pacana caldera range from 50 m to 140 m thick and decrease to 20 m at 20 km at 45 km distance, respectively (Lindsay et al., 2001b). Cerro Overo maar is only 4 – 6 km to the west of La Pacana caldera and thus rests atop a relatively thick deposit of Atana, which crops out along the walls of the crater (Figure 49). The sub-maar outcrops of the Atana ignimbrite are a buff-colored, massive, homogenous, and poorly-welded tuff rich in crystals (30 -50 % by volume) and poor in lithic fragments and pumice (Figure 52). The mineralogy consists of plagioclase (20-30 %), brown to bronze biotite (5-8%), characteristic euhedral pink quartz (3-8%), subhedral black Fe-Ti oxides (1-3%), sanidine (<1%), and hornblende (<1%). Also characteristic in thin section is occasional subhedral sphene (e.g., Gardeweg & Ramirez, 1987). Zircon is sparse, but present. Pyroxene is very rare in samples from near Cerro Overo, although it is present in larger proportions in other sections of the Atana (Lindsay et al., 2001b). Crystals of quartz and plagioclase are commonly fragmented and frequently display embayments, resorption, and/or sieve textures. Original crystals appear to have been generally in the 1 – 3 mm range, with some outliers exceeding 5 mm. The matrix is composed of fine ash shards and devitrified ash and is slightly welded. In thin section, a eutaxitic texture (glassy matrix flowing around phenocrysts) is visible. Pumice clasts, when present, are dominantly rhyolitic with an identical mineralogy as the bulk rock. Lower in the outcrop, a 10-20 m portion of the exposed ignimbrite is white when fresh but less-welded and less-indurated (i.e., powdery) than the top of the outcrops and much more friable, able to be crushed in-hand. In the basal section, pumice clasts and lithic fragments are much more abundant, and derived from underlying Toconao ignimbrite. The absolute base of the Atana is not exposed in the crater wall. At the top of the outcrop near the crater rim, the ignimbrite is brown-to-pink and much more consolidated with the same mineralogy as the basal section, but with a very low number of lithic or pumice clasts. The majority (>90%) of non-juvenile material rests within the crater and the ejecta blanket of Cerro Overo is indurated ignimbrite fragments which match the mineralogy and chemistry of the Atana ignimbrite, dominantly the upper, more coherent portion (Figure 48). Occasional small (1-4 cm) coarse-grained volcanic rocks in the ejecta with no clear rock unit affiliation may have been derived from lithic fragments encased in the weak basal unit of the Atana.
The Atana ignimbrite is recognized as the unit in the walls of the Cerro Overo crater by field and petrographic observations, which align nearly identically with the descriptions of Gardeweg & Ramirez (1987) and Lindsay et al. (2001a, 2001b). The pink quartz phenocrysts are distinctive, although not universally distributed. The next underlying unit, the Toconao ignimbrite (4.0 ± 0.9 – 4.49 ± 0.38 Ma) is crystal-poor and distinguished by abundant, nearly aphyric “silky” filiform pumice clasts and a homogenously rhyolitic composition (76–77 wt % SiO₂), likely sourced from the upper “cap” of the same magma chamber which produced the Atana Ignimbrite (Gardeweg & Ramirez, 1987; Lindsay et al., 2001b; Lindsay et al., 2001a) (Figure 50). We can also identify the Atana ignimbrite by the inclusion of Toconao-sourced clasts in the basal portion. However, the Toconao ignimbrite has a much smaller extent (~ 180 km³) and its thickness (average of 30 m) shrinks at times to mere centimeters, so one cannot rely on its existence in identifying the Atana (Lindsay et al., 2001b). Beneath the Toconao is the Pujsa ignimbrite (5.8 ± 0.1 Ma), which could be confused with the Atana due to its similar mineralogy, which includes euhedral, pink quartz (Gardeweg & Ramirez, 1987). However, the stratigraphic position and known distribution (~ 500 km³) of the Pujsa precludes the possibility of it being the wall-rock unit in Cerro Overo maar (Lindsay et al., 2001b). In addition, U-Pb dating of zircon separates from felsic xenolith sample CIUP 08-97 gives a ²⁰⁶Pb/²³⁸U weighted mean age of 4.0 +/- 0.1 Ma (MSWD = 1.0; n = 17) (McClelland, 2014, personal communication), which conforms to previously published ages for the Atana (Gardeweg & Ramirez, 1987; Lindsay et al., 2001b; Lindsay et al., 2001a).

**Underlying Tilocálars & Tujle: 3.2–3.1 Ma Tucúcaro-Patao ignimbrite**

**Cerro Overo Maar**

Olivine: 5 – 15%, average ~ 7%

Vesicles: < 2 – 30 %, frequently higher values are concentrated in alternating bands.

*Petrography: Basaltic Andesite*

Cerro Overo maar produced calc-alkaline, olivine-phyric medium-K basaltic-andesite lava. This monogenetic eruption is the most mafic (average 54.2 wt % SiO₂, 7.42 wt % MgO) volcanic product recognized in the Altiplano-Puna region (21°-24° S) of the CVZ, where compositions are dominantly andesitic to rhyolitic (de Silva & Francis, 1991; Rosner et al., 2003;
The sole phenocryst phase, forsteritic olivine (0.5 – 5 mm, 5 – 15 % by volume), displays a broad range of morphologies, high-Forsterite cores (86 % average) with lower-Forsterite skeletal overgrowth (79 % average), that are rich in melt and mineral (Cr-spinel) inclusions (Figure 71; Figure 40). High forsterite cores are in equilibrium with whole-rocks and appear to be native to the lava (i.e., not xenocrysts), while the low Mg rims appear to have grown rapidly near the surface, possibly during or post-eruption. Olivine crystal morphologies include euhedral, tabular, resorbed, and skeletal aspects (Figure 40). Local volumes can exceed 25% olivine and phenocrysts show slight flow orientation in samples that have experienced plastic motion, which is mirrored in the microphenocrysts (Figure 38). The groundmass consists of mafic glass with microcrysts (≤ 0.25 mm) of calcic plagioclase lathes (An_{65}), euhedral clinopyroxene (augite and diopside), olivine, and Fe-Ti oxides (dominantly magnetite). Microphenocrysts of olivine are euhedral to skeletal and are compositionally identical to the rims of the larger phenocrysts (Figure 72 - Figure 74). The lava ranges from massive to wholly vesicular (from < 2 % to > 50 %), but low vesicularity (< 10 %) is dominant. When present, higher vesicularity is often heterogeneously distributed with concentrated bands (1-3 cm), surfaces, and boundaries (Figure 35).

**Petrography: Xenoliths**

The majority of the xenoliths in Cerro Overo lava are compositionally and mineralogically similar to the Atana ignimbrite in thin section, even where they appear distinct in hand sample. The dominant xenolith type (> 50 %) is light grey with medium vesicularity and phenocrysts consisting of 1-5 mm subhedral crystals of plagioclase and quartz (15-40 %) and seriate textured, dark opaque minerals (10 – 20 %), ranging from < 0.1 mm to > 3 mm. Some samples have plagioclase displaying highly sieved cores. In thin section, the crystal population of the xenoliths is dominated by broken and/or resorbed plagioclase and quartz crystals and opaque minerals with variable sizes and crystal forms. The matrix is a clear glass (40 – 70 %) with minor portions showing acicular microcrystallization of an unidentified mineral. The groundmass of xenoliths differs from that of fresh Atana Ignimbrite. Xenolith groundmass glass is homogenously clear with acicular micro-crystals of unknown mineralogy and halos of brown glass surrounding opaque oxides (Figure 42). The groundmass glass of the Atana Ignimbrite is banded and shows a sense of motion, flowing around phenocrysts and clasts (Figure 51).
Devitrification of the ignimbrite glass in xenoliths results from the glassy matrix being the most easily melted portion of the overall groundmass + minerals + clasts assemblage of the Atana. Thus, the glass is most obviously altered by interaction with the basaltic andesite of the maar, although compositional analyses and mineralogy indicate they are identical. The other notable difference in the xenoliths, in comparison with the Atana ignimbrite, is the absence of crystals of biotite or amphibole. The opaque mineralogy results from a combination of subhedral magnetite and breakdown pseudomorphs of biotite and amphibole, remnants of which are very rarely visible at the cores. The opaque minerals are in various states of destruction, ranging from instances of well-preserved crystal forms to minerals that are shattered, resorbed, and/or “leaking” material into the surrounding glass (Figure 42), locally transforming the glass from clear to a translucent brown.

The next largest population of xenoliths (~ 30 %) has identical mineralogy but is either extremely vesicular (“frothy”) or dense (very low to non-existent vesicularity). Another xenolith sub-population is highly frothy and black in hand sample. In thin section, these black xenoliths display similar relative mineral modality, but have a significantly reduced amount of glass (< 40%), which has been completely stained an iron-brown color which, in some clear-glass samples, is seen as halos around the opaque breakdown crystals. Ostensibly, these xenoliths are of similar or identical origin and reflect different stages of assimilation, alteration, and destruction. The level of alteration or breakdown can be generally discerned from the level of preservation of primary glass (i.e., the pyroclastic eutaxitic texture and how much biotite or hornblende remains). Compositionally, they are dacitic with a minor rhyolitic component (Figure 8). Zircon separates from typical felsic xenolith sample CIUP 08-97 yield a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 4.0 +/- 0.1 Ma (MSWD = 1.0; n = 17) (McClelland, 2014, personal communication), which conforms to published ages for the Atana ignimbrite (Gardeweg & Ramirez, 1987; Lindsay et al., 2001b; Salisbury et al., 2011).

A very minor (<< 1%) portion of basaltic-andesite-hosted xenoliths are of unknown origin, composed of silicate rocks other than felsic ignimbrite. One such xenolith has the appearance of a greenish, altered sandstone with a shell of chilled basalt. This rock is very fine-grained and composed glassy shards and microscopic mineral fragments, and is compositionally similar to arc andesites in both major and trace elements. Another unique xenolith is a black, mafic lava within the basaltic andesite that is physically distinguishable from the host lava due to
a thick (1-2 cm) glassy chill-rim not found around silicic xenoliths. Petrographically, this xenolith is nearly indistinguishable from its host rock and consists of olivine phenocrysts with skeletal overgrowths in a groundmass of mafic glass with microlites of plagioclase and clinopyroxene. This xenolith may be a bomb ejected at a near vertical trajectory which was subsequently re-integrated into the erupted lava while maintaining a glassy chill rim acquired during its short flight.

Geochemistry of Cerro Overo Basaltic Andesite

By Total Alkali – Silica classification, Cerro Overo lava is a calc-alkaline, basaltic-andesite due to its elevated silica content (52.8 – 56.6 wt % SiO₂; 4.1 – 4.7 wt % K₂O + Na₂O) (Figure 8). The high volume of olivine phenocrysts (x̄ = 7 vol %) and high concentration of magnesium (x̄ = 7.4 wt % MgO) perhaps more clearly define the mafic nature of the rock, compared to other Central Volcanic Zone rocks (Figure 11). The ⁸⁷Sr/⁸⁶Sr (0.70628) and ¹⁴³Nd/¹⁴⁴Nd (0.51247, εNd = -3.25) ratios are at the extremes for the region, reflecting a relatively lower level of crustal interaction than the majority of arc-related rocks in the CVZ (Figure 25). Upper-crustal interaction has clearly impacted the lava, resulting in higher SiO₂ and lower MgO in samples with a high number of partially-assimilated silicic xenoliths. An increase in K/Ti between less-evolved (49 – 51 wt % SiO₂) olivine-hosted melt inclusions and the whole rock, which is not expected to deviate significantly during AFC processes (Ariskin, 1999), provides additional evidence for crustal interaction following inclusion entrapment. Mixing models developed by Rosner et al. (2003) based on B-Sr and B-Nd isotopes indicate the isotopic composition of Cerro Overo lava could be produced by a 10-15 % addition of crustal melt to a primary arc magma. This estimate is at the low-end estimate for the average crustal input of 15 to 30% for central Andes arc volcanics (Davidson et al., 1984; Rosner et al., 2003). Oxygen fugacity (fO₂) of Cerro Overo olivine, calculated from olivine composition, ranges from 0.99 – 1.38 ΔFMQ (oxidizing) (Matthews et al., 1999).

Whole rock isotopic values for Cerro Overo maar (⁸⁷Sr/⁸⁶Sr = 0.7062-0.7065) are unradiogenic for the Altiplano-Puna region, but still relatively high for mafic rocks in a global context, reflecting the influence of crustal interactions occurring during ascent through double-thickened silicic crust (⁸⁷Sr/⁸⁶Sr ≥ 0.709). Single crystal olivine ⁸⁷Sr/⁸⁶Sr ratios from Cerro Overo (~0.7041-0.7071) define a broader range than accompanying whole rocks, indicating
preservation of a range of melt compositions in olivine-hosted melt inclusions, which is likely homogenized at the whole rock scale (Figure 75). Rosner et al. (2003) reported isotopic ratios for two samples from Cerro Overo. Values for $^{87}\text{Sr}/^{86}\text{Sr}$ (average 0.70628) are on the lower end for the region and $^{143}\text{Nd}/^{144}\text{Nd}$ (average 0.51244; $\varepsilon\text{Nd} = -3.89$) are at the higher end as expected from the primitive nature of the lava relative to regional volcanics (Rosner et al., 2003). Mantle and MORB are expected to have $\varepsilon\text{Nd} > 0$, and ratios for Cerro Overo (-3.4, -3.1) plot between CHUR and more negative crustal values, bolstering the argument that some crustal assimilation has occurred, but not as extensively as the majority of intermediate arc lavas (Rosner et al., 2003; McLeod et al., 2013). Central Andean stratovolcanoes generally have Pb isotopic ratios that reflect those of underlying crustal domains (i.e. the isotopic composition of the basement rocks), thought to be controlled by various accreted terranes (Mamani et al., 2008; Mamani et al., 2010). Radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (average 18.775) correspond with the Antofalla crustal domain, as defined by Mamani et al. (2010), which is the domain immediately underlying Cerro Overo and a large portion of the Altiplano-Puna Volcanic Complex (Rosner et al., 2003; Mamani et al., 2008).

**Geochronology**

A mid-Pleistocene 77 ka age for Cerro Overo maar has been determined by (U-Th)/He analysis of zircon from entrained felsic xenoliths (Ukstins-Peate, 2012, pers. comm). Previous Holocene estimates of the age of the maar were based entirely from the fresh nature of the lava (De Silva & Francis, 1991). Basaltic rocks this young are notoriously difficult to date, however, and additional checks are needed to confirm, and possibly better constrain this age. Magmatic temperatures, such as those induced by the inclusion of a portion of ignimbrite in a basaltic lava, can readily be assumed to reset the accumulation of He within a crystal of zircon. As such, the (U-Th)/He analytical technique measures how much He has accumulated from radioactive decay since the last time the mineral was above its He-closure temperature (175–193 °C) (Reiners, 2005). However, there is no assurance of a zircon crystal having its He content fully and completely reset, although six of seven measurements yielded similar ages, indicating reset is a reasonable assumption. Regardless, the (U-Th)/He eruption age of 77 ka represents a maximum possible age of eruption/entrainment.
Table 10 - Results from (U-Th)/He analyses and age calculations for zircon grains from a felsic xenolith (sample CIUP 08-097) entrained in basaltic andesite from Cerro Overo maar (McClelland, personal communication).

<table>
<thead>
<tr>
<th>(U-Th)/He data</th>
<th>Sample</th>
<th>Grain#</th>
<th>[U]$^2$</th>
<th>[Th]$^2$</th>
<th>$^{4}$He$^3$</th>
<th>Raw Age 18</th>
<th>Mean F$_T$</th>
<th>F$_T$ Corr. Age$^4$</th>
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<td></td>
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</tr>
</tbody>
</table>

Notes:
1. [z005 was lost during dissolution.]
2. These are the measured U, and Th yields in pico-moles, since individual grains were not weighed they can not be presented in a per gram notation.
3. The measured $^{4}$He yields are in femto-moles instead of pico-moles.
4. The age in italics was not included in the average calculation as it is considered not fully reset.

La Albóndiga Grande Lava Dome

**Petrography**

Lava of La Albóndiga Grande dome is calc-alkaline, olivine-phyric medium-K basaltic-andesite (56 wt % SiO$_2$, 7.3 wt % MgO) and nearly identical in composition to the lava found at Cerro Overo maar (average 54 wt % SiO$_2$, 7.4 wt % MgO). Olivine phenocrysts (5-18 % by volume) show subhedral to euhedral crystal forms with high forsterite cores (average 85.8 Fo %) and lower forsterite (average 77.6 Fo %) skeletal overgrowths and thin rims (Figure 76). Morphologies are varied, including perfectly euhedral, tabular, skeletal, dendritic, and complex, but generally show evidence for rapid growth during the later stages of the magmatic history, at least in part during volcanism. Olivine-hosted melt and mineral (Cr-spinel) inclusions are common. Local concentrations of olivine can exceed 25 % or be as low as 3 %, but samples show an average of 6-10 % olivine across the sample. The groundmass consists of mafic glass with microcrysts (≤ 0.25 mm) of calcic plagioclase lathes (An$_{66}$), euhedral clinopyroxene (augite and diopside), olivine, and Fe-Ti oxides (dominantly magnetite). Microphenocrysts of olivine are euhedral to skeletal and are compositionally identical to the rims of the larger phenocrysts...
Flow textures amongst the phenocrysts or within the groundmass are uncommon and very weak where present.

The lava ranges in vesicularity from massively dense (5 – 8 %) to extremely vesiculated (25 – 40 %), broadly segregated into sections of high or low vesicularity. The majority of vesicles are 0.25 – 5mm, but throughout the lava rare large vesicles up to a few cm can be found. Samples from the now-exposed interior of the dome are dominantly and homogenously vesicular (8 - 15 %) while those immediately below the outer surface of the dome show a wide range in vesicularity (7 – 35 %). The outermost portion of the dome is once again relatively homogenous in vesicularity (~ 30%) with an almost scoriaceous texture. The portions of higher or lower vesicle contents do not show smaller scale patterns, such as the presence of banding in lava around Cerro Overo maar.

CO55 – olv rich upper portion, inhomg. Vesc. 7 – 35 %, Avrg 20%, up to several cms; olv 17-16 %
CO56 – scoriaceous near-surface – homog vesc 30%; 6% oliv, 5-18%
CO62 – dome interior - 8-32 (rare, conc.) %, avrg 15% vesc; 6-13% olivine
CIUP 016 – N side – 8-25 % vesc., avrg 17 %; avrg 7 % olivine, 5-12%

We recovered 3 samples of lava from the dome in 2014, one from the vesicular outer layer and two from the olivine-rich interior (COBA 055, 056, 062). One sample from the north side of the dome was collected in 2008 (CIUP 08-016)

Lava texture (macro) – IUP_2007, 2027, 2030, 2002(glass), 2042 (N-side apron), 2065, 2070, 2072

Geochemistry

By Total Alkali – Silica classification, La Albóndiga Grande lava is a calc-alkaline basaltic-andesite (Figure 8). While the silica content (55.9 – 56.6 wt % SiO₂) is similar as the more evolved (xenolith bearing) Cerro Overo lava samples, La Albóndiga MgO contents (7.16 – 7.45 wt % MgO) are similar to the more mafic glassy lava of the maar (Figure 63). La Albóndiga dome lava also has low Sr (~ 485 ppm) when compared with Cerro Overo lava (486 – 525 ppm), although ultimately the difference is minimal. Otherwise, the two lavas appear to be the same. La Albóndiga Sr isotopic composition (0.70618) is also similar to the Cerro Overo signatures (0.7061 – 0.7064) (Figure 32). As no age data is available for La Albóndiga dome, it is possible the two endmember mafic lavas in the Altiplano-Puna region were emplaced within a few kms of each other at different times. However, similar degrees of surficial weathering suggest they
are of similar age. For all practical purposes, La Albóndiga dome and the Cerro Overo maar can be considered two different surface manifestations of the same magma controlled by similar structural features, if not the exact same zone of crustal weakness.

The Puntas Negras – El Laco Mafic Lava Flow

The Puntas Negras – El Laco lava is a series of Quaternary age, olivine- and clinopyroxene-phyric basaltic andesite flows near the Chile – Argentina border (23.75° S, 67.47° W). The lava has phenocrysts of olivine and clinopyroxene ± plagioclase. Olivine phenocrysts (0.5 – 5 mm) are subhedral to euhedral and frequently (~40-60 %) found in clusters with subhedral clinopyroxene (diopside; 0.25 – 5 mm) intergrown with plagioclase (An60) (Figure 77). Higher forsterite cores (average 83 % Fo) are in equilibrium with the whole rock, while lower forsterite rims (average 69 % Fo) would be in equilibrium with a more differentiated melt (Figure 78). Inclusions of Cr-spinel are found in most olivine crystals, but melt inclusions are relatively uncommon. Lava further from the vent contain phenocrysts (0.5 – 1.5 mm) of plagioclase (An52-69) which are commonly fractured with sieve-textured interiors and clinopyroxene inclusions. This plagioclase is compositionally continuous with those found in glomerocrysts and the groundmass. Anorthite-albite exchange (Kd(An-Ab)) indicates Puntas Negras plagioclase is in equilibrium. The groundmass consists of microphenocrysts of plagioclase (< 0.5 mm; 20-60 %; An60), clinopyroxene (< 0.25 mm; < 5 %; diopside-augite), and opaque oxides (< 0.1 mm; < 2 %) in a dark glass (20-50 %). Crystals show weak flow orientations in most, but not all samples. No xenoliths were observed in the Puntas Negras – El Laco lava, and a single quartz xenocryst shows extensive resorption and is mantled with a clinopyroxene reaction rim, indicative of prolonged residence within the mafic lava.

More in-depth field studies are required to determine the number of discrete flows or eruptive events at this location, but the lava can be divided into two main parts based on composition, petrography, and spatial relationships (Figure 64). Lavas closer to the point of origin (the “Upper Flow”) are rich in olivine-clinopyroxene glomerocrysts (2-8 mm) and slightly higher in both SiO2 and MgO (53.4 wt % SiO2, 6.98 wt % MgO) compared with the denser, lower crystallinity “Lower Flow” lavas further from the vent (52.5 wt % SiO2, 6.48 wt % MgO). The more highly crystalline Upper Flow (5 – 12 % olivine) contains nearly twice as much nickel (~ 80
Plagioclase is present almost exclusively as microphenocrysts in the Upper Flow, while the Lower Flows contain phenocrysts (0.5-1.5 mm) of plagioclase (and higher CaO) and less clustering of mafic minerals. The Higher Flows have higher degrees and variability of vesiculation (10 - 40%, average ~ 15 %) than the Lower Flows (3 – 10 % vesicles), and hand samples from the Lower Flows are notably much denser. The ratio of Cr/Ni is higher for the Lower Flows (5.67) than the Upper Flows (3.13) likely reflecting the larger pyroxene to olivine ratio of the Lower Flows. Trace element characteristics used for distinguishing magmatic origin (e.g. Rb/Sr, La/Ta) (e.g. Kay et al., 1994) are more or less constant between the two flow subdivisions (e.g. Nb (~ 17 ppm), Ba (~ 445 ppm), and similar La/Ta). Other shared geochemical characteristics include high K2O (with respect to SiO2), high TiO2 content (1.3 wt %, compared with 0.9 wt % TiO2 for Cerro Overo), and lower Sr/Nd (21.0) per given silica (Cerro Overo = 27.3).

**Upper:** PN samples (N-S) 14, 01, 02, 03, 04

- Olivine-rich (5 -12 %), highly vesiculated (10 – 40%)
- Higher SiO2 (Upper flow is 53.4-53.7 wt %, transitional sample is 52.5 wt %)
- Slightly lower K2O (average 1.39 %) and Na2O (average 3.12 wt %)
- Samples 14, 02, 04 show higher MgO (7.3 wt %), all others (6.1 – 6.8 wt %)
- Higher FeO* (9.05 – 9.36 wt %), lower Al2O3 (15.8 %)
- Lower CaO (8.32%), sample 04 is transitional.
- Significantly higher Ni content (79 ppm vs. 40 ppm in the Lower Flow)
- Lower Sr content (Upper: 567 ppm vs. Lower: 625 ppm)
- Lower La/Yb ratio (12.9 vs. 15.4), Sm/Yb (2.7 vs. 3.1), Sr/Y (23.7 vs. 28.3)

**Lower:** PN samples (N-S) 06, 08, 09, 11, 12

- Lower crystallinity (2 – 5 %), lower vesicularity (3 – 10 %) (notably denser)
- Lower SiO2 (51.7 – 53.2 wt %), not correlated with distance
- Slightly higher K2O (average 1.54 wt %), Na2O (average 3.33 wt %) than the Upper Flow
- Mg) in lower range (6.1 – 6.8 wt %) for all Puntas Negras mafic lava samples
- Lower FeO* (8.73 – 9.19 wt %), higher Al2O3 (16.4 wt %)
- Higher CaO (8.86 wt %) than the Upper Flows, sample 05 is transitional.
- Significantly Higher Cr/Ni (5.67 vs. 3.13), due to a higher pyroxene/olivine ratio.
El País Lava Flow

El País lava has plagioclase phenocrysts (18 %; 0.25 – 1 mm) and glomerocrysts (16 %; 0.5 - 8 mm across) of light green clinopyroxene, yellow-brown orthopyroxene, and plagioclase in a groundmass of dark volcanic glass and plagioclase microcrysts (< 0.1 mm) (Figure 79). The lava is massive and nearly vesicle-free. The glomerocrystals are composed of 85 % two pyroxenes, present in roughly equivalent amounts, and approximately 15 % plagioclase. The glomerocrysts show some flow-orientation with the larger (> 2 mm) clusters roughly concentrated in bands. Orthopyroxene (0.5 – 1 mm) is slightly pleochroic, subhedral enstatite, which appears in shades of light grey in crossed-polars (Figure 80). Clinopyroxene (0.5 – 1 mm) is subhedral augite with high birefringence, which frequently displays simple twinning and, less often, sector-zoning. This sector-zoning represents relatively minor intracrystalline variations in Al content (2.6 – 4.5 wt %). Plagioclase phenocrysts (18 %; 0.25 – 1 mm) are anhedral to subhedral and found both in glomerocrysts and free floating. Plagioclase commonly have sieved cores with glassy and/or opaque micro-inclusions. Many are fractured and resorbed along their boundaries. Within the glomerocrystic clusters, plagioclase appears to be in the process of being consumed by the surrounding pyroxene. Anorthite-albite exchange coefficients \( K_D(\text{Ab-An}) = 0.11 – 0.19 \) for the An\(_{75}\) phenocryst plagioclase population indicate these crystals are out of equilibrium \( K_D(\text{Ab-An}) = 0.27 \pm 0.05 \) for equilibria exchange at \( T > 1050^\circ\text{C} \) \( K_D \) test from Putirka, 2008). The groundmass consists of microphenocrysts of plagioclase (< 0.5 mm; An\(_{55}\)), which show strong alignment with flow and are in equilibrium with the whole-rock composition in a matrix of dark-brown volcanic glass. Vesicles are rare, with the exception of elongated, flow-oriented “pull-apart” voids (Figure 81). Small crystals of pyroxene (< 0.25 mm), found in the groundmass, appear to be derived from the glomerocrysts.

Tilocálar Norte and Tilocálar Sur Volcanoes

Petrography

Both Tilocálar volcanoes erupted aphyric, fresh, dark grey, and less-evolved andesites to basaltic andesite (Figure 8), which display evidence for rapid cooling. Lavas exhibit 10-30% vesicularity (< 1 – 2mm) in the flows and up to 80 % vesicularity in pyroclastic sections of Tilocálar Sur. These lavas contain rare (< 3-5 %) microphenocrysts of clinopyroxene (0.5 – 0.7 mm; green augite) and plagioclase (0.5 – 0.8 mm; An\(_{35}\) – An\(_{48}\)) and display either glassy
inclusions or poikilitic textures. In addition, lava from Tilocálar Norte contains rare microphenocysts of slightly pleochroic, subhedral orthopyroxene (0.5 – 1.5 mm). Extremely rare crystals (< 1mm) of olivine have been found in a scoriaceous sample from the explosion crater, but only in the crushed rock (> 250 μm separate). Large phenocrysts are absent (or extremely rare). Vesicles are sub-spherical and angular. Lavas from both volcanoes contain amygdules of gypsum, less commonly calcite, and possibly cristobalite. The groundmass of the lava predominantly consists of a homogenous, clear brown glass (20 – 50 %) and microlitic plagioclase lathes (10-30 %; 0.05-0.3 mm) immersed in the glass (“hyaloophitic” texture) that commonly show subparallel flow-alignment. Other microlites include subhedral green clinopyroxene (0.01 – 0.1 mm; < 2%) and opaque cubic minerals, likely magnetite (0.01 – 0.1 mm; < 1-3 %). Opaque minerals are more abundant in lava from Tilocálar Sur. Tilocálar Norte rocks contain rare microlites of orthopyroxene (0.01 – 0.2 mm). Occasional clusters of slightly pleochroic acicular microcrystals (< 0.1 mm) are present in the groundmass glass from both volcanoes, which may be amphibole.

**Geochemistry & Age**

Aphyric andesite of Tilocálar Norte (63.6 wt% SiO₂, 2.44 wt % MgO) is compositionally more evolved than that of Tilocálar Sur (58.7 wt% SiO₂, 3.56 wt % MgO). Tilocálar andesites show a calc-alkaline affinity with medium potassium contents (Norte: 2.86 wt % K₂O; Sur: 1.94 wt % K₂O) and lie within the modern arc suite for major element composition (Figure 8). Notably, lavas of Tilocálar Norte and Sur have highly elevated Sr contents (886 ppm and 1189 ppm, respectively), Ba contents (930 ppm and 752 ppm), and are enriched in other incompatible elements (La - Sm), likely evidence these lavas originated as relatively small fractions of partial melt. However, large ion lithophile elements (LILEs) Cs and Rb and actinides Th and U are relatively depleted (Figure 82). Another notable compositional feature of Tilocálar volcanoes is a significantly higher degree of rare earth element fractionation (La/Yb = 39 -66) than the arc (typically La/Yb = 15-20 at equivalent silica content). Tilocálar Norte has higher La/Yb (56.5 – 65.5) than most lavas from Tilocálar Sur (La/Yb = 39.3 – 48.5), with the exception of one sample from the easternmost flow lobe of Tilocálar Sur, which is an older (stratigraphically lower) andesite with La/Yb = 61. Heavy rare earth element (HREE) depletion may reflect the presence of residual garnet in the magmatic source region, which preferentially sequesters HREEs, and/or fractionation of amphibole (e.g., Kay et al., 1991).
The Tilocálar volcanoes erupted during the late Pleistocene to Holocene. Lavas from both Tilocálar Norte and Sur were dated at < 1 Ma by the Laboratorio de Geocronología del Servicio Nacional de Geología y Minería (Sernageomin) using whole rock K-Ar, which were found to be enriched in radiogenic Argon (\(^{40}\text{Ar}\)) (Gardeweg & Ramirez, 1982). Lavas from Tilocálar Sur dated using \(^{40}\text{Ar}/^{39}\text{Ar}\) of whole rocks indicate a Late Pleistocene age ranging from 730 ± 50 ka to 460 ± 50 ka (Gonzalez et al., 2009). The underlying Tucúcaro ignimbrite is welded dacite with a \(^{40}\text{K}/^{40}\text{Ar}\) age of 3.2 ± 0.3 Ma (Gardeweg & Ramirez, 1982), and the Patao ignimbrite is 3.1 ± 0.2 Ma (Gonzalez et al., 2009).

**Cerro Tujle Maar**

Lava erupted at Cerro Tujle maar is a glassy and aphyric calc-alkaline andesite (58.8 wt% SiO\(_2\), 3.45 wt % MgO) that is petrographically and compositionally similar to lava from the Tilocálar volcanoes. Cerro Tujle lavas exhibit 2 – 10 % vesicularity (≤ 0.4 mm) and contain 2-5 % microphenocrysts of plagioclase (≤ 0.2 mm) and ≤ 2 % microphenocrysts of ortho- and clinopyroxene (≤ 0.3 mm) (Figure 83). Large phenocrysts are absent (Figure 83). Plagioclase crystals are euhedral lathes with compositions ranging An\(_{48}\) – An\(_{64}\) (average An\(_{59}\)) and show no preferred orientation. Pyroxene crystals are subhedral to sub-rounded with compositions split evenly between diopside and magnesian enstatite (Figure 83) and display micro-inclusions of opaque oxides in roughly 20 % of the crystal population. The orthopyroxene is yellow-brown and slightly pleochroic (Figure 84) while clinopyroxene microphenocrysts are clear to light green and display colorful birefringence. The groundmass is a medium-brown glass with microlites (≤ 2 %) of euhedral opaques oxides (≤ 20 μm) and an unidentified acicular mineral (≤ 5 μm) (Figure 83). Vesicles are sub-rounded, irregularly shaped, and show no preferred orientation.

**Cerro Chascón de Purico Complex**

(23.0182° S, 67.6882° W)

_Elevation: 5480 m ASL_

Cerro Chascón de Purico and Cerro Aspero are the youngest two dacitic lava domes (estimated as Holocene by De Silva & Francis, 1991) in the Purico volcanic complex. Cerro Chascón is formed from viscous flows of dacitic lava and contains mafic xenoliths. Lava from this dome is included in this study as the Purico volcanic complex is located above the Altiplano-
Puna Magma Body, therefore this center may reflect similar parental magmatism reaching the upper crust as to the southeast of the Salar de Atacama, with one additional complication – the upper-crustal magma chamber (e.g., Del Potro et al., 2013). Considering this dome as a foil to other centers in this study helps to frame the importance of the sub-regional setting of the other studied lavas.

The sample included in this work is derived from the Cerro Chascón dome and results from mixing between the dominant dacitic material of the complex and the more mafic material found as magmatic inclusions. Dacitic lava from Cerro Chascón is coarse-grained and crystal rich (~ 65% crystals; ~ 40% phenocrysts, 15% microphenocrysts). Phenocryst mineralogy includes plagioclase (~ 20%), quartz (~ 6%), amphibole (~ 5%), clinopyroxene (~ 3%), biotite (~ 3%), oxides (~ 2%), K-feldspar (< 1%), olivine (< 0.5%), orthopyroxene (< 0.1%), and accessory zircon, apatite, and sphene (Burns et al., 2015). The groundmass is a medium vesiculated, high-silica glass (75 wt % SiO₂) with microphenocrysts of plagioclase and amphibole (50 % of total groundmass). Phenocrysts (> 1 mm) display disequilibrium textures, such as sieved plagioclase, quartz with resorption features and clinopyroxene halos, and olivine with amphibole rims. Basaltic-andesitic inclusions are fine-grained and porphyritic (60–66% crystals; ~ 15% phenocrysts, 50–53% microphenocrysts), with a mineralogy consisting of clinopyroxene (~ 5%), amphibole (~ 4%), olivine (~ 3%), oxides (~ 2%), plagioclase (~ 1%), and rare quartz (< 0.5%) and biotite (< 0.1%) (Burns et al., 2015). Groundmass is fine-grained and medium vesiculated with microphenocrysts of plagioclase (44 %) and amphibole (33 %) in a rhyolitic glass (75 wt. % SiO₂).

Mineral Chemistry

Olivine: Cerro Overo Maar & La Albóniga Grande Dome

Olivine phenocrysts and microphenocrysts from the basaltic andesite lava of Cerro Overo maar and La Albóniga dome have virtually identical morphologies and compositions (Figure 40; Figure 76). Phenocrysts range from 0.5 – 4 mm and are generally subequant with skeletal overgrowths at some, but not all, crystal apexes. Forsteritic contents are normally-zoned with cores ranging 84 – 88 Fo% (\(\bar{x} = 86.3 \pm 0.9\) Fo%) and rims on the scale of 5 – 25 \(\mu\)m with 70 – 83 Fo% (\(\bar{x} = 78.7 \pm 3.2\) Fo%) (Figure 72 - Figure 74). High forsterite olivine cores are
also correlated with high Ni and low Mn and Ca contents. The profile of the transition from high Fo% cores to low Fo% rims is relatively steep, indicating compositional zoning is not dominated by diffusive relaxation and the observed zoning patterns reflect original growth partitioning influenced by the magmatic environment (Chapter 3). Calculated Fe-Mg exchange coefficients between olivine phenocrysts and parental liquid (whole rock) compositions ($K_D$; Equation 5) indicate crystal cores are in equilibrium with bulk rock compositions while crystal rims and groundmass microphenocrysts have crystallized from more differentiated liquid (Figure 78). Such a deviation from equilibrium exchange is expected from ongoing olivine crystallization in an evolving melt. The continuous nature of the compositional deviation away from equilibrium (Figure 78) indicates continuous growth from the same liquid. In contrast, olivine phenocrysts from the Puntas Negras – El Laco flow display a compositional gap between core and rim, indicating either a break in crystallization or an immediate and significant shift in magmatic conditions.

\[
K_D (Fe - Mg)_{oliv-\text{liq}} = \left( \frac{X_{Fe\text{liq}}}{X_{Mg\text{liq}}} \right)^{oliv} \left( \frac{X_{Fe\text{oliv}}}{X_{Mg\text{oliv}}} \right)^{liq}
\]

*Equation 5 - Calculation of the Fe-Mg exchange coefficient between olivine and liquid.*

The outer rims ($\leq 25 \mu m$) of the olivine phenocrysts are lower forsterite (average 78.7 Fo %) overgrowths reflecting the final stages of growth immediately preceding and following eruption, resulting from lower temperature crystallization which likely occurred in a more differentiated melt environment. While temperature certainly influences forsterite content (e.g., Donaldson, 1976), lower Mg availability may have also been in part due to syn-eruptive assimilation of upper crustal material. Olivine microphenocrysts in the groundmass are compositionally indistinguishable from phenocryst overgrowth rims and their small size and flow alignment are evidence these grew near the time of eruption, as well. The broader spread in forsterite contents of the phenocryst rims (Table 11) represents a continuum of olivine growth during cooling and continuously changing magma chemistry. Skeletal overgrowth features of Cerro Overo, La Albóndiga, and Puntas Negras olivine phenocrysts likely indicate strong undercooling accompanied by rapid crystal growth (Donaldson, 1976), also visible in fine-scale
zoning patterns of incompatible element phosphorous (Chapter 3). As many as 90% of the olivine phenocrysts visible in a thin section display skeletal (or hopper) morphology to some degree (Figure 38). Crystals without such features may have simply been intersected at a non-ideal angle for highlighting obvious rapid-cooling features (e.g., Faure et al., 2003; Welsch et al., 2012). Skeletal phenocryst morphologies of Cerro Overo olivine are similar to those of microphenocrysts of the Ollagüe-associated mafic center labeled “SC2” (Mattioli et al., 2006), but Cerro Overo lava is a less-evolved overall.

In a few Cerro Overo samples, the olivine phenocrysts have thin, micron-scale (reaction) overgrowths of microcrystalline iddingsite or phlogopite ± magnetite. The interface between the olivine and these reaction rims are generally convoluted and irregular, are more pronounced on skeletal growth features, and can contain a significant portion of Fe-oxides concentrated at the inner regions of the rim. Such rims are significantly more common for phenocrysts from La Albóniga dome, in some instances having replaced > 50% of individual low forsterite rims. Olivine rims with significant reaction overgrowth display elevated Mn/Fe ratios with respect to forsterite content, but are otherwise contiguous with the compositional trends seen in olivine phenocrysts from both the dome and Cerro Overo maar. This deviation is likely due to enhanced Fe-depletion via diffusion relative to Mn in the outer rims of the olivine as Fe-oxides developed adjacent to (and potentially derived from) the phenocrysts. Olivine phenocrysts contain abundant melt inclusions, preserving additional compositional information for the melt at depth. Microbeam analyses of re-homogenized melt inclusions provide evidence of olivine trapping high MgO melt less-contaminated by crustal material than the bulk magma. Trace element characteristics of trapped mafic melts, however, suggests they do not necessarily represent a single parental arc magma, but rather trapping of one of several separate basaltic components introduced to the lower crustal MASH zone (Chapter 2) (Kay & Kay, 1993; Kay & Coira, 2009; Beck et al., 2015).

| Table 11 - Summary of olivine phenocryst compositions in the basaltic andesites of Cerro Overo maar, La Albóniga dome, and the Puntas Negras – El Laco lava flow. Reported values are averages ± one sigma (standard deviation). |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Average Fo%    | Core n<sub>core</sub> | Rim n<sub>rim</sub> | Groundmass n<sub>GM</sub> | Liquid* n<sub>liq</sub> |
| Cerro Overo    | 86.3 ± 0.9      | 107             | 78.7 ± 3.2      | 89             | 79.8 ± 4.4      | 6               | 64.9 ± 0.3      | 15              |
| La Albóniga    | 85.8 ± 1.7      | 51              | 77.6 ± 2.0      | 58             | ±               | 64.9 ± 0.4      | 13              |
Puntas Negras  83.1 ± 2.3  29  68.6 ± 2.4  23  67.7 ± 0.2  8  59.5 ± 1.4  15

*Liquid Fo% is calculated from whole rock (bulk) measurements of MgO and FeO(t).

Internal subgrain domains are not observed in crystal birefringence viewed in crossed-polarized light. High-resolution microprobe imaging of olivine phenocrysts confirms complex internal zoning of P, indicative of stages of rapid skeletal growth followed by slower infilling crystallization (Milman-Barris, 2008; Watson et al., 2015; Chapter 3). Melt and mineral (dominantly Cr-spinel, rarely Fe-Ti oxides) inclusions are common in olivine, ranging from 5 – 30 μm across, with few outlying exceptions. Oxide inclusions are dominantly (> 95 %) subhedral to euhedral Cr-spinel (average Cr#*100= 71), commonly found in clusters or arranged approximately parallel to olivine crystal faces and result from Cr-spinel growth during certain intervals of favorable magmatic conditions. Resorption surfaces or embayments in olivine crystals are common, but usually visible on only one or two crystal faces, implying a possible chemical or thermal gradient, likely due to near-surface introduction of felsic melt as evidenced by upper-crustal xenoliths. Destructive features are visible not only as disruptions in crystal outlines, but also manifest in Fo% with the lower-Fo rims missing or truncated at a crystal edge (Figure 86).

Table 12 - Summary of relevant chemistry for olivine phenocrysts and whole rock chemistry of lava from Cerro Overo maar and the Puntas Negras-El Laco mafic flow. Values are in oxide weight % unless otherwise noted.

<table>
<thead>
<tr>
<th></th>
<th>Fo%&lt;sub&gt;OLV&lt;/sub&gt;</th>
<th>SiO₂</th>
<th>MgO</th>
<th>FeO&lt;sup&gt;t&lt;/sup&gt;</th>
<th>Mg#&lt;sub&gt;WR&lt;/sub&gt;</th>
<th>TiO₂</th>
<th>MnO</th>
<th>Cr ppm</th>
<th>Ni ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. Overo</td>
<td>86</td>
<td>54.7</td>
<td>7.4</td>
<td>7.8</td>
<td>62</td>
<td>0.91</td>
<td>0.12</td>
<td>295</td>
<td>117</td>
</tr>
<tr>
<td>P. Negras</td>
<td>83</td>
<td>52.9</td>
<td>6.7</td>
<td>9.1</td>
<td>57</td>
<td>1.31</td>
<td>0.14</td>
<td>240</td>
<td>58</td>
</tr>
</tbody>
</table>

Overall, the trace element compositions of olivine from Cerro Overo, La Albóndiga Grande, and Puntas Negras – El Laco are most similar to the “Within-Plate-Magmas; Thick” classification described by Sobolev et al. (2007) as Ocean Island Basalts and Large Igneous Provence basalt emplaced over thick lithosphere (> 70 km). Unfortunately, in the extensive review of olivine compositions of Sobolev et al. (2007), continental-margin (i.e., subduction zone) olivine compositions were not included to avoid introducing the complexities of subduction zones into the analyses. The Andean olivine do not show signs of Ni/Co decoupling, a prevalent feature of the thick-lithosphere intraplate magmas analyzed by Sobolev et al. (2007),
many of which are derived from Ni-rich mantle plumes (e.g. the Siberian Large Igneous Provinces). The other exception is in the Cr content of the measured central Andean olivine, as mentioned above.

**Pyroxene**

Crystals of pyroxene are present in the four mafic lavas (olivine-phyric Cerro Overo, La Albóndiga, and Puntas Negras-El Laco, and two pyroxene-bearing El País). For Cerro Overo and La Albóndiga, small crystals (< 0.25 mm) are found in the groundmass as microphenocrysts (< 2%) and presumably grew during the final stages of the magmatic ascent. Compositionally, both lavas show a bimodal distribution of compositionally similar augite and diopside (MgCaSi$_2$O$_6$) with very low Fe contents (Figure 87 A & B; Figure 88). The compositional spread between the two centers is remarkably limited, bolstering the argument Cerro Overo maar and La Albóndiga dome represent two different surface expressions of the same magmatic batch/system.

Groundmass pyroxene crystals from Puntas Negras-El Laco (< 0.25 mm; < 5%) have a similar, but less variable compositions near the augite/diopside classification border (Figure 87C), although with a slightly higher Fe-bearing component, reflecting the overall elevated Fe content of Puntas Negras lava (Figure 89). Phenocrysts from this same flow are Mg-rich augites and show negligible core-rim variations or sector zoning (Figure 87C; Figure 77).

El País lava contains intergrown phenocrysts of ortho- and clinopyroxene with a subordinate plagioclase component in glomerocrystic clusters (Figure 80; Figure 90). There are two distinct pyroxene compositions of calcic, monoclinic Augite ((Mg, Ca)$_2$Si$_2$O$_6$) and magnesian, orthorhombic Enstatite (Mg$_2$Si$_2$O$_6$) with little intra-pyroxene variation (Figure 87; Figure 87D). Minor sector-zoning is displayed in the Al contents of some diopside phenocrysts (Figure 90). On average, diopside contains 3.4 wt % Al$_2$O$_3$ and ranges from 2.6 – 4.5 wt %. This zoning, however, is not well-correlated with variation in any other major clinopyroxene components (Mg, Fe, Ca), indicating these pyroxenes were not grown in particularly dynamic magmatic conditions (Figure 91). The intergrowth of two pyroxenes and plagioclase indicates all three phases were stable concurrently. The complicated textures seen in two dimensions (Figure 90) hint at the great complexity of these accumulations in three dimensions. El País lava does not show seriate texture (i.e., continuous crystal size range) and instead consist of these large (2 – 10 mm) pyroxene-plagioclase crystal conglomerates in a groundmass of plagioclase.
microphenocrysts (0.1 – 0.4 mm) and microphenocrysts (< 0.1 mm) of plagioclase and Fe-oxides in volcanic glass. Relatively stable pyroxene growth and phenocryst cumulates in a more fine-grained matrix indicate this lava was likely derived from a magma storage zone in the middle to upper crust and was delivered to the surface with a crystal cargo. The absence of significant resorption of phenocrysts is evidence that the crystals and melt are genetically and/or compositionally related. Magma differentiating in storage (AFC processes) near the brittle-ductile transition is a common source of lava in the central Andes (e.g., Stern, 2004) and is consistent with an origin of El País as a mafic component of the long-lived, intermediate arc-andesite volcanism commonly seen at stratovolcanoes in the Andes (e.g., Davidson et al., 1991).

Microcrystals of pyroxene in west-of-the-arc monogenetic lavas from Tilocálar Norte, Tilocálar Sur, and Cerro Tujle maar have bimodal augite-diopside and magnesian enstatite compositions (Figure 92). The diopside-augite clinopyroxene crystals form continuous ranges across the same compositions as Cerro Overo and La Albóndiga groundmass pyroxenes (Figure 88). The orthopyroxene enstatite from Cerro Tujle maar (Figure 92B) is identical in composition to the orthopyroxene of El País lava (Figure 87D). The enstatite from Tilocálar Norte y Sur (Figure 92A & C) is slightly more magnesian than El País orthopyroxene (Figure 87D). Tilocálar Sur pyroxene (Figure 92C & D) shows the greatest range of microcrystic pyroxene overall and vesiculated lava sampled from the gas explosion crater on the south slope of the volcano (Figure 22; Figure 23) contains only clinopyroxene crystals (Figure 92D).

**Tectonic & Structural Interpretations**

The stress regime of the Altiplano-Puna region was dominated by NW-SE to E-W shortening and uplift (vertical extension) through the Miocene to early Pliocene (Allmendinger et al., 1997). Around 2 – 3 Ma, the stress regime transitioned into a more complex mixture of both compression and extension, which were likely associated with delamination of the lithospheric root (Kay et al., 1994).
Minor Volcanism within the Frontal Arc

_Cerro Overo & La Albóndiga Grande_

Cerro Overo maar is located at the axis of an eastward-verging asymmetric antiform known as the _Cordón Altos de Toro Blanco_, which extends 21 km north-south (~12°) between _Chiliques_ and _Aguas Calientes_ stratovolcanoes. The Toro Blanco ridge is mainly comprised of folded and uplifted ignimbrite (the uppermost unit is the ~4 Ma Atana) and is overlain by volcanic deposits associated modern arc volcanism, indicating its formation between the start of ignimbrite flare-up in the Miocene and before development/migration of the Andean arc to its current location. The lithology of the core of the fold is unknown. The orientation of the _Toro Blanco_ ridge, its eastward vergence, and apparent timing indicate it is likely this feature is related to the compressional stresses at the boundaries of the Atacama crustal block (Figure 6). A large thrust fault, the Miscanti Fault, is located some 12 km to the west, and it is possible the _Cordón Altos de Toro Blanco_ is a splay fault of this larger system (Figure 93). Crustal faulting and folding of this sort provide opportunities for magma to rapidly reach the surface while reducing the time for magmatic interaction with country rock where the rotational deformation component produces localized extension or, at least, less vertical stress (e.g., Aron et al., 2008; Gonzalez et al., 2009; Lin et al., 2016). At least three of the other volcanic centers addressed in this work (Tilocálar Norte, Tilocálar Sur, and Cerro Tujle maar) are similarly erupted in a region of localized extension within contractional structural features such as the Miscanti Fault (Figure 17). Cerro Overo maar is also located along the mapped trajectory of the Calama-Olacapato-El Toro (COT) lineament, a regional left-lateral transverse fault system that cuts through the crust with a NW-SE orientation (Figure 5). The lineament is generally mapped as “inferred” as it passes through the volcanic arc (i.e., below Cerro Overo), although its appearance to the NW and SE of the arc make it highly likely that the fault system continues beneath the maar (e.g., Matteini et al., 2002; Riller et al., 2006). With our current knowledge, it is impossible to know the precise involvement of these two structural features in aiding the ascent and emplacement of Cerro Overo magma. Field and mapped relationships between structures and minor volcanism, however, are consistent with a role for upper crustal structures to allow less-evolved magma batches reaching the surface in this region of the central Andes.

The Cerro Overo maar itself is a relatively fresh volcanic crater, as indicated by the persistent steep walls of the crater (e.g., Ross et al., 2011). Shallower (< 200 m) explosion(s),
which formed the crater, limit the extent of ejecta around the maar and any deeper explosive activity will have created brecciated magma-country rock mixtures through upward-directed debris blasting and subsidence (Palladino et al., 2015; Valentine et al., 2015). Thus, basaltic andesitic maar ejecta is substantially contaminated with only uppermost crustal material (i.e., the Atana Ignimbrite; Gardeweg & Ramirez, 1987). A handful of xenoliths with other compositions exist, although their sources are unclear. The deep crust of the Andes is complex and relatively unknown in any form other than density features (e.g., McLeod, 2013). In addition, the basal portion of the Atana Ignimbrite carries a significant amount of lithic fragments and xenoliths itself (Gardeweg & Ramirez, 1987; Lindsay, 2001a). Occasional brecciated hand samples found around the maar indicate breccia-generating, diatreme pipe-forming blasts occurred during eruption (White & Ross, 2011; Palladino et al., 2015), but little is known of the maar at > 80 m depth, although a comprehensive study of global maar occurrences suggest that the diatreme extends ~ 2 km downward before connecting with a feeder dike (Palladino et al., 2015). Monogenetic eruptions of mafic lavas at maars is commonly attributed to small magma batches ascending from depths of 10s of km (as opposed to being fed by sub-volcanic reservoirs; e.g. Palladino et al., 2015). Localized extension along compression-related features of the Altiplano-Puna (Aron et al., 2008) provide ample opportunity for accelerated magma ascent through the upper crust and Cerro Overo magma was almost certainly channeled to the surface by the structural weakness underlying the Cordon Altos de Toro Blanco antiform. Deeper-reaching transverse structural lineaments, which cut the lithosphere, may have provided a pathway for the magma to reach the upper-crustal fault system without experiencing extensive differentiation (Matteini et al., 2002; Norini et al., 2013).

The lack of fine-grained ejecta (tuff, ash) around the maar crater is strong evidence that the explosion that created Cerro Overo maar was not dominated by phreatomagmatic processes as magma-water interaction causes intensive fragmentation of erupted lava (White & Ross, 2011; Valentine et al., 2015). The angular nature of Cerro Overo fracturing also indicates the lava was relatively viscous and degassed. Heavily vesiculated lavas are, however, found around the crater rim in a subordinate population, and likely indicates rapid degassing of the ascending magma as it neared the surface, which may have played an important role in generating the crater-excavating explosion. Substantial subsidence following a minor surficial explosion is ruled out by the presence of diatreme-related country rock – juvenile lava breccia and occurrences of ejected Atana Ignimbrite which, by matching petrology, was derived from at least 40 m depth.
Scoria lapilli horizons have been identified as a product of eruptive phases with little to no involvement of external water, driven mainly by magmatic volatiles (Palladino et al., 2015 and references therein). These scoria horizons, when observed forming, have been associated with Hawaiian-style or violent Strombolian eruptions of mafic lava and typically alternate with tuff-and ash-forming phreatomagmatic volcanism (Houghton et al., 1999; Sotilli et al., 2009; Palladino et al., 2015). However, such scoria-forming eruptive styles are not expected to form craters, but rather cones or flows (White & Ross, 2011; Valentine et al., 2015). Experimental and field observations of maar-diatreme and other crater-forming eruptions indicate some form of molten fuel-coolant interaction is required to cause rapid lava expansion and crater excavation (White & Ross, 2011; Palladino et al., 2015; Valentine et al., 2015, and references therein). Effusive eruptions following intersection of an ascending dike with the surface are well documented and do not require crater-forming explosive activity (e.g., Iceland).

Nearby, at the southwestern edge of the exposed antiform (23.527° S, 67.685° W), a large dome of olivine phyric basaltic-andesitic lava has been exposed at the edge of a basin (drop-block?) (Figure 34). This dome, herein referred to as La Albóndiga Grande, displays nearly identical mineralogy and composition as the lava at Cerro Overo maar, but without the flow features, variable vesicularity, or upper crustal xenoliths found at the maar eruption. Similar petrography and composition, along with spatial correlation and degree of weathering, indicate these two features are likely built of the same magmatic material and will be treated as such in this work. The eruption at this dome was clearly not explosive. The majority of the dome is a coherent mass of mildly vesiculated basaltic andesite and the uppermost surface of the dome displays increased vesicularity indicative of gas release and a small flow of basaltic andesite extending from the main extrusive feature. These physical traits offer clear evidence that it was not a necessity for the basaltic andesite erupted at Cerro Overo maar to form an explosive, crater-excavating eruption by rapid de-volatilization. The most likely candidate, as before, is magma-coolant (water or slurry) interaction inciting thermohydraulic detonation (e.g., Ross et al., 2011; Palladino et al., 2015). The complete lack of ash or tephra around the maar, in this case, may be due to winnowing of fine-grained material by the high winds of the Atacama Desert.

La Albóndiga dome is mentioned in the literature once, although not named, in a description of a volcanic lineament passing through Cerro Overo maar (2.5 km NE of La
Albóndiga), Negro de Barriales dome (10 km NW), and Cerro Tumisa composite cone (15 km NW) (Matthews & Vita-Finzi, 1993). This ‘Tumisa Line’ is parallel and spatially coherent with the regional-scale, NW-SE trending Calama-Olacapato-El Toro (COT) transverse lineament and almost certainly a local expression along this broad lithospheric feature. The COT passing through the area at the foot of Chiliques stratovolcano likely provided a subvertical zone of weakness that acted as a crustal pathway for magma ascent, located along the margin of the depression adjacent to La Albóndiga dome (e.g., Allmendinger et al., 1983; Coira et al., 1993; Kay et al., 1994; Matteini et al., 2002; Norini et al., 2013). The COT lineament has been proposed (e.g., Matteini et al., 2002) to extend as deep as the base of the lithosphere, which would provide a pathway for magma to travel from deep storage to the surface with minimal assimilation and differentiation. Some 6-8 km south of Cerro Overo maar and La Albóndiga dome, a similar alignment of volcanic features (e.g., eruptive craters) of stratovolcanoes Lascar and Chiliques, and a complex series of flows and domes to the southeast follow an orientation trend nearly identical to the Tumisa Line. Further south (~ 17 km from Cerro Overo), the Cordon de Puntas Negras is a ~ 30 km long complex of flows, domes, and composite cones that once again follow a nearly identical NW-SE orientation. These multiple cases of volcanic alignment are taken as evidence of the influence of the COT Lineament on magmatism and volcanic emplacement in the area. The Cordón Altos de Toro Blanco ridge is subparallel to and just east of the series of fold-and-thrust features at the SE margin of the Salar de Atacama (e.g. the Miscanti thrust) and may be a splay of these features beneath the arc itself, providing additional upper crustal weakness to aid in channeling magma around storage zones in the middle to upper crust (Davidson et al., 1991; De Silva & Francis, 1991; Gonzalez-Ferrán, 1995; Kuhn, 2002; Gonzalez et al., 2009; Lin et al., 2016).

The Puntas Negras – El Laco Mafic Lava Flow

The Cordón de Puntas Negras is a transverse volcanic belt situated along the northwest portion of the Calama-Olacapato-El Toro (COT) transversal fault system, one of the most extensive transcurrent lineaments in the Central Andes (Matteini et al., 2002). This fault system and associated volcanism passes through the CVZ frontal arc at ~ 23.5° S at an orientation of roughly 125° (NW – SE), with left-lateral transcurrent displacement (Matteini et al., 2002) (Figure 5). The regional lineation extends from the Eastern Cordillera, near Salta, Argentina
(24.7° S, 65.4° W) and possibly as far west as the subduction trench itself, off the Pacific coast of Chile near the town of Tocopilla (22.1° S, 70.2° W) (Google Earth, 2016; Matteini et al., 2002). The exact location of faulting associated with the COT is not well-mapped, as the majority of it is buried beneath significant volcanic products, such as the massive sheets of caldera-sourced ignimbrites which blanket the region. However, the lineament cuts through the modern main arc and geographically coincides with structural features near Lascar stratovolcano, including the Toro Blanco antiform (Cordón Altos de Toro Blanco), where Cerro Overo maar is located. The ‘Tumisa Line,’ a lineament proposed by Matthews & Vita-Finzi (1993), connects Cerro Overo maar with the Cerro Tumisa stratovolcano complex 17 km to the NW is parallel to the COT and is almost certainly a local manifestation of this regional feature (Figure 94). It seems likely that much, if not all, of the minor volcanism along the COT lineament is structurally-controlled, and that continued work along the COT will identify additional complexities in igneous petrogenesis and regional geodynamics. Also located at the southeastern end of the Cordón de Puntas Negras is a stratovolcano named Cerro Overo with no relationship to the maar addressed frequently in this work. Stratovolcano Cerro Overo, however, is also notable for its modern day deformation that switched from a regime of subsidence to one of inflation in 2003 – 2005 (Henderson et al., 2013).

The expression of Late Cenozoic volcanism along the COT is dominantly large stratovolcanoes (NW to SE: Cordón Puntas Negras, Rincon, Tul Tul-Del Medio-Pocitos, Quevar, and Tastil) and a caldera structure (Aguas Calientes, Miocene), although a relatively quick review of satellite imagery reveals a scattering of small flows, maars, domes, and other minor volcanic features, commonly assumed to be Quaternary in age, although few in-depth studies exist (Google Earth, 2016; Allmendinger et al., 1983; Matteini et al., 2002). Only one stratovolcano, the Tuzgle volcano, located just north of the lineament in the central Puna plateau, has thus far been associated with Quaternary volcanism along the COT (Coira & Mahlburg Kay, 1993).

Compositionally, the Cordón de Puntas Negras complex as a whole follows the same major element trends as the contemporary central Andean arc front, although minor and trace elements yield evidence for magma sources, including at least some component of intraplate melting (e.g., Kay et al., 1994). With respect to the full range of volcanism along the COT, lavas of the Cordón de Puntas Negras have relatively high K2O and 87Sr/86Sr, and low Rb/Cs, Ta/Th,
La/Yb, and $^{143}$Nd/$^{144}$Nd (Matteini et al., 2002). The northwestern portion of the volcanic belt is characterized as calc-alkaline magmas partly modified by upper crustal and/or (trench) sediment accumulation (Matteini et al., 2002). More eastern portions of the COT transverse volcanism have a lower crustal signature more indicative of MASH-derived magmas potentially generated by melting of the underthrust Brazilian craton (Matteini et al., 2002). Quaternary mafic volcanism at the far SE of the lineament, such as the basaltic–andesitic scoria cones and lava flows of San Geronimo and Negro de Chorillos, have a shoshonitic affinity, similar to the Oligo-Miocene and Plio-Pleistocene back-arc mafic volcanism occurring at the northeastern edge of the Altiplano (Argentina/Bolivia) and the southeastern edge of the Puna plateau (Chile/Argentina) (Kay, 1994; Matteini et al., 2002; Hoke & Lamb, 2007; Risse et al., 2013). These manifestations of mafic volcanism have been linked to melting following delamination of lower crust and are distinct from the magma generated at the main subduction arc (Hoke & Lamb, 2007; Risse et al., 2013).

The Puntas Negras-El Laco mafic lava flows sampled near the Chile-Argentina border (23.76 S, 67.47 W) represent mafic volcanism related to both the arc and intraplate magmatism along the COT lineament and retains characteristics of both subduction fluid mitigated melting above the slab and intraplate melting instigated by loss of the lithospheric root behind the arc. Olivine-rich lava at Cerro Overo maar and the associated Albóndiga Grande dome addressed in this work, are similar manifestations of fault-controlled minor mafic volcanism associated with the COT lineament and likely derived from asthenospheric melting above the subducted slab.

Minor Volcanism West of the Arc

Tilocálar Norte y Sur

The Tilocálar volcanoes are evidence of magma reaching the surface in a bulk compressional regime that, as the least principal stress is vertical, would favor formation of subhorizontal sills over vertical feeder dikes (e.g., Gonzalez et al., 2009). Study of tectonic expression has revealed surficial extensional features in the region southeast of the Salar de Atacama which is otherwise dominated by compression (Kuhn, 2002; Lin et al., 2016). Variable
eastward propagation of the hanging wall and the rotational component of the Salar de Atacama crustal block (i.e., the indenter) have created along-strike segmentation of the various ridges in the basin, which is ideal for development of localized extension (Kuhn, 2002; Aron et al., 2008). A rotational aspect of compression creates changes in stresses and produces fold-axis-parallel, vertical weak zones in the upper crust, which could offer pathways for magmatic ascent (Kuhn, 2002; Aron et al., 2010). Magmatic overpressure may have also been critical in overcoming the gravitational load and allows melt to reach the surface. While ideas have been put forth regarding the source, transport, and storage of the Tilocálar magma, little work has addressed the volcanoes themselves, particularly in regard to composition. Notable exceptions are the original petrographic and volcanological descriptions of Gardeweg & Ramirez (1982) in Spanish, the source for most subsequent catalogue descriptions (De Silva & Francis, 1991; Gonzalez-Ferrán, 1995), and a few $^{40}$Ar/$^{39}$Ar ages by Gonzalez et al. (2009). The lack of previous in-depth studies of these volcanoes is understandable as they are particularly remote and located some 20 km south of the tiny village of Tilomonte (population unknown) and reachable only by rugged powerline access-roads.

**Cerro Tujle Maar**

Cerro Tujle (also written as Tucle or Tugle) is a remote, isolated maar located SE of the Salar de Atacama along the hinge zone of the *Cordón de Tujle* anticline ~21 km to the northeast of the Tilocálar volcanoes (Figure 19). The crater of Cerro Tujle maar is approximately 60 m deep and elliptical, ~ 335 m across E-W and ~ 270 m across N-S. A thin (1.5 m thick or less) apron of dark-colored juvenile ejecta surrounds the crater and extends to a maximum of 350 m from the crater to the SE. The Cordón de Tujle anticline has alternatively been labeled as “Tilocálar Ridge,” “Tolonchar Ridge,” or “Toloncha-Socaire Ridge” in the literature, the name *Cordón de Tujle* has been selected for this work as it is the name which appears in structural maps of the southern Salar de Atacama region (e.g., Kuhn, 2002; Gonzalez et al., 2009). Regardless of nomenclature, the 500 m high sigmoidal ridge is part of the series of east-vergent subparallel fault-propagation-folds and fault-bend-folds that comprise the thin-skinned deformation zone at the southeastern corner of the Salar de Atacama (Aron et al., 2008; Arriagada et al., 2006; Gonzalez et al., 2009). The north-dipping, east-vergent asymmetric *Cordón de Tujle* anticline is almost certainly a fault-propagation fold of a west-dipping blind
reverse fault (e.g., Jordan et al., 2007; Gonzalez et al., 2009), although no geophysical evidence exists to support field and remote sensing observations on which this assessment is based. This buried fault has acted as a magma conduit, with some activity focused along its hinge zone. Both the maar Cerro Tujle and the minor composite cone Cerro Tolonchar, 11 km to the south-southwest, are aligned along the hinge zone of the anticline. In the region, local changes in stresses and which produced fold-axis-parallel vertical weak zones that were accompanied by buckling at the surface and which provided magma pathways from fault plane to surface (Kuhn, 2002; Gonzalez et al., 2009; Aron et al., 2010).

Summary of Mafic Lavas in the CVZ

Cerro Overo Maar & La Albóndiga Grande Dome

_Cerro Overo_ is a solitary maar (i.e., excavated volcanic crater and associated ejecta), which has erupted olivine-phyric basaltic-andesite within the main arc of the Central Andes during the Quaternary. The maar is located at the base of _Chiliques_ stratovolcano and near the southern shores of hypersaline _Laguna Lejía_, along the _Cordón Altos de Toro Blanco_ antiform ridge (Figure 34). Produced by a potentially phreatomagmatic explosion, the crater is approximately 600 m across and 80 m deep at its greatest extents. This glassy, olivine-bearing basaltic-andesite is currently recognized as the least evolved lava (54 wt % SiO₂, 7.4 wt % MgO) from a young volcanic eruption in the 21 – 24° S segment of the Central Volcanic Zone (De Silva, 1991) (Figure 8). Cerro Overo maar may also represent the least evolved eruption of subduction-generated lava within the modern arc of the entire Central Andes (17° - 28° S).

Three whole-rock major and trace element analyses of Cerro Overo have been previously published, as well as a couple isotopic measurements. No published work has specifically focused on the volcanic center (Thorpe, 1984; de Silva & Francis, 1991; Gonzalez, 1995; Rosner, 2003; Matthews et al., 2009). Age analyses of zircon from entrained silicic xenoliths generated using (U-Th)/He methods indicates a thermal reset age, presumably caused by, of 77 ka (Ukstins-Peate, 2012, pers. comm). This age is consistent with previous broad assessments as Quaternary based on the “youthful morphology” of the maar crater (e.g. De Silva & Francis, 1991; Gonzalez-Ferrán, 1995).
The maar is ringed by a partially-eroded, thin (cms) ejecta blanket, which may have originally extended up to 3 km from the eruption site (Figure 34). The lava is a glassy, olivine-bearing basaltic andesite with abundant silicic xenoliths and scattered xenocrysts (Figure 41 - Figure 44). Vesicularity is low to medium when present, although the majority of the ejecta is poorly-vesiculated and glassy (Figure 53; Figure 48). The source of the felsic xenoliths (evident from geochemistry, petrography, and U-Pb dating) is dominantly (> 95 %) the immediately underlying Atana ignimbrite, although a few outliers have been recorded (Figure 58). Despite contamination with upper crustal material, the low $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70628) and high $^{143}\text{Nd}/^{144}\text{Nd}$ (0.51244; -3.89 εNd) ratios indicate less crustal involvement than other arc magmas in the region (Figure 32). Cerro Overo erupted at the axis of a N-S antiform, the *Cordón Altos de Toro Blanco*, and along the path of the NW-SE trending Calama-Olacapato-El Toro (COT) structural lineament as it passes through the CVZ frontal arc (Figure 34). Structural control was undoubtedly a significant factor in preventing extensive contamination and fractionation of Cerro Overo magma as is ubiquitous with other Altiplano-Puna lavas erupted through the double-thickened crust (60 – 80 km) of the central Andes. Studies of the COT lineament and east-vergent thrust faults show they are composed of structures fundamentally controlled by the sub-Andean basement (Mazzuoli et al., 2008; Norini et al., 2013; Lin et al., 2016), indicating it is possible for Cerro Overo magma to have been tapped from a lower-crustal source. The relatively un-altered nature of the lava makes it a valuable target for identifying the origin and early evolution of arc rocks in the region. Olivine-hosted glassy melt inclusions provide additional insight on the nature of magma(s) beneath the thickened crust of the central Andes (Figure 75).

*La Albóndiga Grande* is an ~ 60 m high extrusive dome of olivine-bearing basaltic andesite (56 wt % SiO₂, 7.3 wt % MgO, ) located approximately 2.2 km SW of Cerro Overo maar, at the western limb of the *Cordón Altos de Toro Blanco* antiform (Figure 34). Lava at La Albóndiga is nearly petrographically and geochemically identical to Cerro Overo maar lava, although it lacks the ubiquitous silicic xenoliths and flow features found at the nearby maar (Figure 76). Lava texture is generally more homogenous than that of Cerro Overo maar with only rare alignment of (micro)phenocrysts and significant vesicularity only present near the outer crust of the dome. La Albóndiga lava appears more oxidized than Cerro Overo, although this is likely due to its prominence in the landscape and resulting increased exposure to the elements. However, as no age data has yet been generated for the dome, a temporal gap
remains a possibility. Major and trace elements as well as the Sr isotopic composition of La Albóndiga lava is indistinguishable from Cerro Overo, indicating the two lavas share a similar source and petrogenetic history, at minimum (Figure 95 - Figure 101). Generally, the composition of the dome plots amongst the more silicic Cerro Overo samples and among the maar samples with evidence for partial assimilation of xenocrysts. The two eruptive centers may represent different surface manifestations of a single batch of magma, broadly supported by the rarity of mafic lava in the region and close proximity of the volcanic features. Additional evidence for the close maar-dome relationship includes equal mineral modality, similar olivine phenocryst morphology, and insignificant variations in phenocryst chemistry (Table 11). Overall, the unique (endmember) composition and structurally-controlled location shared by both La Albóndiga and Cerro Overo lava provide strong evidence the two lavas are closely related, if not two different extrusions of the same magmatic batch.

The Puntas Negras – El Laco Mafic Lava Flow

We sampled a previously un-described olivine- and pyroxene-phyric lava flow in 2014 that was identified by satellite imagery at the far southeast extent (23.75° S, 67.47° W) of the Cordón de Puntas Negras. The basaltic andesite flow originates at the edge of the Puntas Negras volcanic complex and flows southward approximately 10 km along the northeast extent of the El Laco volcanic complex, toward Salar El Laco (Figure 64). A 1964 paper by W. Zeil briefly describes this flow as a “Late-Holocene olivine basalt” and includes it on a map of the distribution of young volcanism in northern Chile. No other references in the literature have been found at this time. Due to its geographical ambiguity and lack of appearance on official maps, this minor volcanic center is referred to as the “Puntas Negras-El Laco flow,” although its name has been shortened to simply “Puntas Negras” on some charts and tables to save space.

The Puntas Negras mafic lava is olivine-clinopyroxene-phyric, medium-high-K calc-alkaline basaltic andesite (53 wt % SiO₂, 6.7 wt % MgO) with both intraplate and arc lava characteristics (Figure 8). The elevated K₂O content and La/Ta ratio relative to silica place this lava just within the compositional field of back-arc intraplate lavas developed from melting initiated by lithospheric delamination (as defined by Kay et al., 1994). The trace element patterns, however, indicate at least some subduction influence, as evidenced by relative depletion of fluid-immobile elements (Figure 102; Figure 103).
The Puntas Negras mafic lava is a blocky flow (subangular fragments > 64 mm) at the surface; a texture caused by fracturing of the viscous (congealing) upper layer of the lava. Deeper in the flow, the rock is continuous and shows signs for following the topography and has lava tubes near the flow flanks. Such features are expected for a relatively fluid basaltic lava. No pyroclastics, ejecta, or any other evidence for explosive eruption are present, although one cannot rule out the possibility of such products having been buried beneath subsequent lava flows. The source of the Puntas Negras lava is not immediately clear, although flow directions do suggest its location at a local small topographic high point (Figure 64). The Puntas Negras – El Laco mafic lava is located along the regional COT lineament and it can be readily assumed this zone of crustal weakness has exerted at least some degree of structural-control over the location of this eruption. The mafic lava represents a transitional magmatic compositional regime at the rear (eastern) margin of the modern arc where melt generation occurs both by fluid-flux melting above the slab (standard subduction style) and melting of lower crustal material from the upwelling of hot asthenosphere, which follows delamination of the lowermost lithosphere. Eventually, this lava will likely be buried under additional eruptions within the Puntas Negras Volcanic Complex, which is largely controlled by the COT lineament, in general.
Conclusions

Minor volcanism in the central Andes is mainly restricted to fields of monogenetic eruptions in the back-arc, representing unfocused, non-sustained magmatism (e.g. Kay et al., 1994; Davidson & De Silva, 1995). Within the arc regime itself, where long-lived magma plumbing systems produce landscape-dominating stratovolcanoes, monogenetic volcanism is rare and commonly restricted to flank eruptions (Gonzalez-Ferrán, 1995; Mattioli et al., 2006; Mamani et al., 2010). Cerro Overo maar, mafic lava in the Puntas Negras Volcanic Complex, and the Tilocálar Group of minor volcanoes form a cross-section of the uncommon monogenetic lavas found within the arc of the central Andes. While this list is certainly incomplete, it outlines a diversity of chemistry and eruptive styles. The semi-explosive, olivine-bearing basaltic andesite of Cerro Overo maar and the associated La Albóndiga dome is representative of an arc magma composition without minimal processing in the middle-upper crust via storage in subvolcanic chambers or extensive mixing with more felsic (i.e. crustal) material. Cerro Overo and La Albóndiga are associated with an anticlinal feature which may be the result of thrust-faulting within the arc and is along the path of the Calama-Olacapato-El Toro (COT) fault lineament. The olivine and clinopyroxene rich basaltic andesite of the Puntas Negras Volcanic Complex is similarly less-evolved, but is located at the eastern margin of the arc and displays chemical characteristics representative of a contribution from melt generation in the back-arc. The Puntas Negras – El Laco lava flow is located along the COT fault lineament. Volcanoes of the Tilocálar Group, a series of aphyric andesites found west of the arc, are all highly correlated with contractional features at the southeast margin of the Salar de Atacama. The shared commonality between the three lava groups is an association with faulting or zones of crustal weakness (Figure 186). Such features provide pathways through the crust for small magma batches, leading to monogenetic eruptions within the arc of a high diversity of lava compositions.
Chapter 2: Geochemical characteristics of Quaternary monogenetic volcanism across the central Andean arc.
Abstract

Fault-controlled monogenetic volcanic centers across the subduction arc of the Central Andes (~ 23° S) have the potential to illuminate the nature of parental melts delivered to the crust. Volcanism in this region is dominated by felsic and intermediates lavas as the thickened crust (55 – 65 km) and vast volumes (> 500,000 km³) of mid-crustal magma beneath the Altiplano-Puna high plateau region make it difficult for mafic magmas to reach the surface (Davidson & De Silva, 1991; Beck et al., 1996; Perkins et al., 2016). However, small volumes of relatively undifferentiated lava have been delivered from the lower crust to the surface along zones of crustal weakness without extensive processing by crustal assimilation and/or extended storage in sub-volcanic magma chambers. Monogenetic eruptions of less-differentiated lava provide important constraints on compositions normally obscured by crustal processing in the Central Andes. Basaltic andesite sampled within the frontal arc (Cerro Overo maar) is a regional mafic end-member (54.6 wt% SiO₂, 7.35 wt% MgO, 0.70628 ⁸⁷Sr/⁸⁶Sr) and approximates the composition of parental arc magmas derived from partially-molten lower crustal regions where mantle-derived magmas interact with the surrounding lithosphere and undergo density differentiation (MASH zones). Basaltic olivine-hosted melt inclusions from Cerro Overo provide a glimpse of less-evolved melt composition from this region and suggest mobilization of MASH magma by injection of basaltic melt. Basaltic andesite sampled from the eastern (back) margin of the frontal arc (Puntas Negras – El Laco) is another regional mafic endmember (52.8 wt% SiO₂, 6.71 wt% MgO, 0.70590 ⁸⁷Sr/⁸⁶Sr), representing a mantle-derived magma composition that is transitional between subduction arc magmatism and intraplate magmatism of the back-arc. Aphyric intermediate monogenetic lavas sampled west of (before) the frontal arc display Adakite-like signatures (e.g. high Sr/Y and Sm/Yb), and represent small melt volumes with a significant contribution from high-pressure, direct melting of metabasaltic lithospheric root, introduced to the mantle by either forearc subduction erosion or delamination. These three magmatic regimes, all of which have been proposed based on theoretical modeling, are observed at monogenetic centers and approximate different end-member compositions being delivered to the lower crust of the Central Andes from which the range of intermediate main arc volcanism in the Altiplano-Puna region is ultimately derived.
Introduction

The suite of Quaternary, within-arc minor mafic volcanic centers studied in this work provides a unique opportunity to examine melt generation regimes and the nature of magma(s) being delivered to the lower crust beneath the subduction arc of the Altiplano-Puna high plateau region of the Central Andes. Transverse faults cutting to the base of the lithosphere and reverse faults in the upper crust provide pathways for eruption of magmas not commonly observed at the surface in the central Andean arc. At first glance, volcanism in the Altiplano-Puna Volcanic Complex (21° - 24° S) of the central Andes is a relatively uniform and dominated by intermediate subduction arc volcanism and felsic ignimbrite volcanism derived from massive upper crustal magma storage systems (De Silva & Francis, 1991; Kay et al., 2011; Perkins et al., 2016). However, the presence of magmatic xenoliths, small-volume back-arc volcanic eruptions, and endmembers derived from geochemical mixing models strongly suggest a larger magmatic diversity exists at depth, which is lost due to magmatic processing during the ascent of melt through the double-thickened crust (McLeod et al., 2013; Key et al., 1994; Wörner & Blum-Oeste, 2016). Less-evolved magmatic components provide the clearest view to parental melt(s) of the arc, and are involved in mafic-recharge and magma remobilization, thermal priming and construction of the crust, and magma mixing. An improved understanding of the small-volume, underrepresented components of the subduction system ultimately informs our interpretations of the geodynamics and arc magmatism of the Central Volcanic Zone.

A generalized view of magma differentiation in the lithosphere of the Central Andes involves a widespread lower-crustal mixing (> 40 km), assimilation, storage, and homogenization (MASH) zone and one or more stages of prolonged storage in the middle (40 – 15 km) to upper crust (< 15 km) where magmas experience additional assimilation and fractionation crystallization (AFC) processes in long-lived, sub-volcanic plumbing systems (Thorpe et al., 1984; Rogers & Hawkesworth, 1989; Davidson et al., 1991; Zandt et al., 1996; Allmendinger et al., 2007; Richards & Villeneuve, 2002; Stern, 2004; Mattioli et al., 2006; Prezzi et al., 2009; Reubi & Blundy, 2009; Salisbury, 2011; Tassara & Echaurren, 2012; Quade et al., 2014; Delph et al., 2017). The partial melt MASH zone (~ 4 – 9 % melt), where melts generated in the asthenosphere interact with the lithosphere and undergo high pressure differentiation, has been imaged by ambient noise tomography at the crust-mantle boundary (~ 60 km) across the southern Puna (Delph et al., 2017). Along with hydrous melting of the asthenosphere above the
slab, intraplate mantle melts are generated by adiabatic upwelling of the asthenosphere following delamination of the lithospheric root, which leads to increased injection of basaltic material in the arc and back-arc (Coira et al., 1993; Kay et al., 1994; Lustrino, 2005; Elkins-Tanton, 2007; Hoke & Lamb, 2007; Murray et al., 2015; Delph et al., 2017). Behind the arc, mafic delamination-generated magmas erupted in monogenetic fields in the Late Miocene–Quaternary along weaknesses in the crust and display a range of marginal arc-to-intraplate signatures (Kay et al., 1994; Murray et al., 2015). Increased magmatic input to the crust has also led to the development of large volumes of 15 – 30 % intermediate partial melt (crystal mush) approximately at the ductile-brittle transition (~ 20 km), which adds to processing of arc magmas and has produced large volumes of silicic ignimbrite instigated by mafic recharge concentrated in the Miocene (~ 20 – 12 Ma) and the Plio-Pleistocene (~ 4 – 2 Ma) (Zandt et al., 2003; Del Potro et al., 2013; Ward et al., 2014; Perkins et al., 2016).

Here we present quantitative chemical analyses of monogenetic arc-related volcanism from the central Andes to quantify the petrogenetic histories of different styles and compositions of minor volcanism across the arc and their relationship to central Andean magmatism. The volcanic centers in this study include olivine- and/or pyroxene bearing lava from within the frontal arc, up to the eastern (back-arc) margin and a compositionally distinct group of aphyric andesites found west of the arc, which erupted within a contractional deformation regime. Using major and trace elements, radiogenic isotopes, and geothermobarometry modeling, we show a minimum of two different magmatic lineages have reached the surface with the aid of structural control. Olivine-bearing basaltic andesite from Cerro Overo maar and the associated La Albóndiga Grande lava dome represent a mafic endmember for the arc lavas commonly erupted at stratovolcanoes in the Central Volcanic Zone of the Andes, confirming the suggestion of De Silva & Francis (1991). A small-volume, olivine- and clinopyroxene-bearing lava flow from within the Cordon de Puntas Negras represents magma generated in the transition zone from fluid-flux subduction arc melting to intraplate magma genesis related to removal of the crustal root. Aphyric andesitic lavas from Tilocálar Norte, Tilocálar Sur, and Cerro Tujle maar represent a minor melt fraction partially derived from metabasaltic rocks within the garnet-stability zone. Trace element patterns displaying a mix of adakite-like and slab-dehydration melting signatures suggest involvement of both the asthenosphere and depleted eclogite, possibly the foundering lithospheric root, fore-arc subduction erosion, or direct melting of the slab. The old and cold nature of the Nazca plate...
subducting at the Central Andean margin and radiogenic Sr isotopic ratios of the lavas suggest the source is the base of the crust or lithosphere, and not the slab itself. Isotopic ratios of Pb are able to distinguish that the melt origin is not sedimentary, but not from which lithospheric domain the lavas were derived. Likely, the metabasaltic material was introduced to the mantle by forearc subduction erosion or delamination of the lithospheric root. These findings emphasize the varied nature of magmas being delivered to the lower crust of the central Andes and better constrain the nature of the mafic endmember(s) in this region.

**Behind-the-Arc Monogenetic Volcanism**

Monogenetic volcanic fields are found behind the arc at the northeast and southeast margins of the Altiplano-Puna plateaus, in Bolivia near Salar de Uyuni and in northwestern Argentina, east of El Negrillar, respectively (Davidson & De Silva, 1992; 1995; Kay et al., 1994; Matteini et al., 2002; Hoke & Lamb, 2007; Mazzuoli et al., 2008; Risse et al., 2013) (Figure 5). Both fields are east of the modern arc and have erupted lavas with a variety of ages and compositions, including young mafic components (northern: 44 – 64 wt % SiO₂; southern: 52 – 60 wt % SiO₂), the least-evolved of which are high-K, intraplate shoshonitic basalts from the Cretaceous or the Oligo-Miocene (Kay et al., 1994; Davidson & De Silva, 1995; Hoke & Lamb, 2007). Most of the basaltic, mantle-generated magmatism is focused along discontinuities or weaknesses in the lithosphere. Generally, lavas from the main arc of the CVZ are distinguishable from the behind-arc groups by lower K content and higher La/Ta ratios (Figure 104; Figure 106) (Kay et al., 1994). Ratios of Ba/Nb versus Nb (Figure 107) and Ti versus Zr (Figure 109) are also useful in distinguishing back-arc and arc compositions, although these distinctions are somewhat more ambiguous and less common in published works (e.g. Mazzuoli et al., 2008). The La/Ta ratio is a quantification of the intensity of the Nb-Ta trough characteristic of melting related to metasomatism of the slab at high pressures due to the preferential inclusion of Nb and Ta in the structure of high pressure Fe-Ti-oxide phases (rutile) (Brenan et al., 1994). Intraplate lavas are generated from the high heat and decompression of upwelling asthenosphere, which leads to melting without interaction with slab-derived fluids. Thus, the La/Ta ratio of volcanic rocks can distinguish between this and subduction arc magmatism. The La/Yb ratio is a quantification of the fractionation of the light rare earth element (LREE) La and the heavy rare earth element (HREE) Yb. The fractionation of LREE/HREE is controlled by the
presence of garnet, which preferentially retains HREE over LREE, in the residual mineral assemblage. Thus, the La/Yb ratio loosely represents the depth of melt generation, as garnet is a high-pressure phase and can be assumed to be more prevalent in the restite of melting at greater depth. In this way, La/Ta versus La/Yb (Figure 106) is particularly useful in identifying separate magmatic regimes across the arc and back-arc, beyond simply classifying behind-arc volcanism by geography alone.

In northwestern Argentina (the southern Puna plateau), most of the monogenetic mafic volcanic centers behind the main arc belong to an Andean intraplate group (i.e. characteristics of OIBs but not subduction lavas) with high K and La/Ta < 25 (Kay et al., 1994). The La/Yb ratios of these rocks are relatively low (≤ 25), suggesting melts are generated at comparatively shallow depths (below thin lithosphere). A subset of the southern Puna group, particularly those centers closer to the arc, define a back-arc calcalkaline grouping with high K and 60 > La/Ta > 25 (Kay et al., 1994). These rocks are essentially potassic arc magmas which plot in an overlapping La/Ta versus La/Yb field with compositions from the main subduction arc (Figure 106). Moving eastward from the arc, a transitional group shows features of both intraplate and arc melting (30 > La/Ta > 25; Kay et al., 1994), representing either mixing of primary melts or mantle melting influenced by both decompression/heat input and slab fluid addition. The volumetrically smallest contribution to back-arc volcanism at the southern margin of the Puna are a handful of extremely high-K shoshonitic basaltic eruptions, mainly associated with faulting along the Calama-Olacapato-El Toro (COT) or Archibarca lineaments (Kay et al., 1994; Marrett et al., 1994; Matteini et al., 2002; Risse et al., 2008). The shoshonites show intermediate to low La/Ta ratios (≤ 40) and higher La/Yb ratios (~ 30-50) resulting from small volumes of intraplate partial melt generation at high pressures (Kay et al., 1994). These back-arc shoshonites are the only instances of tholeiitic volcanism reported from the Central Volcanic Zone of the Andes (Kay et al., 1994; Hoke & Lamb, 2007) (Figure 12).

Ar-Ar dating indicates the majority of southern Puna back-arc mafic volcanism occurred 10 – 0 Ma, in the Late Miocene to Holocene (Trumbull et al., 2006; Risse et al., 2008). Periods of increased activity around 6.0, 4.5, and 2.0 Ma are concurrent with major eruptions of ignimbrite from Cerro Galán caldera (centered at 25.95° S, 66.93° W), which themselves have been linked with episodic delamination of the eclogitic lithospheric root (Risse et al., 2008; Folkes et al., 2011; Kay et al., 2012). High-K shoshonitic basalts, on the other hand, are dominantly Oligo-
Miocene in age and their origin is not as well constrained (Kay et al., 1994; Trumbull et al., 2006; Hoke & Lamb, 2007). Shoshonites at the northeast margin of the Puna, in SW Bolivia, have been loosely correlated with slab steepening throughout the Miocene and melting in the upwelling asthenosphere following delamination events in the Late Miocene onward (Hoke & Lamb, 2007). The < 7 Ma behind-arc mafic volcanism in northwestern Argentina (25° - 27° S) has been well-correlated with asthenospheric upwelling and increased heat input to the crust due to delamination or foundering of material from the base of the lithosphere (Coira et al., 1993; Kay et al., 1994; Risse et al., 2013). This geodynamic explanation supports development of non-subduction related magmas (i.e. not formed by flux-melting involving slab fluids) in a subduction setting due to changing subduction geometry and an introduction of hot material to the base of the crust. Delamination can also explain why the Puna region has a higher average elevation than the Altiplano to the north, despite an ~10 km thinner crust beneath the Puna (Yuan et al., 2002), due to dynamic isostatic uplift caused by upwelling hot upper mantle (Risse et al., 2013). Upwelling mantle and the increase in heat being delivered to the crust may have also been one of the major mechanisms in creating the massive mid-crustal magma bodies which fueled the large silicic caldera eruptions of ignimbrite in the Miocene (Kay et al., 1994). Dacitic ignimbrite erupted at Cerro Galán has been modeled as ~ 50:50 mixtures of enriched mantle ($^{87}$Sr/$^{86}$Sr ~ 0.7055) and crustal ($^{87}$Sr/$^{86}$Sr ~ 0.715–0.735) melts resulting from delamination (Kay et al., 2012). An essentially intraplate origin for the ignimbrite of the Altiplano-Puna region is also discernable in La/Ta classification of volcanic rocks (Figure 106).

Ratios of La/Ta for across-arc monogenetic volcanism of this study range 25 to 40 for within-arc volcanism, encompassing both arc-derived lava (Cerro Overo), and transitional arc – back-arc lava (Puntas Negras – El Laco) and from La/Ta = 67 up to as high as 115 for minor lavas sampled west of the main arc (Tilocálar Norte, Tilocálar Sur, Cerro Tujle) (Figure 106). K$_2$O content at a given silica is within the arc range for Cerro Overo and the west-of-the-arc Tilocálar Group volcanism, but the mafic Puntas Negras lavas shows marginally back-arc K content (Figure 104). Cerro Overo represents mafic endmember lava for arc volcanism, Puntas Negras – El Laco mafic lava represents a transitional arc/intraplate end-members, and the west-of-the-arc volcanism from the Lomas de Tilocálar area represent a separate, adakite-like magma composition, possibly formed from direct melting of the slab or delaminated lithospheric root.
Geochemistry of Monogenetic Volcanism across the Arc

Table 13 - Summary of average major-element compositions in wt % for rocks of this study.

<table>
<thead>
<tr>
<th>Location</th>
<th>Rock Type</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeOtot</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo</td>
<td>Basaltic Andesite</td>
<td>54.59</td>
<td>0.91</td>
<td>16.14</td>
<td>7.81</td>
<td>0.12</td>
<td>7.35</td>
<td>8.10</td>
<td>3.22</td>
<td>1.27</td>
</tr>
<tr>
<td>La Albóndiga</td>
<td>Basaltic Andesite</td>
<td>56.17</td>
<td>0.87</td>
<td>15.50</td>
<td>7.79</td>
<td>0.12</td>
<td>7.32</td>
<td>7.55</td>
<td>3.15</td>
<td>1.21</td>
</tr>
<tr>
<td>C. Overo Melt Inclusions</td>
<td>Olivine-hosted Melt inclusions</td>
<td>49.68</td>
<td>1.19</td>
<td>18.86</td>
<td>7.23</td>
<td>0.10</td>
<td>7.27</td>
<td>10.05</td>
<td>3.79</td>
<td>1.14</td>
</tr>
<tr>
<td>C. Overo Xenoliths</td>
<td>Dacite - rhyolite</td>
<td>67.88</td>
<td>0.57</td>
<td>15.31</td>
<td>3.62</td>
<td>0.08</td>
<td>1.20</td>
<td>4.22</td>
<td>3.69</td>
<td>3.30</td>
</tr>
<tr>
<td>Atana Ignimbrite</td>
<td>Dacite - rhyolite</td>
<td>69.88</td>
<td>0.48</td>
<td>15.06</td>
<td>2.79</td>
<td>0.08</td>
<td>0.88</td>
<td>3.04</td>
<td>3.98</td>
<td>3.68</td>
</tr>
<tr>
<td>Puntas Negras</td>
<td>Basaltic Andesite</td>
<td>52.76</td>
<td>1.31</td>
<td>16.15</td>
<td>9.11</td>
<td>0.14</td>
<td>6.71</td>
<td>8.61</td>
<td>3.23</td>
<td>1.47</td>
</tr>
<tr>
<td>El País Lava Flow</td>
<td>Basaltic Andesite</td>
<td>56.32</td>
<td>1.08</td>
<td>15.78</td>
<td>8.66</td>
<td>0.13</td>
<td>5.62</td>
<td>7.39</td>
<td>3.08</td>
<td>1.53</td>
</tr>
<tr>
<td>Cerro Chascón Dome</td>
<td>Dacite – Basaltic Andesite</td>
<td>58.76</td>
<td>1.16</td>
<td>16.48</td>
<td>6.86</td>
<td>0.09</td>
<td>3.45</td>
<td>6.44</td>
<td>4.23</td>
<td>2.01</td>
</tr>
<tr>
<td>Cerro Tujle (trachy)</td>
<td>Dacite – andesite</td>
<td>63.40</td>
<td>0.84</td>
<td>15.86</td>
<td>4.70</td>
<td>0.06</td>
<td>2.44</td>
<td>5.23</td>
<td>4.13</td>
<td>2.86</td>
</tr>
<tr>
<td>Tilocálar Norte</td>
<td>Andesite</td>
<td>58.72</td>
<td>1.09</td>
<td>16.02</td>
<td>6.36</td>
<td>0.08</td>
<td>3.56</td>
<td>7.35</td>
<td>4.22</td>
<td>1.94</td>
</tr>
<tr>
<td>Tilocálar Sur</td>
<td>Andesite</td>
<td>58.47</td>
<td>0.74</td>
<td>17.53</td>
<td>7.03</td>
<td>0.12</td>
<td>3.42</td>
<td>7.16</td>
<td>3.03</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Cerro Overo Maar & La Albóndiga Dome

Consanguineous lavas of Cerro Overo maar and the adjacent La Albóndiga Grande extrusive dome are medium-K calc-alkaline, high Ni basaltic andesites (55 wt % SiO₂; 7.4 wt % MgO; 4.5 wt % K₂O + Na₂O) which mark the endmember mafic composition for post-Miocene arc rocks of the central Andes (Figure 8; Figure 12; Figure 112) (frontal arc data from GEOROC, accessed 2015 & Mamani et al., 2010). Cerro Overo displays enrichment in MgO (average 7.35 wt % MgO) and Ni (120 ppm) with respect to silica relative to the arc trend, due to the presence of the high Ni content of olivine phenocrysts, which are rarely found in other arc lavas (e.g. Mattioli et al., 2006; Mamani et al., 2010). Intra-lava variations for Cerro Overo samples show a small compositional range from more mafic glassy and fully juvenile products (e.g. bombs, scoria) to more evolved compositions (higher SiO₂, lower MgO, etc.) of xenolith- and/or xenocryst-bearing samples. La Albóndiga dome lavas plot within the Cerro Overo maar
compositional grouping for most major elements. Both lavas share mineralogy, with olivine phenocryst cores averaging Fo86 and groundmass plagioclase of An65. Lack of significant Europium anomalies indicate minimal plagioclase fractionation. On primitive mantle-normalized diagrams of incompatible elements, La Albóndiga plots nearly indistinguishably from the least-evolved Cerro Overo maar lavas (Figure 95).

**Compositional Variation between Maar & Dome Lava**

Relative to Cerro Overo maar rocks, La Albóndiga dome lavas display elevated silica and depleted Sr content, similar to the xenolith-bearing lavas of Cerro Overo maar, despite displaying MgO content similar to the uncontaminated juvenile maar lavas (Figure 98; Figure 97). Samples from the scoriaceous outer surface of La Albóndiga dome are slightly more evolved (56.6 wt % SiO2, 7.16 wt % MgO) than the glassy lava from the interior of the dome (55.9 wt % SiO2, 7.45 wt % MgO), suggesting that interaction with surrounding wall rock at the margin of the ascending magma may have resulted in elevated silica content of the lava dome (Figure 97). Xenolith-bearing lavas from Cerro Overo maar, however, display enrichments of elements concentrated in the crust, relative to chondrite-normalized values for La Albóndiga dome, including incompatible light elements (e.g. Cs, Ba), U, and Pb (Figure 95). Somewhat conflicting data on the level of crustal interaction between the two volcanic features may be an indication that while both maar and dome experienced a small degree of upper-crustal contamination, the assimilated material differed slightly in nature. A lack of xenocrysts or xenoliths in lava extruded at La Albóndiga dome, despite slightly more differentiated lava composition at the exterior of the dome suggests middle-upper crustal contamination of La Albóndiga magma occurred as assimilation of a more easily assimilated, liquid portion of felsic melt only (i.e. melting of ignimbrite groundmass glass) (Figure 97). The enrichment in certain trace elements seen in xenolith-bearing Cerro Overo rocks, however, reflects additional incorporation of the mineral assemblage of the wall rocks during eruption of the maar, such as plagioclase (Sr), apatite (U, Th, Sr, Pb), and amphibole and biotite mica (Ba, Cs, Rb, Sr). Hydrous minerals, which sequester the incompatible large ion lithophile elements (LILEs) (Bebout et al., 2007), such as the mica and amphibole ubiquitous in the Atana ignimbrite (e.g. Gardeweg & Ramirez, 1987), are extensively altered to opaque oxides within the xenoliths of Cerro Overo maar (Figure 42). The less-violent, extrusive eruption of basaltic andesite at La Albóndiga Grande precluded extensive fracturing of country rock and subsequent inclusions of the full mineral assemblage.
**Comparison with Compositions of the Frontal Arc**

Volcanic rocks of the Quaternary Altiplano-Puna subduction arc display (sub) trends defined by higher or lower TiO$_2$ and FeO* (all Fe expressed as FeO) content with respect to any proxy for differentiation (e.g. MgO or SiO$_2$) (Figure 113; Figure 114). Cerro Overo and La Albóndiga plot together as an endmember composition (7.8 wt % FeO*, 0.90 wt % TiO$_2$) for a trend with lower TiO$_2$ and FeO, while olivine-phyric basaltic andesite from the Puntas Negras – El Laco flow define an endmember composition (9.1 wt % FeO*, 1.31 wt % TiO$_2$) for a higher TiO$_2$ and FeO* arc trend. The major element trend with Cerro Overo as the endmember is defined by compositions measured from Lascar stratovolcano (23.4° S, 67.8° W) and the San Pedro – San Pablo volcanic complex (21.9° S, 68.5° W) (Mamani et al., 2010). The trend with Puntas Negras rocks as the volcanic endmember also includes Irrutupuncu (20.7° S, 68.6° W), Ollagüe (21.3° S, 68.2° W), and Licancabur (22.9° S, 67.9° W) stratovolcanoes (Mattioli et al., 2006; Mamani et al., 2010). There exists a similar, but less clearly-defined trend in MnO content with Cerro Overo defining a lower MnO endmember and Puntas Negras – El Laco defining a higher MnO endmember. This distinction in TiO$_2$ and FeO* trends is likely due to differences in oxygen fugacity (i.e. redox state), reflected in differences in the amount and character of Fe-Ti oxides precipitated, and thus fractionated during evolution. Such a conclusion is supported by the mineralogy of Cerro Overo versus that of Puntas Negras – EL Laco. Olivine phenocrysts from Cerro Overo maar contain mineral inclusions of almost exclusively Cr-spinel (occasional Fe-Ti oxides are present at crystal rims), while Puntas Negras olivine phenocrysts contain mineral inclusions of both spinel and Fe-Ti oxides throughout the host crystals, reflecting favorable Fe-Ti oxide growth throughout the period of olivine crystallization.

Cerro Overo Pb isotopic ratios are within the common orogenic CVZ isotopic field, showing a slight enrichment in $^{208}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb relative to the majority of the main arc (Figure 29 - Figure 31). La Albóndiga Pb isotopes plot among the relatively non-radiogenic results from Cerro Overo maar, but display less negative εNd, again indicative of the lower degree of crustal contamination experienced by the dome lava (Figure 31). The $^{206}$Pb/$^{204}$Pb ratios from both centers (18.763 – 18.772) straddle the upper bounds of the Antofallo isotopic domain (18.551 – 18.770) defined by Mamani et al. (2008; 2010). It has been suggested that these isotopic ratios reflect the crustal basement through which the arc lavas are erupted, as Pb
isotopic ratios are highly sensitive to small-volume contamination (e.g. Wörner et al., 1992; Mamani et al., 2008; Mamani et al., 2010). This is unsurprising from a spatial point of view, as the two works of Mamani et al. (2008) focused on developing high-resolution maps of crustal domains based on Pb isotopes have Cerro Overo straddling the easternmost boundary of the Antofallo crustal domain. The Puntas Negras – El Laco mafic lavas even further east of Cerro Overo display \(^{206}\text{Pb}/^{204}\text{Pb}\) ratios from 18.789 – 18.812, which lie above and outside the Antofallo domain. These isotopic domains are correlated with the Crustal Structure Index (3D density structure) of the Andes, and the \(^{206}\text{Pb}/^{204}\text{Pb} = 18.770\) line may mark an actual physical divide within the basement, possibly a suture or fault boundary between different basement lithologies (Mamani et al., 2008).

\[\varepsilon_{\text{Nd}} = \left[ (^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}})/(^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}) - 1 \right] \times 10,000\]

\[^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}} = 0.512638\] (Dickin, 1995)

**Olivine-Hosted Melt Inclusions from Cerro Overo**

The composition(s) of mafic melt inclusions (\(n = 17\)) hosted in olivine phenocrysts from Cerro Overo maar basaltic andesite cluster around a medium-K, calc-alkaline basalt (49.7 wt % SiO\(_2\); 7.3 wt % MgO; 4.9 wt % K\(_2\)O + Na\(_2\)O) which represents a potential parental melt (Figure 112). Melt inclusion compositions have been normalized to equilibrium (\(K_D(\text{Fe-Mg}) = 0.30 \pm 0.03\)) with the host olivine via the methods of Danyushevsky et al. (2002), which resulted in minimal corrections. The melt inclusion compositions show slightly lower FeO* than the whole rock even after corrections for diffusive Fe loss. The melt inclusion compositions are on the border between calc-alkaline and tholeiitic classification (Figure 12). The corrected olivine-hosted melt inclusions have lower SiO\(_2\) and FeO* content at similar MgO (6.75 – 8.01 wt % MgO) as Cerro Overo (6.80 – 7.83 wt % MgO), falling nearly perfectly on-trend in plots involving Mg# (Mg# =Mg\(^{2+}\)/ (Mg\(^{2+}\)+Fe\(^{2+}\)); i.e. the FeO*/Mg ratio is nearly identical) (Figure 115). There is also strong continuity in the K\(_2\)O trend between central Andean arc rocks, Cerro Overo, and the olivine-hosted melt inclusions (endmembers along the differentiation pattern). Relative to Cerro Overo whole rock, olivine-hosted melt inclusions display enrichment in P\(_2\)O\(_5\), Na\(_2\)O, CaO, and TiO\(_2\), and low relative MnO content (Figure 116; Figure 117; Figure 118; Figure 114; Figure 119). Whole-rock Al\(_2\)O\(_3\) (16.1 wt %) is less than melt inclusions (18.9 wt %) at similar MgO values (Figure 120). The melt inclusions also display enrichments in Na, Ca, and Al content relative to
the whole rock. These compositional trends cannot be universally explained by fractionation of olivine, plagioclase, magnetite, or clinopyroxene, and may represent variable crustal assimilation, magma mixing or mingling, or accumulation of elements incompatible in the olivine lattice in the immediate proximity of the growing mineral, which were subsequently trapped in the inclusions (e.g. Milman-Barris et al., 2008). However, the higher values of Al, Na, Ti, and P in the mafic melt inclusions all cluster tightly (with the exception of one analysis which reflects whole rock values), suggesting these compositions represent a widespread magmatic composition and not highly localized, crystal-scale enrichment.

If the lava erupted at Cerro Overo maar were derived directly from the trapped mafic melt by olivine fractionation alone, the compositions (MgO vs. SiO₂) of olivine, melt inclusions, and Cerro Overo lava would lie along a linear trend. From this trend, the amount (%) of fractionation could easily be calculated using the lever rule. However, such a relationship does not exist, indicating some degree of magma mixing or crustal assimilation is required if the melt inclusion and host lava compositions are indeed related (Figure 121). A possible common parental magma could be a basalt with approximately 48.7 wt % SiO₂ and 10.5 wt % MgO from which the melt inclusion composition was derived by around 5 – 9 % olivine fractionation and the Cerro Overo bulk rock composition was created from mixing with as much as 35 % (felsic) crustal material (least evolved maar lava: 20 %, average maar lava: 35 %) (Table 13). The olivine fractionated from the included melt may simply represent the average amount of olivine crystallized from the included melt along the walls of the inclusions (e.g. Baker, 2008; Kent et al., 2008). Based on an estimate of mixing with 35 % upper crustal material, the hypothetical parental melt would have had an ⁸⁷Sr/⁸⁶Sr ratio of ~ 0.70437, a value approaching the lower ⁸⁷Sr/⁸⁶Sr isotopic ratios measured in single olivine-hosted melt inclusions (0.70367 – 0.70432) (Equation 6). At first glance, 35 % crustal melt appears to be an extremely high estimate, considering the relatively undifferentiated nature of Cerro Overo rocks and other published estimates of an average crustal contamination ranging from 12 to 30 % for andesitic arc rocks of the central Andes (Davidson et al., 1991; Trumbull et al., 1999; Bourdon et al., 2000; Rosner et al., 2003). However, the upper limit of crustal input (~ 30 %) is constrained by the nature of felsic ignimbrites of the upper crust, themselves impure crustal melts (i.e. largely derived from fractionation of arc magma) (Rosner et al., 2003). The dynamic and static mixing models based on B-Sr and B-Nd isotope systematics established by Rosner et al. (2003) estimate lava with the isotopic composition of Cerro Overo could be produced with 10-15% addition of crustal melt to
a primary arc magma. An addition of 35 % ignimbrite, itself only 30 % derived from crustal material and 70 % from highly differentiated arc magma would result in a total of \(0.30 \times 35\% = 10.5\%\) addition of melt that is ultimately of continental crustal providence.

Melt inclusion analytical totals were within error of 100 wt %, and thus water content could not be estimated by difference. However, experimental studies have shown evidence for rapid water exchange between olivine-hosted melt inclusions and the host magma, and water content of the inclusions is therefore likely to represent a (partially) degassed composition (Portnyagin et al., 2008). Water estimates mentioned in this study were derived from plagioclase compositions and thus represent minimum, (near) eruptive estimates as (most of) the equilibrium plagioclase in the rocks of this study are groundmass crystals.

Another possible source for olivine-hosted melt inclusions is capturing of melt not directly related to subduction arc magmatism (i.e. melting in the mantle wedge instigated by slab metasomatism and dehydration). Melting of mafic material in the lower crust or lithosphere or alternative styles of melting (e.g. decompression, heating) of the asthenosphere have the potential to create primary mafic melts unrelated to the Cerro Overo parent magma, or other arc magmas, even in relatively small batches (e.g. Kay et al., 1994; Lustrino, 2005; Kent et al., 2008; Moyen, 2009). Melt inclusions do show elevated Nd, Sr, Ba, Zr, and P\(_2\)O\(_5\) relative to the whole rock and a lower La/Sm ratio, all suggesting the included melt was derived from a smaller melt fraction than the bulk Cerro Overo lava (Figure 123). The Sr/Y ratio, which is greater for melt inclusions at similar Y content to the whole rock (Figure 124), indicates the inclusion melts were formed at greater depth than the bulk host rock. Additionally, Zr and Ti characteristics of the melt inclusions, which broadly separate arc from back-arc (i.e. intraplate-influenced) magmatism (Pearce & Peate, 1995) place the melt inclusions well within the back-arc field, similar to the Zr-Ti composition of the transitional Puntas Negras – El Laco lava flow(s) (Figure 109). The relative (to the arc suite) Ba depletion (Figure 125) and enrichments in K\(_2\)O (Figure 105), Ti (Figure 126), and P (Figure 116) indicate that the inclusions were less influenced by metasomatism (i.e., fluid flux) of the mantle wedge, which should enrich primary arc basalts in fluid mobile LILEs (e.g. Ba) and deplete the melt in HFSEs, Ti, and P (e.g. Richards & Kerrich & references therein). Finally, the isotopic composition melt inclusions, based single olivine crystal \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios (~0.70376 – 0.70719) define a broader range than whole rock ratios (0.7062 – 0.7065) for Cerro Overo. These less-evolved \(^{87}\text{Sr}/^{86}\text{Sr}\) values (0.70376-0.70432) are the lowest
reported for the Altiplano-Puna region of the central Andes, but may represent the isotopic composition of magma(s) being delivered to the lower crust not directly parental to the majority of arc magmas. Unfortunately, Ta concentration data is not available for inclusions, making it impossible to employ the La/Ta intraplate vs. arc distinction for the central Andes defined by Kay et al. (1994) and widely applied in more recent publications (e.g. Matteini et al., 2002; Hoke & Lamb, 2007). However, the La/Ta index is essentially a loose quantification of relative Ta depletion due to melt generation in the presence of high-pressure Fe-Ti-oxide phases (rutile), which preferentially sequester Ta over La (Brenan et al., 1994; Pearce & Peate, 1995). The ratio of La/Nb, however, should provide a substitute for distinguishing melting in the presence of rutile as Nb is also preferentially included into Fe-Ti oxide phases in the residual mineralogy of metasomatized oceanic slab at high pressure (Brenan et al., 1994). Plots of La/Nb ratio La concentration (Figure 108) show that the compositions of mafic olivine-hosted melt inclusions of Cerro Overo plot firmly within the arc-signature field, and not the back-arc intraplate field. This is also true for Ba/Nb versus Nb content (Figure 107). Thus, the melt inclusions appear to have a similar slab metasomatism-related origin as Cerro Overo basaltic andesite itself, although may have experience significant alteration by MASH processes at the base of the crust (e.g. Delph, 2017).

Equation 6 – Calculation for the initial composition ($X_A$) of a two-component mixture from composition of the resultant mixture ($X_{AB}$) and the added contaminant ($X_B$). The fraction of $X_A$ remaining in the mixture is denoted by $r$ ($\leq 1$).

$$X_A = \frac{1}{r} (X_{AB} - (1 - r)X_B)$$
Table 14 – Calculated compositions for a hypothetical parental magma $X_A$ from which the average Cerro Overo lava composition could be derived solely by assimilation of felsic upper crustal material (crustal contamination). Here, the Atana Ignimbrite is used as an approximation for the dacitic material which dominates the upper crust of the Altiplano-Puna region of the central Andes (Riller et al., 2006; Kay et al., 2010). Major element variations within the variably-contaminated lava erupted at the maar can be described by < 10 % addition of upper-crustal ignimbrite, but isotopic variations by only < 5 % contamination.

<table>
<thead>
<tr>
<th>Ignimbrite addition</th>
<th>Fraction of $X_A$ in Cerro Overo lava</th>
<th>SiO$_2$ (wt %) of $X_A$</th>
<th>MgO (wt %) of $X_A$</th>
<th>$^{87}$Sr/$^{86}$Sr of $X_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>0.95</td>
<td>54.02</td>
<td>7.66</td>
<td>0.70604</td>
</tr>
<tr>
<td>10%</td>
<td>0.90</td>
<td>53.38</td>
<td>8.00</td>
<td>0.70584</td>
</tr>
<tr>
<td>15%</td>
<td>0.85</td>
<td>52.67</td>
<td>8.39</td>
<td>0.70563</td>
</tr>
<tr>
<td>20%</td>
<td>0.80</td>
<td>51.87</td>
<td>8.82</td>
<td>0.70539</td>
</tr>
<tr>
<td>25%</td>
<td>0.75</td>
<td>50.96</td>
<td>9.31</td>
<td>0.70511</td>
</tr>
<tr>
<td>30%</td>
<td>0.70</td>
<td>49.93</td>
<td>9.87</td>
<td>0.70480</td>
</tr>
<tr>
<td>35%</td>
<td>0.65</td>
<td>48.73</td>
<td>10.51</td>
<td>0.70444</td>
</tr>
<tr>
<td>40%</td>
<td>0.60</td>
<td>47.33</td>
<td>11.27</td>
<td>0.70401</td>
</tr>
<tr>
<td>45%</td>
<td>0.55</td>
<td>45.68</td>
<td>12.16</td>
<td>0.70351</td>
</tr>
</tbody>
</table>
| 50%                 | 0.50                                 | 43.7                   | 13.23             | 0.70292                     

**Oxygen Fugacity of Cerro Overo Melt Inclusions**

In their empirical calibration of a Sulphur valence oxygen barometer, Matthews et al. (1999) measured sulfur valence states and calculated magmatic oxidation states (i.e. oxygen fugacity, $f_{O_2}$) for Cerro Overo maar and adjacent Lascar stratovolcano using olivine-spinel and magnetite-ilmenite, respectively (Table 15). Matthews et al. (1999) correlated variation in sulfur speciation (S$^2-$ v. SO$_4^{2-}$) as a function of log $f_{O_2}$ and used this model to calculate $f_{O_2}$ conditions under which melt inclusions were trapped preceding magma mixing and/or assimilation of country rock. They targeted undegassed glassy melt inclusions trapped within minerals (olivine for Cerro Overo, hornblende for Lascar) as they typically have much higher S content than matrix glass and can be used to determine pre-eruptive sulfur content (Matthews et al., 1999; Kent et al., 2008). In olivine-hosted melt inclusions from Cerro Overo, Matthews et al. found a wide range of S (SO$_4$/ΣS = 0.08 – 0.79), which they attributed to a rapid shift in sulfur speciation correlated with changing $f_{O_2}$ (Matthews et al., 1999). Additionally, the calculated Cerro Overo melt inclusion oxidation states were matched by hornblende hosted inclusions at Lascar (Matthews et al., 1991).

Using the olivine-spinel oxygen barometer, Matthews et al. (1999) found an approximately 2 log unit decrease in $f_{O_2}$ between Fo$^{87}$ and Fo$^{80}$ olivine from Cerro Overo, with
some scatter in the data. This result is mirrored in a positive correlation between olivine Fo content and sulfur valence. Eruption temperature was assumed to be 1050 – 1150, based on 1-pyroxene thermometry and pressure of 3-10 kbar (Matthews et al., 1999); an assumption bolstered by the more extensive thermometry calculations of this study (Table 17). Matthews et al. then used the observed relationship between olivine forsterite content and $fO_2$ to calculate the oxygen fugacity of glassy inclusions, based on the immediately adjacent host olivine composition (1999) (Table 15).

The scatter in Matthew et al.'s data may be due to analyzing melt inclusions which cover a wider suite of pre-eruptive compositions than assumed. The effects of re-distribution of Fe and Mg through the host crystals by diffusion was not considered either, and some of the targeted inclusions may have become trapped while the magma was crystallizing olivine of a composition different from what is currently seen, which was later erased by Fe-Mg diffusion. Inclusions originally trapped in Fo$_{90}$ and Fo$_{84}$ will likely both be hosted in Fo$_{87}$ due to subsequent homogenization of olivine at high T (e.g. Shea et al., 2015). For example, Matthews et al. calculated a range of molar SO$_4$ of 0.08 – 0.79 for four glassy inclusions from Cerro Overo olivine ranging from Fo$_{83.6}$ – Fo$_{84.7}$, which they attribute to varying $\Delta$FMQ (0.99 – 1.38) inducing a sharp change in Sulphur speciation (1999 and references therein). However, two inclusions with an identical $\Delta$FMQ of 1.38 were measured to have molar SO$_4$ of 0.25 and 0.79, a broad range considering olivine Fo content is correlated with sulfur valence state.

In applying their sulfur valence oxygen barometer, Matthews et al. also targeted inclusions in hornblende phenocrysts from the stratovolcanoes Lascar (23.367° S, 67.738° W) and Cerro Tumisa (23.459° S, 67.811° W), both adjacent to Cerro Overo (1999). These hornblende are interpreted to have originated in more reduced mafic magmas which experienced quenching and oxidation upon injection into the dacitic magma chambers underlying the stratovolcanoes (Matthews et al., 1999; Matthews et al., 1994). The calculated values for $\Delta$FMQ (1.07 – 1.82) from the hornblende-hosted inclusions from both volcanoes is not only significantly different from the magnetite-ilmenite $\Delta$FMQ calculations for the host magma (2.13 – 3.15), but is also in agreement with the calculated $\Delta$FMQ (0.99 – 1.38) for olivine-hosted inclusions from Cerro Overo (Matthews et al., 1999) (Table 15). These values, at minimum, suggest a similarity in the oxidation state(s) of the source magma for these three volcanic centers, and could be an indication that the mafic magma erupted at Cerro Overo is, in fact,
representative of the hot, less-evolved material commonly implicated as activating Andean stratovolcano eruptions when injected into subsurface magma chambers.

Table 15 - Measured $S$ valence of glass inclusions and calculated oxygen fugacity ($f_{O_2}$) for host olivine from olivine spinel pairs from Cerro Overo and Lascar or for whole-rock compositions from Fe-Ti oxides for Lascar. From Matthews et al. (1999).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Host mineral</th>
<th>Fo (olivine)</th>
<th>Molar SO$_2$/S</th>
<th>ΔFMQ</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO. OVERO</td>
<td>SM9436</td>
<td>Olivine basaltic andesite</td>
<td>Olivine</td>
<td>83.6</td>
<td>0.08 ± 0.10</td>
<td>0.99</td>
</tr>
<tr>
<td>G1</td>
<td></td>
<td>Olivine</td>
<td>84.7</td>
<td>0.25 ± 0.14</td>
<td>1.38</td>
<td>Olivine compn.</td>
</tr>
<tr>
<td>G2</td>
<td></td>
<td>Olivine</td>
<td>84.7</td>
<td>0.79 ± 0.04</td>
<td>1.38</td>
<td>Olivine compn.</td>
</tr>
<tr>
<td>G3</td>
<td></td>
<td>Olivine</td>
<td>84.1</td>
<td>0.56 ± 0.05</td>
<td>1.17</td>
<td>Olivine compn.</td>
</tr>
<tr>
<td>LASCAR</td>
<td>Sencor ignimbrite</td>
<td>Olivine basaltic andesite</td>
<td>Olivine</td>
<td>80.7</td>
<td>0.83 ± 0.04</td>
<td>2.10</td>
</tr>
<tr>
<td>LA124</td>
<td></td>
<td>Olivine</td>
<td>81.5</td>
<td>0.81 ± 0.05</td>
<td>1.99</td>
<td>Olivine compn.</td>
</tr>
<tr>
<td>Glass5</td>
<td></td>
<td>Olivine</td>
<td>81.1</td>
<td>0.88 ± 0.04</td>
<td>2.04</td>
<td>Olivine compn.</td>
</tr>
<tr>
<td>Glass7</td>
<td></td>
<td>Hornblende andesite</td>
<td>Hornblende</td>
<td>0.77 ± 0.11</td>
<td>2.91</td>
<td>Magnetite-ilmenite</td>
</tr>
<tr>
<td>Glass8</td>
<td></td>
<td>Hornblende andesite</td>
<td>Hornblende</td>
<td>0.82 ± 0.10</td>
<td>2.44</td>
<td>Magnetite-ilmenite</td>
</tr>
<tr>
<td>LAS1219</td>
<td></td>
<td>Hornblende andesite</td>
<td>Hornblende</td>
<td>0.84 ± 0.10</td>
<td>2.44</td>
<td>Magnetite-ilmenite</td>
</tr>
<tr>
<td>Glass10</td>
<td></td>
<td>Pyroxene</td>
<td>0.82 ± 0.10</td>
<td>2.44</td>
<td>Magnetite-ilmenite</td>
<td></td>
</tr>
<tr>
<td>Glass11</td>
<td></td>
<td>Pyroxene</td>
<td>0.84 ± 0.10</td>
<td>2.44</td>
<td>Magnetite-ilmenite</td>
<td></td>
</tr>
</tbody>
</table>

Cerro Overo Xenoliths & the Atana Ignimbrite

Felsic xenoliths are prevalent within the basaltic andesite of Cerro Overo maar, although nearly non-existent in the otherwise similar lava of La Albóndiga Grande dome. The vast majority of the Cerro Overo xenoliths are dacitic and can be linked by mineralogy and geochemistry to the immediately underlying Atana Ignimbrite, suggesting nearly all of the xenoliths and xenocrysts were accumulated immediately before and during the turbulent phreatomagmatic eruption which produced the maar crater. Total alkali silica classification of felsic xenoliths from Cerro Overo maar (and ignimbrite samples) show dominantly dacitic composition (65 - 68 wt % SiO$_2$; 6.0 - 7.5 wt % Na$_2$O+K$_2$O) with a subordinate rhyolitic population (70 - 75 wt % SiO$_2$; 7.5 - 8.5 wt % Na$_2$O+K$_2$O) (Figure 8). The Atana Ignimbrite dacitic with a
minor rhyolitic component thought to represent the highly differentiated magma chamber “cap” (Gardeweg & Ramirez, 1987; Lindsay et al., 2001a). In the field, rhyolitic ignimbrites were sampled outcropping at or immediately below the crater rim of Cerro Overo maar while dacitic samples were collected from the 5 – 30 m of crater wall rock exposed as a nearly homogenous, crystal-rich white ignimbrite. A rough estimation of excavated volume of ignimbrite suggests the rhyolitic component should make up less than 10% of the material removed during crater formation, and is ≤ 5% of the xenoliths sampled from Cerro Overo.

Several types of xenoliths are present, dominated by (≥ 60%) light grey, plagioclase, oxides, and quartz-bearing dacite (65-68 wt % SiO₂; 6-7 wt % Na₂O+K₂O) ranging from isolated quartz or feldspar xenocrysts to meter-scale, coherent xenoliths. Another ~ 30% of the sampled xenoliths are a dark-colored glassy material with either a frothy texture or a dense, low-glass content displaying nearly identical chemistry and mineralogy to the light-grey dacitic xenoliths. These appear to be more well-integrated (assimilated) examples of the same material. Some are discrete blocks with sharp boundaries, while others show a range of disaggregation to fluidal mixing with the host rock. In some instances, anti-xenoliths of mafic lava are found within larger felsic xenoliths, fully enclosed in silicic glass. Additional uncommon xenolith types include pyroxene-bearing andesite, a greenish fine-grained rock with andesitic composition, pepperitic material which appears to be a baked gradient between mm-cm scale mafic blebs and fine-grained felsic material, and glassy, frothy textured xenoliths of unclear origin, ranging from light grey to black. Quartz xenocrysts in Cerro Overo lava lack alteration rims, indicating relatively short residence times in the higher temperature mafic host lava. Feldspar xenocrysts show the same degree of fracturing and sieve textures as the phenocrysts within the ignimbrite, which is a diagnostic characteristic of the Atana and is inherited from their storage in the upper-crustal Altiplano Puna Magma Body (e.g. Lindsay et al., 2001a; Folkes et al., 2011; Frey & Lange, 2011). Dacitic xenoliths are chemically and mineralogically similar to the immediately underlying Atana Ignimbrite, although with a more variable amount of glass, and the xenoliths display pseudo-morphed replacement of biotite and amphibole crystals by Fe-oxides.

Ignimbrite and associated dome compositions throughout the Central Volcanic Zone are rhyo-dacitic and show wide scatter in several major and trace element trends (Lindsay et al., 2001a; Kay et al., 2010). The Atana Ignimbrite represents a relatively well-defined highly differentiated endmember in the continuous arc trend (Figure 8; Figure 11). The Atana is a high-
K, calc-alkaline rock with very low FeO* content (rhyolitic component: 1.7 – 2.8 wt % FeO*; dacitic: 3.3 – 4.2 wt % FeO*) and a wide range in Na₂O & CaO (& Al₂O₃) content, but not K₂O (Figure 117; Figure 118; Figure 120; Figure 112). Although the ignimbrite can be classified as a high-K lava (Figure 112), total alkali content (K₂O + Na₂O) with respect to silica follows a lower concentration trend than the arc lavas erupted at stratovolcanoes, presumably related to heavy fractionation of plagioclase and microcline in the upper crustal Altiplano-Puna magma body, the postulated source of major ignimbrite eruptions in the region (Gardeweg & Ramirez, 1987; De Silva, 1989b; Lindsay et al., 2001; De Silva et al., 2006; Schnurr et al., 2007; Kay et al., 2010; Kay et al., 2012). Other AFC-related trends include very low Al₂O₃ content (~ 12.7 wt %) in some samples due to substantial fractionation of plagioclase and depleted P₂O₅ content due to apatite crystallization. Plagioclase fractionation in the ignimbrites (e.g. Kay et al., 2010) has also resulted in depletion in Ba (Figure 125) and Sr (200 – 300 ppm) (Figure 127), resulting in the highest Rb/Sr of the region (0.39 – 1.46) (Figure 128), and some of the most negative Europium anomalies (Eu/Eu* = 0.51 – 0.79, average 0.68) in the central Andes (Figure 130). Europium anomalies displayed in intermediate arc volcanism generally range from 0.73 to 0.88 and mafic endmember rocks of Cerro Overo maar show small negative Eu anomalies, ranging from 0.84 to 0.89 (Figure 130).

Atana Ignimbrite Pb isotopic ratios are highly enriched (i.e. radiogenic) with respect to all other rocks of this study, but still within the range of CVZ isotopic compositions (Figure 29 - Figure 31). The ²⁰⁶Pb/²⁰⁴Pb of the Atana Ignimbrite (18.978) is higher than any of the crustal domains defined by Mamani et al. (2008; 2010), indicating the isotopes are strongly influenced by ingrowth of radiogenic Pb from the high U and Th content of ignimbrites of the upper crust. Normalized trace element and REE diagrams (Figure 10) and isotopic composition (Nd, Sr) also indicate the dominant xenolith type is sourced from the Atana ignimbrite, which is identifiable in outcrop along the crater walls (Figure 10). The ⁸⁷Sr/⁸⁶Sr, ratios (0.70950 – 0.70968) and Nd isotopic composition (¹⁴³Nd/¹⁴⁴Nd = 0.51223; εNd = -8.02) measured in Cerro Overo xenoliths are consistent with a dominantly crustal origin and fall within the broad isotopic range reported throughout the Atana Ignimbrite (⁸⁷Sr/⁸⁶Sr = 0.7094–0.7131; ¹⁴³Nd/¹⁴⁴Nd = 0.51222 – 0.51230; εNd = -8.15 – -6.59) (Lindsay et al., 2001a).
The Puntas Negras – El Laco Mafic Lava Flow

An olivine- and clinopyroxene-bearing, high-K basaltic andesite lava flow (53 wt % SiO₂; 6.7 wt % MgO; 4.7 wt % K₂O + Na₂O) in the Cordon de Puntas Negras defines another mafic endmember composition for volcanism in the Altiplano-Puna region (Figure 8). This small flow, the Puntas Negras – El Laco mafic lava, has an arc-intraplate transitional composition, and is inferred to be derived from melts with origins of both fluid-flux melting above the slab and back-arc intraplate magmatism, based on work from Kay et al. (1994). Their survey of (high-K) behind-the-arc rocks of the southern Puna defined a back-arc calc-alkaline group with La/Ta > 30, an intraplate group with La/Ta < 25, and classified volcanic samples with La/Ta between 25 and 30 as transitional compositions (Figure 106). Magma generation within this transitional regime involves an intermediate amount of partial melting beneath a relatively thin (~ 50 km) continental lithosphere with an intraplate signature due to a melt contribution caused by upwelling hot asthenosphere following removal of the lithospheric root (Coira & Kay, 1993; Kay et al., 1994; Matteini et al., 2002; Hoke & Lamb, 2007). The Puntas Negras – El Laco lava is less-differentiated than the main arc front volcanics, displaying higher MgO (average 6.71 wt %) and lower SiO₂ (52.8 wt %) (Figure 8). They display both lower MgO and SiO₂ than rocks from Cerro Overo maar (7.4 wt % MgO, 55 wt % SiO₂). Puntas Negras lavas have, however, experienced a lesser degree of crustal contamination than the basaltic andesite of Cerro Overo maar, as indicated by Th/Nb ratios (average Puntas Negras Th/Nb = 0.31, CVZ arc front range = 0.5 – 1.9) and less-radiogenic Nd and Sr isotopic compositions relative to indices of differentiation (Figure 28), suggesting the higher MgO of Cerro Overo is due to a lower degree of mafic mineral fractionation. Puntas Negras – El Laco lava also marks an endmember volcanic composition higher in Fe (9.1 wt % FeO*) and Ti (1.31 wt % TiO₂) than the basaltic andesite of Cerro Overo (Figure 113; Figure 114). The higher FeO*/MgO may reflect fractionation of higher forsterite olivine fractionation, preferentially depleting Mg.

These rocks are basaltic andesites which straddle medium- and high-K classification (Figure 112; Figure 12). Elevated K₂O content and La/Ta < 30 relate the Puntas Negras basaltic andesite with back-arc volcanics based on the established indices of Kay et al. (1994). In addition, the mantle-normalized Nb-Ta deficit seen in magmas produced from fluid flux melting of the asthenosphere is not as pronounced for basaltic andesite from Puntas Negras as it is for the arc-related mafic lava of Cerro Overo maar (Figure 102). The mantle-generated
characteristics of this lava are partially overprinted by influence from the thickened crust, evidenced by slight negative Eu anomalies (Eu/Eu* < 0.92), radiogenic Sr (> 0.7055) and Pb and nonradiogenic Nd (εNd < −1.9) isotopic ratios (Figure 25). Pb isotopic ratios of Puntas Negras are within the CVZ isotopic field and similar to Cerro Overo maar, showing an enrichment in \(^{208}\text{Pb}/^{204}\text{Pb}\) and \(^{206}\text{Pb}/^{204}\text{Pb}\) relative to the main arc (Figure 29 - Figure 31).

The Puntas Negras – El Laco mafic lava is divisible into at least two sub-sections: an Upper Flow which is olivine-rich (5 -12 %) and highly vesiculated (10 – 40%), and a (notably denser) Lower Flow with lower crystallinity (2 – 5%), lower vesicularity (3 – 10%) and a greater plagioclase content (Figure 131). The Upper Flow displays higher SiO\(_2\) (Upper: 53.4 – 53.7 wt %, Lower: 51.7 – 53.2 wt %), MgO (Upper: 7.3 wt %, Lower: 6.3 wt % average), and FeO* content (Upper: 9.05 – 9.36 wt %, Lower: 8.73 – 9.19 wt %), and lower Al\(_2\)O\(_3\) (Upper: 15.8 %, Lower: 16.4 %), total alkalis (Upper: 4.51 wt %, Lower: 4.87 wt % K\(_2\)O + Na\(_2\)O), and CaO content (Upper: 8.32 wt%, Lower: 8.86 wt %) (Figure 11) (Table 16). The Upper-Lower subdivision divides the full length of the flow into a near-vent and far-from-vent lava, but there is limited variability within each unit. There were either two different eruptive events, or two pulses in one eruption with different compositions. The Upper Flow displays a significantly higher Ni content (79 ppm vs. 40 ppm) and lower Cr/Ni ratio (3.13 vs. 5.67), indicative of the higher olivine relative to pyroxene content, also seen petrographically (Figure 132; Figure 133). The elevated Mg and Fe content of the Upper Flow are also due to olivine concentration, while the higher concentrations of Ca, Al, alkalis, and Sr (625 ppm vs. 565 ppm) in the Lower Flow are due to the increased concentration of plagioclase, as is the slightly less negative Europium anomaly (Table 16). The Upper flow also displays lower values of Sr/Y (23.7 vs. 28.3), La/Yb (12.9 vs. 15.4), and Sm/Yb (2.7 vs. 3.1). Both flows, however, show similar values for incompatible elements Nb (117ppm) and Ba (443 ppm), which are both elevated with respect to the arc and other lavas of this study (generally 5 – 10 ppm). The La/Ta ratio, which indicates an intraplate melting origin to the Puntas Negras magma (Kay et al., 1994), is consistent across both flows, as are normalized trace or rare-earth element patterns (Figure 102). The differences in the two flow lobes is likely due to assimilation, crystallization, and/or fraction (AFC) processes, further supported by petrographic differences. Potentially, the compositional differences represent the eruption of an inhomogeneous magma batch which had gravitationally fractioned the lighter minerals (i.e. plagioclase) to the top and first erupted portion and concentrated heavier olivine crystals in its deeper portions.
Table 16 - Select physical and compositional differences between the Upper and Lower flow divisions of the Puntas Negras - El Laco lava, presented as average values.

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<tr>
<th>Puntas Negras</th>
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<th>Lower</th>
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<td>2 - 5 %</td>
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<td>Vesicularity</td>
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<td>3 - 10 %</td>
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</table>

Geochemistry of El País Lava

El País lava flow is an ortho- and clinopyroxene-bearing basaltic andesite (56.3 wt % SiO$_2$; 5.62 wt % MgO) with one of the more mafic compositions found in the Altiplano-Puna arc, with the exception of Cerro Overo maar and the Puntas Negras-El Laco flow (Figure 8). El País lava is representative of the least-evolved lavas erupted at stratovolcanoes after experiencing storage and processing in supravolcanic magma chambers (storage zones), compositionally similar to the least-evolved lavas reported from the nearby Lascar stratovolcano (Figure 115). El País lava was sampled west of the arc (23.79° S, 67.97° W), north of the Cordón de Tujle, but
appears to be a an erosional remnant from a larger flow, possibly a distal lobe of Corral Negro, an eroded volcanic complex on the western margin of the modern frontal arc, immediately southwest of Laguna Miscanti (Ramirez & Gardeweg, 1987; González-Ferrán, 1994) (Figure 19). This lava is medium-K and calc-alkaline and distinct from the rest of the volcanism addressed in this study as out-of-equilibrium plagioclase crystals and inter-grown orthopyroxene- clinopyroxene-plagioclase-oxide glomerocrysts are evidence for prolonged magma storage in a sub-arc magma chamber (Figure 80) (e.g. Davidson et al., 1991; Mattioli et al., 2006; Petrinovic et al., 2006; Petrone, 2010). Spatially associated lavas from the Corral Negro complex have been dated to 4.6 +/- 2.3 Ma by K-Ar, suggesting these lavas were produced in the Pliocene, during the final stages of ignimbrite volcanism (Ramirez & Gardeweg, 1987; González-Ferrán, 1995; De Silva, 1989a; 1989b). A map published by Gonzalez et al. (2009) has this lava simply marked as “Late Pleistocene Lava.”

El País lava displays alkali content at the low end for the arc, similar to the Cerro Overo end-member. FeO* and TiO$_2$ content are elevated with respect Cerro Overo maar, more similar to the compositions of the Puntas Negras mafic lava (Figure 89; Figure 114). Ni content is also relatively high (63 ppm), similar to the more olivine-depleted and plagioclase-rich Lower Flow of the Puntas Negras – El Laco lava (Figure 132). Sr, Nd, Zr, Rb/Sr, and Ba fall along or near the modern main-arc trend and suggest relatively minor fractionation of plagioclase, also apparent in the Europium anomaly (0.86), which is only slightly more negative than that of Cerro Overo maar (Figure 130). Trace element characteristics fall within the main arc field (Figure 9) and form a primitive mantle-normalized pattern with Nb-Ta depletion and showing slightly more differentiation than Cerro Overo (Figure 134). Indices of La/Ta, Ba/Nb, and Sr/Y ratios all indicate the El País lava is a part of the main arc melting regime (Figure 106; Figure 107; Figure 124), formed from mantle melting mitigated by slab fluids. The La/Sm ratio of El País lava, representing light incompatible element enrichment, is slightly higher than Cerro Overo and slightly lower than Puntas Negras – El Laco lava, indicating a derivation from an intermediate degree of partial melting (Figure 123).

West of the Arc: Tilocálar Norte y Sur & Cerro Tujle Maar

Aphyric intermediate lavas erupted west of the Altiplano-Puna frontal arc in the Lomas de Tilocálar area (the Tilocálar Group) display high Al$_2$O$_3$ (> 15.5 wt %) and Na$_2$O (> 4.0 wt %)
content, relative depletions in certain fluid-mobile elements (Cs, Rb, Th, U), a high degree of heavy rare earth element (HREE) and Y depletion relative to light REEs, and substantial enrichment in certain incompatible elements, such as Sr and Ba (Figure 110; Figure 135; Figure 82). These volcanoes are situated along subparallel fault-propagation-folds and fault-bend-folds at the southeast margin of the Salar de Atacama, where localized extension has focused magmatism along bends in compressional deformation features (Aron et al., 2008; Gonzalez et al., 2009). Tilocálar Sur minor composite volcano (58.7.3 wt % SiO₂; 3.56 wt % MgO) and Cerro Tujle maar (58.8 wt % SiO₂; 3.45 wt % MgO) have erupted medium-K, calc-alkaline lavas which straddle the andesite to trachy-andesite classification fields (Figure 8; Figure 12; Figure 112). These rocks are less-evolved than most of the frontal arc for most major elements, with high alkali element concentrations due to elevated Na₂O content (~ 4.2 wt %). Lavas from the Tilocálar Norte flow complex are high-K, calc-alkaline, less-evolved dacites (63.4 wt % SiO₂; 2.44 wt % MgO) which also plot within the main arc for most major element trends (Figure 8). The Tilocálar Group volcanics display high FeO* and TiO₂ content, with Cerro Tujle maar showing the most elevated Fe content relative to Tilocálar rocks with similar silica content (Figure 113; Figure 114). Al₂O₃ content is high, ranging 15.7 – 16.7 wt %. The composition of the Tilocálar Group volcanoes is distinct from the main subduction arc trend in enrichments of incompatible components, such as P₂O₅ (Figure 116), Sr (Figure 127), Ba (Figure 125), and Nd (Figure 136), and greatly fractionated REEs (Sr/Y = 78 – 97, La/Yb = 35 – 66) (Figure 134; Figure 135; Figure 110).

While marginally within the main subduction arc major element trends, normalized trace element patterns of the Tilocálars and Cerro Tujle clearly display the deep Nb-Ta trough (La/Ta > 60) indicative of melting of metasomatized mafic rock at high pressure. While this indicates a subduction arc-related magmatic origin, trace and minor element patterns indicate these magmas were derived from a distinct source to the majority of the arc front in the Altiplano – Puna region (e.g. Cerro Overo maar). Trace element ratios indicative of melt fractionation (i.e. not caused by crystallization), such as Sr/Y, La/Sm, La/Yb, and Dy/Yb, are all elevated relative to the main arc for the Tilocálar Group volcanism at the southeastern margin of the Salar de Atacama (Figure 110; Figure 111). In addition, Ti and Zr characteristics of this group place them well within the compositional field for back-arc rocks and not the arc itself (Figure 109), as does Sr/Y versus Y content (Figure 124). However, for La/Ta versus La/Yb (Figure 106), which distinguishes arc from back-arc and different melting regimes (Kay et al., 1994;
Mazzuoli et al., 2008), the Tilocálar Group volcanic rocks plot as their own field with high values for both trace element ratios.

The La/Sm ratio, when compared with La content, is higher than the majority of the arc rocks and indicate the Tilocálar Group lavas were derived from relatively small melt fractions (Figure 123). Very low Rb/Sr (≤ 0.06) and small europium anomalies (Eu/Eu* ≥ 0.9) indicate minimal fractionation of plagioclase, which is present in the lavas only as groundmass crystals, indicating plagioclase crystallization was suppressed. Relative enrichment of Ba (Figure 82) is also likely related to suppression of plagioclase crystallization due to high temperature melt (e.g. Lange et al., 2009). Depletions in other fluid-mobile incompatible elements, such as Cs, Rb, Th, and U (Figure 82) indicate the melt source was depleted and/or dehydrated by the time the Tilocálar Group magmas were generated (e.g. Rudnick & Fountain, 1995; Rollinson & Tarney, 2005). Enrichment in P2O5 per evolution indicators (e.g. MgO, SiO2, etc.) relative to the arc front trend suggests the magmas did not precipitate out significant amounts of apatite (Figure 116). A lack of apatite crystals observed in the lava itself suggests the phase did not crystallize at any point.

Relatively high εNd (average -4.6) for both Tilocálers and Cerro Tujle for their level of differentiation hint at a source unenriched in the Nd isotopic composition of the upper crust (Figure 25; Figure 28). Values for 87Sr/86Sr ratios of Tilocálar Group lavas are radiogenic, ranging 0.70647 to 0.707017, yet are relatively unevolved (i.e. low) in the context of CVZ arc rocks (e.g. Mamani et al., 2010 and references therein). The contextually low Sr isotopic ratios and higher Nd isotopic ratios indicate low degrees of crustal involvement (i.e. melting and assimilation) in the Tilocálar Group magmas, further supported by trace element indicators, such as low Rb concentration and high Ba/Rb and Rb/Cs ratios (see Hildreth & Moorbath, 1988; Matteini et al., 2002). Pb isotopic ratios for the Lomas de Tilocálar lavas plot within the orogenic CVZ arc field, but show less radiogenic Pb (206Pb, 207Pb and 208Pb are derived from decay chains beginning with 238U, 235U and 232Th, respectively), indicating little involvement of upper crustal rocks, which are enriched in U and Th and thus show more radiogenic signals (Figure 29 - Figure 31). Lower radiogenic Pb also indicates the Tilocálar Group does not include a significant contribution from either a high U/Pb, Th/Pb enriched mantle lithospheric source or ancient continental crust. Pb isotopic ratios are more sensitive by mass balance than Nd or Sr ratios, and the
**Geothermometry, Barometry, and Hygrometry**

Temperature and pressure estimates were modeled for each monogenetic volcano from mineral, glass, and whole rock compositional data obtained by EMP and ICP-MS analysis, respectively (Table 17). With the exception of the olivine-spinel thermometry (Wan et al. 2008; Coogan et al., 2014), the thermometry and barometry model results use updated calibrations from the RiMG review for volcanic systems by Putirka (2008). Additional thermometry based on the T-dependent partitioning of Al between cogenetic olivine and spinel was developed by Wan et al. (2008) using experimental datasets and later updated and expanded in its range by Coogan et al. (2014). Thermometry results indicate 2-stage phenocryst growth in the olivine-bearing lavas, followed by syn- or post-eruptive growth of additional low forsterite olivine and groundmass plagioclase. For the aphyric lavas of the Tilocálar Group, results indicate relatively high eruptive temperatures of 1050 - 1100° C for the andesitic-dacitic compositions of the lavas.

Geobarometry results were, indicating equilibrium pressure values within the range of the middle-upper crust (0 – 30 km depth), but with large margins of error. These results can be interpreted to represent the absence of extended magma storage in “chambers,” mush zone, or along fault planes at specific depths. For equations listed in this section, unless otherwise noted, $X_b^a$ is the cation fraction of $b$ in the phase $a$. For example, $X_{CaO}^{Plg}$ represents the cation fraction of CaO in plagioclase. Cation Proportion is the wt % of an oxide divided by the molecular weight per cation (e.g. for Al$_2$O$_3$, the weight of AlO$_{1.5}$ = 50.98), and Cation Fraction per component is that component's cation proportion divided by the sum of all cation proportions.

*Table 17 (next page)* - Summary of average thermometry, barometry, and hygrometry results for different small-volume mafic lavas of the Altiplano-Puna region of the Central Andes and olivine-hosted melt inclusions from Cerro Overo maar (C.O. Melt Incs). The left column lists the components used in each set of calculations. The errors reported refer to the immediately preceding thermometer, barometer, or hygrometer and are the precision of the model itself. Estimates for H$_2$O content are based on groundmass plagioclase compositions and thus represent the water content at the time of eruption. The depths reported are calculated from an assumed lithospheric pressure gradient of 3.7 km/kbar. Abbreviations are as follows: Pyx = pyroxene, Cpx = clinopyroxene, Plag = plagioclase, Mantle $T_p$ = mantle potential temperature, $a_{SiO_2}$ = silica activity.
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<tr>
<th></th>
<th>Cerro Overo</th>
<th>CO Melt Incs.</th>
<th>La Albóniga</th>
<th>Puntas Negras</th>
<th>El País Lava</th>
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<td>N/A</td>
<td>1088</td>
<td>1171</td>
<td>1084</td>
<td>1042</td>
<td>1048</td>
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<tr>
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<td>1091</td>
<td>1173</td>
<td>1078</td>
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<td>1044</td>
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<tr>
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<td>±36</td>
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<td>±36</td>
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<td>1276</td>
<td>1199</td>
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</tr>
<tr>
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<td>±27</td>
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<td>N/A</td>
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<td>1323</td>
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<tr>
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<th>P: aₛₒ₂ (kbar)</th>
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<th>12.3</th>
<th>4.8</th>
<th>7.1</th>
<th>4.4</th>
<th>5.2</th>
<th>0.4</th>
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<td><strong>BAROMETRY</strong></td>
<td>Error (kbar)</td>
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<td>±2.9</td>
<td>±2.9</td>
<td>±2.9</td>
<td>±2.9</td>
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<td>±2.9</td>
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<td>17.8</td>
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<td>6.7</td>
<td>17.4</td>
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<td>±10.7</td>
<td>±10.7</td>
<td>±10.7</td>
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<td>±1.8</td>
<td>±1.8</td>
<td>±1.8</td>
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<tr>
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<td>±6.7</td>
<td>±6.7</td>
<td>±6.7</td>
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<td>N/A</td>
<td>N/A</td>
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<tr>
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<td>N/A</td>
<td>N/A</td>
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<td>N/A</td>
<td>N/A</td>
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<td>N/A</td>
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<td>N/A</td>
<td>N/A</td>
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<td>N/A</td>
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**HYGROMETRY**

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<td>± 1.1</td>
<td>± 1.1</td>
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<td>± 1.1</td>
<td>± 1.1</td>
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**Liquid-Only Thermometry**

Liquid-only or glass thermometers are models for calculating equilibrium temperatures from bulk compositional data with no contributions from discrete silicate phases (i.e. minerals). Such models generally yield results with systematic errors but very high correlation coefficients (Putirka, 2008). For example, the liquid thermometer of Helz & Thornber (1987) captured 84% ($R^2 = 0.84$) of temperature variation within an experimental data set ($n = 1536$) with the simple model $[T(°C) = 23.0\times\text{MgO}_{\text{liq}} + 1012 °C]$, dependent only on bulk MgO content (wt %). Such models are incredibly useful for investigating lavas which are aphyric or lack the necessary phase assemblages for more complicated thermometers. More complicated models involve input values for other compositional components, and those which have pressure or H$_2$O dependencies can be employed to solve for these factors if an accurate temperature estimate is independently available. These thermometers essentially estimate the temperature at which a melt with the input composition was last in equilibrium with whatever phases exerted the strongest control on Mg # (Putirka, 2008). For lavas with Mg-rich phases, such as Cerro Overo, La Albóndiga, Puntas Negras, and El País, this represents a temperature when the melt was in equilibrium with the main phenocryst phases. For the relatively aphyric Cerro Tujle, Tilocálar Norte, and Tilocálar Sur, these estimates more likely represent the near-eruptive temperature as Mg# would be fully controlled by the bulk composition. Considering these lavas show little to no evidence for upper crustal assimilation, they care likely in equilibrium with their bulk chemistry.

The compositional values used as inputs for liquid-only thermometry are whole-rock measurements from ICP-MS analysis. As such, they are not representative of the volcanic glass seen in the final rock products, but rather the full groundmass + minerals assemblage. The
thermometry calculations represent the temperature at which the full assemblage presumably would have been in equilibrium. Calculated temperatures from liquid-only thermometry do not deviate greatly from mineral-based calculations. For example, model temperatures for basaltic andesite from Cerro Overo maar averaged 1169°C for liquid-only thermometry, 1207°C for olivine-liquid methods, and 1153°C from Al exchange between olivine and spinel (Table 17). These temperature estimates cover ~50°C and are all approximately within error of each other, suggesting they all represent the same process: equilibrium precipitation of olivine from a mafic melt. Olivine-hosted melt inclusion compositions from Cerro Overo phenocrysts yield a higher temperature (1205°C) than the whole-rock, as would be expected for trapping melt earlier in the history of the magma. For the olivine-bearing lavas of Cerro Overo, La Albóndiga, and Puntas Negras-El Laco, Mg-Fe exchange coefficients show that olivine cores are in equilibrium with whole-rock compositions and the modeled liquid thermometry temperatures represent the interval of olivine crystallization in the melt. For pyroxene-phyric El País lava, the calculations represent the temperatures at which pyroxene phenocrysts were precipitating. For the aphyric lavas of Cerro Tujle and the two Tilocálar volcanoes, the model temperature represents the temperature of the rocks pre-cooling (eruption).

Table 18 - Summary of whole-rock thermometry, barometry, and H2O content estimation results from six different liquid thermometers (Putirka, 2008; Helz & Thornber, 1987). Some thermometers require a P input while others are dependent only on composition. The small standard deviations (within error for the thermometers) are a testament to appropriate P input. The reported pressure is the average value (+2.9 kbar) from the silica activity barometer (Beattie, 1993; Putirka, 2008) calculated iteratively along with H2O content (±1.1 wt %), using whole-rock and plagioclase compositions as constant input values.

<table>
<thead>
<tr>
<th>Location</th>
<th>Avrg T (°C)</th>
<th>StdDev (± σ)</th>
<th>Min (°C)</th>
<th>Max (°C)</th>
<th>P (kbar)</th>
<th>H2O (wt %)</th>
<th>n</th>
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<td>33.1</td>
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<td>1225</td>
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<td>46.1</td>
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<td>1266</td>
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<td>La Albóndiga</td>
<td>1163</td>
<td>32.9</td>
<td>1092</td>
<td>1195</td>
<td>4.8</td>
<td>2.5</td>
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<td>Puntas Negras</td>
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<td>30.8</td>
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<td>1214</td>
<td>7.1</td>
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<td>18.2</td>
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<td>1147</td>
<td>4.4</td>
<td>2.6</td>
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<td>1117</td>
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<td>3</td>
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<td>Tilocálar Sur</td>
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<td>15.1</td>
<td>1079</td>
<td>1140</td>
<td>4.7</td>
<td>2.1</td>
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The Silica Activity Barometer

The activity of silica \(a_{SiO_2}^{liq}\) in silicate liquids (Equation 7) can be used as a barometer or thermometer for igneous systems (Equation 8) as it is buffered at constant P and T (Beattie, 1993; Putirka, 2008). The activity of a chemical component is functionally equivalent to its effective concentration. Activity models are designed to account for deviations in a complex system caused by the interaction of different chemical components. In an ideal system, the activity of a component will equal the mole fraction, but as geologic systems are notoriously non-ideal, calibrated models based on activity are valuable and worth consideration. The calibration of Putirka (Equation 8) can reproduce P ± 2.9 kbar for large experimental data sets (2008), which is a broad approximation of around 11 km depth in natural systems. The barometer in this case should not be considered an estimate of exact pressure values, but is rather more useful in giving a sense of relative pressure of equilibration. Using temperatures calculated from olivine-liquid thermometry and the corresponding compositions, I calculated P values representing the pressure of equilibrium for each respective melt + phenocryst assemblage (Table 17). For lava without an olivine phase, the temperature input was from whole-rock thermometry values, and the results are less precise (Putirka, 2008).

Results for barometric modelling based on silica activity (Table 17) range from 1.8 kbar (~ 6.7 km) for Tilocálar Sur to 12.3 kbar (~45.5 km) for olivine-hosted melt inclusions from Cerro Overo maar. Calculated equilibrium pressures for lava from Cerro Overo, La Albóndiga, and El País cluster around 5 ± 1 kbar (~ 20 km depth), which roughly corresponds to the ductile-brittle transition (e.g. Perkins et al., 2016); the rheological boundary which distinguishes the upper crustal regime and has been broadly implicated as the stalling depth for both the sub-volcanic magma storage zones of arc volcanoes and the dactitic crystal mush of the Altiplano-Puna Magma Body (Thorpe et al., 1984; Davidson et al., 1991; Davidson & De Silva, 1992; Chmielowski et al., 1999; Babeyko et al., 2002; Zandt et al., 2003; Stern, 2004; Mattioli et al., 2006; Petrinovic et al., 2006; Riller et al., 2006; Prezzi et al., 2009; Reubi & Blundy, 2009; Salisbury, 2011; Tassara & Echaurren, 2012; Del Potro et al., 2013; Ward et al., 2014; Perkins et al., 2016; Delph et al., 2017, etc.). Lava from Cerro Tujle maar and Tilocálar Sur yield pressures of 3.3 kbar (~ 12 km) and 4.7 kbar (~ 17 km). This relative consistency in calculated equilibrium pressures may represent that the majority of magma batches are delivered rapidly from around 20 km depth to the surface through pathways of weakness in the brittle upper crust. The P calculated from silica activity would represent the last depth at which the magma batch was ascending slowly.
enough to reach barometric equilibrium. Puntas Negras and El País lavas are the only ones that show petrographic evidence for magma storage (e.g. large crystals out of equilibrium), or interaction with a magmatic storage zone. All low-forsterite olivine rims and other late-stage mineralization will likely have occurred after this 20 km equilibrium. The other possibility is that storage at ~20 km depth is a common feature of mantle-derived magmatism around the globe and the calibration of the barometer to natural samples consistently produces such results.

\[
a_{\text{SiO}_2}^{\text{liq}} = (3X_{\text{SiO}_2}^{\text{liq}})^{-2}(1 - X_{\text{Al}_2\text{O}_3}^{\text{liq}})^{7/2}(1 - X_{\text{TiO}_2}^{\text{liq}})^7
\]

*Equation 7 – Activity for SiO\(_2\) in silicate liquids which can be used to describe > 60 % of P-T variation in experimental data sets over the range 0.001-70 kbar (~0 – 260 km depth) and 825-2000 °C for 31.5 – 70 wt % SiO\(_2\) (Beattie, 1993; Putirka, 2008). This variable can be employed in more complex barometry and thermometry modeling without the need for other phase data (Putirka, 2008).*

\[
P(\text{kbar}) = 231.5 + 0.1867T(\degree\text{C}) + 0.12444T(\degree\text{C})\ln(a_{\text{SiO}_2}^{\text{liq}}) - 528.5(a_{\text{SiO}_2}^{\text{liq}})^{1/2} + 103.3(X_{\text{TiO}_2}^{\text{liq}}) + 69.9(X_{\text{Na}_2\text{O}_{0.5}}^{\text{liq}} + X_{\text{K}_2\text{O}_{0.5}}^{\text{liq}}) + 77.3\left(\frac{X_{\text{Al}_2\text{O}_3}^{\text{liq}}}{X_{\text{Al}_2\text{O}_3}^{\text{liq}}} + X_{\text{SiO}_2}^{\text{liq}}\right)
\]

*Equation 8 – The re-calibrated silica activity barometer reported by Putirka (2008) which is based on liquid composition, temperature, and the activity of silica (Equation 7) in silicate liquids as devised by Beattie (1993).*

**Two-Pyroxene Thermometry**

El País is the sole lava sampled as a part of this work with co-crystallized ortho- and clino-pyroxene phases. In this rock, diopside and enstatite have intergrown with plagioclase in glomerocrystic clusters (Figure 90). Two-pyroxene thermometers based on major element partitioning (Equation 9; Equation 10) were employed to estimate both pressure and temperature through iterative calculation. The results produced from these models represent the thermodynamic conditions at which the two pyroxene phases last established equilibrium exchange. Five different two-pyroxene thermometers (Putirka, 2008) gave crystal equilibration temperatures ranging 1015 – 1047 °C with an average temperature of 1034°C (Equation 9). Two separate geobarometry calculations (Putirka, 2008) gave pressure estimates of 4.2 ± 3.7 and 4.3 ± 2.8 kbar (Equation 10), equivalent to approximately 16 ± 9 km depth. These enstatite-diopside
thermometers and barometers assume that the crystals are in equilibrium with each other for accuracy. All pyroxene included in these calculations were tested for equilibrium, indicated by Fe-Mg exchange, $K_D^{\text{Fe-Mg}} = 1.09 \pm 0.14$ (Putirka, 2008). Two-pyroxene thermobarometers do not require an input for H₂O content, and can thus be used as a check for other pyroxene-based calculations (see below) which require an approximation or iterative calculation to provide water content as an input in the absence of quantitative data. The depth and temperature calculations for El País lava (1035°C, 4.3 kbar) roughly correlate to those expected for storage or stalling in a subvolcanic magma chamber and the eruption of an intermediate lava, although the errors are broad.

The two-pyroxene barometric estimates of 4.3 kbar are similar to the whole-rock (silica activity) barometry results of 3.3 kbar for the same lava. Near the ductile-brittle rheological boundary, these results indicate the large (2 – 8 mm) pyroxene phenocrysts of El País were stable in the upper crust long enough to be in equilibrium. As many of the larger pyroxene crystals of both compositions show resorption features around their outer edges, it is possible they are antecrysts included in the magma as it passed through a storage zone. The fact that they are pyroxenes and not the plagioclase, amphibole, and biotite commonly found in ignimbrite eruptions (e.g. De Silva et al., 2006), El País lava is most likely related to the magmatic plumbing of the arc stratovolcanoes, and not the Altiplano-Puna Magma Body. Plagioclase, liquid, and groundmass clinopyroxene based thermometry all produce higher temperature estimates for the same El País lava, further supporting a crystal-cargo type origin for the large pyroxene glomerocrysts. However, the error of precision for the two-pyroxene thermometer is relatively large ($\pm 56^\circ$ C), so this interpretation is tenuous at best as the two-pyroxene results are within error of other estimates of eruptive temperature.

\[
\frac{10^4}{T(\text{°C})} = 11.2 - 1.96\ln\left(\frac{X^{\text{opt}}_{\text{EnF}}}{X^{\text{opt}}_{\text{EnFy}}}\right) - 3.3\left(X^{\text{opt}}_{\text{Ca}}\right) - 25.8\left(X^{\text{opt}}_{\text{CrCsTs}}\right) + 33.2\left(X^{\text{opt}}_{\text{Mn}}\right) - 23.6\left(X^{\text{opt}}_{\text{Na}}\right) - 2.08\left(X^{\text{opt}}_{\text{En}}\right) - 8.33\left(X^{\text{opt}}_{\text{Dr}}\right) - 0.05P(\text{kbar})
\]

(A)
Equation 9 - Two-pyroxene thermometers from the calibrations of Putirka (2008). Equation (A) recovers $T$ to $\pm 56^\circ C$ and Equation (B) recovers $T$ to $\pm 60^\circ C$ for experimental data (Putirka, 2008).

\[
\frac{10^4}{T(\circ C)} = 13.4 - 3.4 \ln \left( \frac{X_{EnF_s}^{\text{cpx}}}{X_{Opt}^{\text{cpx}}} \right) + 5.59 \ln \left( X_{Mg}^{\text{cpx}} \right) - 8.8 \left( Mg \#^{\text{cpx}} \right) + 23.85 \left( X_{Mn}^{\text{opt}} \right) + 6.48 \left( X_{FmAl_2SiO_8}^{\text{opt}} \right) - 2.38 \left( X_{Di}^{\text{opt}} \right) - 0.044 P(\text{kbar})
\]

Equation 10 - Two-pyroxene barometers from the calibrations of Putirka (2008). Equation (A) is $T$-independent and recovers $P$ to $\pm 3.7$ kbar for experimental data (Putirka, 2008). Equation (B) is $T$-dependent variation which recovers $P$ to $\pm 2.8$ kbar for experimental data (Putirka, 2008).

\[
P(\text{kbar}) = -279.8 + 293 \left( X_{Al(VI)}^{\text{opt}} \right) + 455 \left( X_{Na}^{\text{opt}} \right) + 229 \left( X_{Cr}^{\text{opt}} \right) + 519 \left( X_{Fm_2Si_2O_6}^{\text{opt}} \right) - 563 \left( X_{En}^{\text{opt}} \right) + 371 \left( X_{Di}^{\text{opt}} \right) + 327 \left( \alpha_{En}^{\text{opt}} \right) + \frac{1.19}{K_f}
\]

\[
P(\text{kbar}) = -94.25 + 0.0457 T(\circ C) + 187.7 \left( X_{Al(VI)}^{\text{opt}} \right) + 246.8 \left( X_{Fm_2Si_2O_6}^{\text{opt}} \right)
\]

\[
-212.5 \left( X_{En}^{\text{opt}} \right) + 127.5 \left( \alpha_{En}^{\text{opt}} \right) - \frac{1.66}{K_f} - 69.4 \left( X_{En,Fs}^{\text{opt}} \right) - 133.9 \left( \alpha_{Di}^{\text{opt}} \right)
\]

Clinopyroxene-Liquid Thermobarometry

Mafic volcanic rocks rarely crystallize both orthopyroxene and clinopyroxene simultaneously, making thermometers and barometers calibrated to single pyroxene assemblages potentially quite valuable. Phenocrysts of diopside from El País and Puntas Negras-El Laco lava flows provide viable targets for single pyroxene-liquid calculations for $P$ and $T$ of equilibration. Unfortunately, groundmass pyroxene crystals from Cerro Overo, La Albóniga, and Puntas Negras-El Laco do not pass the test for equilibrium with the whole rock (liquid), based on Fe-Mg exchange, or $K_0(\text{Fe-Mg})_{\text{cpx-liquid}}$, which should be $0.27 \pm 0.14$ (Putirka, 2008). Liquid-only calculations meant to apply in the presence of clinopyroxene (Equation 16B) can still be attempted for these lavas, especially since independent $P$ estimates are available, but these numbers will be reported with caution. El País lava contains large phenocrysts of clinopyroxene in equilibrium with the whole-rock. The Tilocálar Group (Cerro Tujle, Tilocálar Sur, and Tilocálar Norte) eruptions all contain microcrystic clinopyroxene in their groundmass, presumably grown.
during or near eruption. Thermometry and barometry calculations from microcrystic pyroxene requires careful Electron Microprobe analyses, but can be useful in calculating the temperatures of magmas in the upper crust.

Pressure calculations for El País lava yield an average of 6.0 ± 1.6 kbar (Equation 14A) and 10.6 ± 3.2 kbar (Equation 14B), both barely within error of the two-pyroxene calculations and corresponding to depths of 22 ± 5.9 km and 39 ± 11.8 km. These values are indicative of depths corresponding to the middle-to-upper crust of the central Andes, where magma storage has been theorized to be common due to a rheological boundary layer (Davidson et al., 1991; Stern, 2004 and references therein). The massive Altiplano-Puna Magma Body slightly to the north of the El País lava has been geophysically imaged occupying this portion of the thickened crust, suggesting a widespread depth of stalling (Del Potro et al., 2013; Perkins et al., 2016). Temperature calculations for El País lava give an average of 1102 ± 42 °C for cpx-liquid thermometry (Equation 16A), 1127 ± 45°C for liquid-only thermometry (Equation 16B), and 1191 ± 87° for cpx-only calculations (Equation 15D). These values cover a significant range and are notably distinct from the two-pyroxene thermometry results. Two interpretations are possible. The first is, simply, that one or both sets of thermobarometers is incorrect. The second is that clinopyroxene began precipitating in El País magma at a higher temperature and greater depth before reaching final equilibrium with the orthopyroxene in the upper crust. Regardless, the results suggest this magma stalled or was stored in the upper crust before remobilization and eruption.

Clinopyroxene-liquid thermobarometry yields results for the Tilocálar Group monogenetic volcanism indicating high (for andesite-dacite compositions) temperatures of 1060 – 1090°C for clinopyroxene crystallization at pressures of 6 – 8 kbar (~ 22 – 30 km depth) (Table 17). Clinopyroxene-only temperature models yield even greater crystallization temperatures of 1120 - 1150°C, within the range of temperatures normally attributed to basaltic magmas. Elevated temperatures for these mafic magmas is supported by the mineralogy, which lacks amphibole and contains plagioclase only as microcrysts and microphenocrysts within the groundmass glass, and the only weakly negative Europium anomalies (Eu/Eu* > 0.91) for all three lavas which suggests plagioclase crystallization has been suppressed throughout their petrogenesis. Differentiation of a magma is normally accompanied, even driven by decreasing magmatic temperature, which induces crystallization and leads to increased polymerization of
silica chains. The High-T nature of these lavas suggested by clinopyroxene-based thermometry is evidence the primary melts from which the Tilocálar Group magmas evolved possessed an intermediate composition (Moyen, 2009). Melting of basaltic or metabasaltic material has been experimentally demonstrated to produce primary magma with intermediate composition (Martin et al., 2005 and references therein). The Tilocálar Group magma compositions and high temperatures could have been produced from melting of the metamafic basement of the central Andes or even direct melting of the subducted slab itself.

Cerro Tujle: $6.0 \pm 1.6$ kbar (Equation 14A) and $10.7 \pm 3.2$ kbar (Equation 14B). Temperature calculations give an average of $1081 \pm 42$ °C for cpx-liquid thermometry (Equation 16A), $1089 \pm 45$ °C for liquid-only thermometry (Equation 16B), and $1122 \pm 87$° for cpx-only calculations (Equation 15D).

Tilocálar Sur: $3.4 \pm 1.6$ kbar (Equation 14A) and $6.2 \pm 3.2$ kbar (Equation 14B). Temperature calculations give an average of $1090 \pm 42$ °C for cpx-liquid thermometry (Equation 16A), $1096 \pm 45$ °C for liquid-only thermometry (Equation 16B), and $1141 \pm 87$° for cpx-only calculations (Equation 15D).

Tilocálar Norte: $7.5 \pm 1.6$ kbar (Equation 14A) and $12.3 \pm 3.2$ kbar (Equation 14B). Temperature calculations give an average of $1060 \pm 42$ °C for cpx-liquid thermometry (Equation 16A), $1061 \pm 45$ °C for liquid-only thermometry (Equation 16B), and $1151 \pm 87$° for cpx-only calculations (Equation 15D).

All of these equations have been solved iteratively, with P, T, and compositional dependecies inherent in each result. Thermobarometry equations for pyroxene crystals from Cerro Overo, La Albóndiga, and Puntas Negras-El Laco could not be solved iteratively due to extremely low sodic pyroxene values driving natural log (ln(x)) factors to infinity. If we assume a near-surface pressure (i.e. 0 kbar), we can still calculate temperatures from the thermometers for cpx-only (Equation 15D) calculations. Puntas Negras-El Laco phenocrysts, which are marginally in equilibrium with the whole-rock, give a calculated average T of $1115 \pm 45$° C. This value agrees quite well with the average T of $1124 \pm 22$ °C calculated from Al partitioning between olivine and Cr-spinel (see below). As the decidedly not-in-equilibrium groundmass crystals yielded a similar result of $1108 \pm 87$° C, I have decided to also cautiously report thermometry results for Cerro Overo and La Albóndiga. Microphenocrysts from Cerro Overo
maar yielded a temperature of 1137 °C and those from La Albóndiga yielded 1130°C, both ± 87°C (Equation 15D). Perhaps surprisingly, these values also correlate quite well with the average values (1134 and 1122 °C, respectively) determined from Olivine-Spinel thermometry (see below). Regardless, considerations for the P and T history of these lavas should be deferred to thermometers and barometers which rely on phases which meet the base equilibrium requirements.

**Plagioclase-Liquid Thermobarometers and Hygrometers**

Thermobarometers based on component exchange between liquid and plagioclase feldspar can prove particularly useful for estimating multiple magmatic parameters as they are commonly dependent on pressure, temperature, and H2O content. If one or more of these factors can be determined independently, then the other two variables can be computed iteratively (Putirka, 2008). In addition, plagioclase is a common mineral phase in mafic-intermediate volcanic rocks, commonly occurring in the groundmass as microphenocrysts or microlites if not as a major phenocryst phase. All the rocks considered in this study contain some amount of plagioclase, making plagioclase-liquid thermometers a valuable tool for comparing all the monogenetic lavas. In addition, the temperature of plagioclase saturation and the resultant anorthite content of the crystals can be predicted for feldspar crystals from liquid composition alone (Equation 13B) as a check against other thermometry calculations. Plagioclase-liquid temperature and pressure estimates were modeled using plagioclase feldspar composition data, obtained by EPMA, and whole-rock (liquid) compositions obtained by ICP-MS along with the spreadsheets designed by Keith Putirka (accessed 2015) to accompany his updated plagioclase-liquid thermobarometer calibrations (2008). Results are summarized in Table 17, and basic statistics for plagioclase thermometry only is presented in Table 19.
Table 19 - Calculated plagioclase equilibrium temperatures (°C) average, standard deviation, and range for n analyses using the plagioclase-liquid thermometer (Equation 13A), ± 36 °C, developed and updated by Putirka (2005; 2008). The "$T_{ plag}$ Predicted" column lists the temperatures calculated via Equation 13B, which predict ± 37 °C when plagioclase should crystallize from input liquid composition at a given P (Putirka, 2008).

<table>
<thead>
<tr>
<th>Location</th>
<th>Avg T (°C)</th>
<th>StdDev (± σ)</th>
<th>Min (T° C)</th>
<th>Max (T° C)</th>
<th>n</th>
<th>$T_{ plag}$ Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo</td>
<td>1096</td>
<td>3.6</td>
<td>1088</td>
<td>1114</td>
<td>42</td>
<td>1092</td>
</tr>
<tr>
<td>La Albóndiga</td>
<td>1091</td>
<td>1.6</td>
<td>1088</td>
<td>1094</td>
<td>34</td>
<td>1088</td>
</tr>
<tr>
<td>Puntas Negras</td>
<td>1173</td>
<td>5.6</td>
<td>1154</td>
<td>1184</td>
<td>41</td>
<td>1171</td>
</tr>
<tr>
<td>El País</td>
<td>1078</td>
<td>5.5</td>
<td>1073</td>
<td>1096</td>
<td>15</td>
<td>1084</td>
</tr>
<tr>
<td>Cerro Tujle</td>
<td>1040</td>
<td>3.5</td>
<td>1019</td>
<td>1045</td>
<td>15</td>
<td>1042</td>
</tr>
<tr>
<td>Tilocálar Norte</td>
<td>1044</td>
<td>5.4</td>
<td>1023</td>
<td>1051</td>
<td>25</td>
<td>1048</td>
</tr>
<tr>
<td>Tilocálar Sur</td>
<td>1096</td>
<td>7.0</td>
<td>1079</td>
<td>1105</td>
<td>41</td>
<td>1102</td>
</tr>
</tbody>
</table>

Microphenocrystic plagioclase is found in the groundmass of all the targeted lavas of this work, and as macrophenocrysts in El País lava and the Puntas Negras-El Laco flows.

Anorthite-Albite exchange provides a test for equilibrium, a requisite state for accurate thermobarometry. The accepted equilibrium constant $K_D (\text{An} - \text{Ab}) = \frac{X_{Ab}^{pl}X_{Al2O3}^{liq}}{X_{An}^{pl}X_{NaO0.5}^{liq}X_{SiO2}^{liq}} = 0.27 ± 0.05$ for plagioclase and liquid in equilibrium for $T > 1050°C$ and $0.10 ± 0.11$ for $T < 1050°C$ (Putirka, 2008; Hamada & Fuji, 2007). All groundmass plagioclase crystals investigated passed this test, along with the large plagioclase from Puntas Negras-El Laco, but phenocrystic plagioclase from El País lava is significantly out of equilibrium with the whole-rock ($K_D (\text{An} - \text{Ab}) = 0.15$) and so the thermobarometry results for these crystal are not reported, although the results varied from groundmass plagioclase calculations by only 10 – 20°C.

Equilibrium pressures and H2O content required an iterative approach with initial guesses informing subsequent calculations whose results were then fed back into the initial input. The calculations I used for iteration included not only plagioclase-based approaches, but also H2O-dependent silica-activity barometry (see above) as these results ultimately concern the state of the whole-rock. This algorithmic approach continued until input/output values “stabilized” for barometry and hygrometry. As a check, I compared pressure and temperature-dependent Anorthite-Albite content predictions (Equation 11) with Anorthite-Albite content calculated from measured plagioclase composition cation fractions (An = CaO/(CaO + NaO0.5 + KO0.5) and Ab = NaO0.5/(CaO+NaO0.5+KO0.5)). As another check on thermometry results, Equation 13B (Putirka, 2005; 2008) calculates the temperature at which plagioclase should crystallize for a given liquid composition and pressure. Predicted and calculated plagioclase
temperatures (Table 19) agree exceptionally well for all samples investigated, indicating the estimated P and H$_2$O content inputs were appropriate. Iteratively calculated H$_2$O$^{liq}$ content is included in temperature calculations, passing on the ± 1.1 wt % error inherent in the hygrometer model (Equation 12). Including this uncertainty as changes in input H$_2$O$^{liq}$ content shifts thermometer results by an average of ± 50 °C, which is not a significant departure from the error for temperature recovery of ± 48°C (Equation 11A) and ± 36°C (Equation 13A), calibrated by Putirka (2008) to experimental data sets. Temperature estimates from Equation 13A, considered by Putirka (2008) as the most reliable plagioclase-liquid thermometer, compare reasonably with other thermometry results (Table 17).

Plagioclase-based barometers function well for some subsets of calibrated data, but are not broadly applicable as the Ca-Na exchange basis is nearly constant for many compositions over a wide P-T range (Putirka, 2008). That said, calculated values for plagioclase equilibration pressure (Equation 11B) generally conform to petrographic observations. The pressures calculated for Cerro Overo maar (0.6 kbar) and La Albóndiga dome (-0.5 kbar) are within error (± 1.8 kbar) of zero, indicating equilibration at or very near the surface. Cerro Overo and La Albóndiga calculations give plagioclase equilibrium temperatures some 40-90 °C lower than those determined from olivine-glass and olivine-spinel thermometry. These results align well with the observed petrography, which shows high-forsterite olivine cores which have experienced lower Fo content (i.e. lower T) growth near eruption. Plagioclase in these lavas is only present as microcrystalline lathes within the groundmass glass which show flow orientation and are absent from chilled rims (when present) around felsic xenoliths, evidence that plagioclase growth only occurred near eruption. The temperatures calculated from plagioclase – liquid exchange for these two lavas (~ 1090°C) is the lowest result for all thermometers and correlates with a post-eruptive cooling temperature of basaltic andesite.

Barometry results for the Puntas Negras mafic lava based on plagioclase phenocrysts yielded an average of 6.9 kbar (~ 25.5 km depth) and an average crystallization temperature of ~1170°C. These results indicate plagioclase equilibration near the base of the brittle upper crust at temperatures lower than olivine crystallization and within error of both clinopyroxene growth and the whole-rock (liquid) thermometer calculations (Table 17). The magmatic history outlined here suggests either accumulation of plagioclase crystals from a pre-existing magma differentiation zone near ~ 20 km or storage of the magma at this depth. Many of the larger
plagioclase phenocrysts display sieved cores with more coherent outer layers, suggesting that plagioclase may have been accumulated and subsequently re-equilibrated, with additional crystallization on the outermost portions of the crystals. This was likely achieved by a period of (relatively brief) magma stalling at ~20 km depth with temperatures of around 1150 - 1180°C, at which time the magma re-equilibrated with its acquired plagioclase cargo. Such a history would also explain why the earlier erupted (stratigraphically lower) lavas show ubiquitous larger (> 0.4 mm) plagioclase crystals with sieved cores while the later (Upper) flows only display microphenocrysts (< 0.25, > 0.1 mm) and groundmass plagioclase lathes, particularly if magma stalling was also accompanied by gravitational differentiation of mineral phases, concentrating olivine near the bottom of the magma column and, thus, in the Upper flows. Hygrometry estimates for Puntas Negras lava based on plagioclase composition are significantly lower (~ 0.7 wt % H2O) than the estimates for Cerro Overo (~ 2.5 wt % H2O) or the Tilocálar Group lavas (~ 2.9 wt % H2O). The lower estimated water content correlates well with the more tholeiitic (i.e. reducing) nature (Figure 12) of the Puntas Negras and a partially intraplate melt origin with a lower degree of slab fluid involvement as the arc and before-arc rocks (e.g. Ochs & Lange, 1999; Hoke & Lamb, 2007).

El País microphenocryst plagioclase-liquid calculations, in contrast, yielded equilibrium pressure of 3.0 kbar (~11.1 km depth) and temperatures averaging 1084°C; much less than the whole-rock (liquid) estimate of 1127°C and the clinopyroxene-liquid estimate of 1102°C and 8.7 kbar (~ 32.2 km depth) (Table 17). Two-pyroxene thermometry for El País lava, however, yielded 1034 ± 56°C, and two-pyroxene barometry yielded a pressure of 4.3 ± 2.8 kbar (~15.9 km depth), both within range of the plagioclase calculations. Macrophenocrysts from El País lava are not in equilibrium with the whole-rock, suggesting they are acquired cargo, and yield slightly higher temperatures and pressure than the microphenocrysts, but these values cannot be considered valid. The sum of results for the El País lava suggests storage of the basaltic andesitic magma in the upper (< 20 km) crust at around 1050°C, at which time the ortho- and clinopyroxene re-established equilibrium and plagioclase growth initiated in the groundmass. As the larger feldspar crystals are out of equilibrium, they were likely acquired by the magma after this storage period, perhaps as the magma mobilized.

Tilocálar Group plagioclase-liquid thermometry results are similar to whole-rock and clinopyroxene-liquid thermometry for all three centers. All three estimates are proposed to
estimate lava temperature immediately preceding and during eruption, at which time microcrysts were forming in the groundmass glass. All thermometry results for Cerro Tujle maar span 1040 - 1090°C, for Tilocálar Norte they range 1040 - 1060°C, and for Tilocálar Sur the calculated temperatures range 1090 - 1100°C and barometry calculations yield upper crustal results (< 20 km) (Table 17). In total, these estimates support a model of a relatively crystal-free, high-temperature but intermediate composition lava being quickly delivered (i.e. with no stalling or storage) to the surface.

\[
\frac{10^7}{T(K)} = 6.12 + 0.257\ln\left(\frac{\text{An}^{\text{pl}}}{\text{Ca}^{\text{liq}} \left(\text{Al}^{\text{liq}}\right)^2 \left(\text{Si}^{\text{liq}}\right)^2}\right) - 3.166[\text{Ca}^{\text{liq}}] + 0.2166[\text{H}_2\text{O}^{\text{liq}}] \\
- 3.137\left(\frac{\text{Al}^{\text{liq}}}{\text{Al}^{\text{liq}} + \text{Si}^{\text{liq}}}\right) + 1.216[\text{Ab}^{\text{pl}}]^2 - 2.475 \times 10^{-2}[P(\text{kbar})]
\]

\[
P(\text{kbar}) = -42.2 + 4.94 \times 10^{-2}[T(K)] + 1.16 \times 10^{-2}T(K)\ln\left(\frac{[\text{Ab}^{\text{pl}} \text{Al}^{\text{liq}} \text{Ca}^{\text{liq}}]}{[\text{An}^{\text{pl}} \text{Na}^{\text{liq}} \text{Si}^{\text{liq}}]}\right) \\
- 382.3[\text{Si}^{\text{liq}}]^2 + 514.2[\text{Si}^{\text{liq}}]^3 - 19.6\ln[\text{Ab}^{\text{pl}}] - 139.8[\text{Ca}^{\text{liq}}] \\
+ 287.2[\text{Na}^{\text{liq}}] + 163.9[\text{K}^{\text{liq}}]
\]

Equation 11 – Plagioclase-liquid models for thermometry (A) and barometry (B) from the calibrations of Putirka (2005) used to iteratively solve the pressure input for feldspar thermometry by comparing measured anorthite content with that predicted by these equations. These models recovered temperatures ± 48°C from experimental data sets used in calibration (Putirka, 2008).

\[
\text{H}_2\text{O(\%wt)} = 25.95 - 0.0032T(°C) \ln\left(\frac{X^{\text{pl}}_{\text{An}}}{X^{\text{liq}}_{\text{CaO}} \left(X^{\text{liq}}_{\text{AlO}_3}\right)^2 \left(X^{\text{liq}}_{\text{SiO}_2}\right)^2}\right) \\
- 18.9\left(X^{\text{liq}}_{\text{K}_2\text{O}}\right) + 14.5\left(X^{\text{liq}}_{\text{MgO}}\right) - 40.3\left(X^{\text{liq}}_{\text{CaO}}\right) + 5.7\left(X^{\text{pl}}_{\text{An}}\right)^2 + 0.108P(\text{kbar})
\]

Equation 12 - Globally-calibrated model for predicting melt water content from plagioclase and liquid compositions, pressure, and temperature. This model recovered H\textsubscript{2}O content ± 1.1 wt % for experimental hydrous data (Putirka, 2008).
Equation 13 - Plagioclase-liquid thermometers with the updated calibrations from Putirka (2008). Equation (A) calculates a temperature of crystallization for given plagioclase/liquid compositions, including input P and H2O content. Equation (B) calculates the temperature at which plagioclase should crystallize from the input liquid composition at a given pressure. These models recovered temperatures ± 36°C and ± 37 °C, respectively from experimental data sets used in calibration (Putirka, 2008).

\[
\frac{10^4}{T(K)} = 6.4706 + 0.3128\ln\left(\frac{X_{An}^{pl}}{X_{CaO}^{liq} \left(X_{AlO_1.5}^{liq}\right)^2 \left(X_{SiO_2}^{liq}\right)^2}\right) - 8.103\left(X_{SiO_2}^{liq}\right) \\
+ 4.872\left(X_{Ko_{0.5}}^{liq}\right) + 1.5346\left(X_{Ab}^{pl}\right)^2 + 8.661\left(X_{SiO_2}^{liq}\right)^2 \\
- 3.341\times10^{-2}\left(P(\text{kbar})\right) + 0.18047\left(H_2O^{liq}\right)
\]

(A)

\[
\frac{10^4}{T(K)} = 10.86 - 9.7654\left(X_{SiO_2}^{liq}\right) + 4.241\left(X_{CaO}^{liq}\right) - 55.56\left(X_{CaO}^{liq}X_{AlO_1.5}^{liq}\right) \\
+ 37.50\left(X_{Ko_{0.5}}^{liq} X_{AlO_1.5}^{liq}\right) + 11.206\left(X_{SiO_2}^{liq}\right)^3 \\
- 3.151\times10^{-2}\left(P(\text{kbar})\right) + 0.1709\left(H_2O^{liq}\right)
\]

(B)

Equation 14 - Clinopyroxene-Liquid thermometers as calibrated by Putirka (2008). Input variables are presented as cation fractions X\text{\textsubscript{A}}\text{\textsubscript{B}} where A = the component (i.e. phase) and B = the atomic or molecular concentration targeted. Equation (A) recovers P to ± 1.6 kbar and Equation (B) recovers P to ± 3.2 for experimental data (Putirka, 2008).

\[
P(\text{kbar}) = -48.7 + 271\frac{T(K)}{10^4} + 32\frac{T(K)}{10^4} \ln\left[\frac{X_{NaAlSiO_6}^{cpx}}{X_{NaO_{0.5}}^{liq} X_{AlO_1.5}^{liq} \left(X_{SiO_2}^{liq}\right)^2}\right] \\
- 8.21\ln(X_{FeO}^{liq}) + 4.61\ln(X_{MgO}^{liq}) - 0.96\ln(X_{Ko_{0.5}}^{liq}) - 2.21\ln\left(X_{DiHd}^{cpx}\right) \\
- 3\ln(Mg \#^{liq}) + 56(X_{NaO_{0.5}}^{liq} + X_{Ko_{0.5}}^{liq}) + 0.76\left(H_2O^{liq}\right)
\]

(A)

\[
P(\text{kbar}) = -40.73 + 358\frac{T(K)}{10^4} + 21.69\frac{T(K)}{10^4} \ln\left[\frac{X_{NaAlSiO_6}^{cpx}}{X_{NaO_{0.5}}^{liq} X_{AlO_1.5}^{liq} \left(X_{SiO_2}^{liq}\right)^2}\right] \\
- 105.7\left(X_{CaO}^{liq}\right) - 165.5\left(X_{NaO_{0.5}}^{liq} + X_{Ko_{0.5}}^{liq}\right)^2 - 50.15\left(X_{SiO_2}^{liq}\right)\left(X_{FeO}^{liq} + X_{MgO}^{liq}\right) \\
- 3.178\ln\left(X_{DiHd}^{cpx}\right) - 2.205\ln(X_{EnF_{0.5}}^{cpx}) + 0.864\ln(X_{Al}^{cpx}) + 0.3962\left(H_2O^{liq}\right)
\]

(B)

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Equation 15 - Three barometers and a thermometer based on clinopyroxene composition only, from the calibrations of Putirka (2008). Equation (A) recovers P to ± 1.7 kbar, Equation (B) recovers P to ± 2.0 kbar, Equation (C) recovers P to ± 1.5 kbar, and Equation (D) recovers T to ± 87°C for experimental data (Putirka, 2008).

\[ P(\text{kbar}) = 3205 + 0.3847T(\text{K}) - 518\ln T(\text{K}) - 5.62\left(\frac{X_{\text{Mg}}^{\text{Clpx}}}{X_{\text{Na}}^{\text{Clpx}}}\right) + 83.2\left(\frac{X_{\text{Na}}^{\text{DiHd}}}{X_{\text{Mg}}^{\text{DiHd}}}\right)^2 + 68.2\left(\frac{X_{\text{Al}^{\text{Clpx}}}{X_{\text{Al}^{\text{Clpx}}}^{\text{AlVd}}}\right) + 2.52\ln\left(\frac{X_{\text{Clpx}}^{\text{K}}}{X_{\text{K}}^{\text{Clpx}}}\right) - 51.1\left(\frac{X_{\text{DiHd}}^{\text{EnF}}}{X_{\text{DiHd}}^{\text{EnF}}}\right)^2 + 34.8\left(\frac{X_{\text{EnF}}^{\text{Clpx}}}{X_{\text{EnF}}^{\text{Clpx}}}\right)^2 \]

\( P(\text{kbar}) = 1458 + 0.197T(\text{K}) - 241\ln T(\text{K}) + 0.453\left(H_2O^{\text{liq}}\right) + 55.5\left(X_{\text{AlVd}}^{\text{Clpx}}\right) + 8.05\left(X_{\text{Clpx}}^{\text{EnF}}\right) - 277\left(X_{\text{K}}^{\text{K}}\right) + 18\left(X_{\text{Jd}}^{\text{Jd}}\right) + 44.1\left(X_{\text{DiHd}}^{\text{DiHd}}\right) + 2.2\ln\left(X_{\text{Clpx}}^{\text{Jd}}\right) - 17.7\left(X_{\text{Al}}^{\text{Al}}\right)^2 + 97.3\left(X_{\text{Fe(Mg)}^{\text{Fe(Mg)}}}\right)^2 + 30.7\left(X_{\text{Mg(Mg)}}^{\text{Mg(Mg)}}\right)^2 - 27.6\left(X_{\text{DiHd}}^{\text{DiHd}}\right)^2 \)

\[ P(\text{kbar}) = -57.9 + 0.0475T(\text{K}) - 40.6\left(X_{\text{Fos}}^{\text{liq}}\right) - 47.7\left(X_{\text{Cat1S}}^{\text{Clpx}}\right) + 0.676\left(H_2O^{\text{liq}}\right) - 153\left(X_{\text{CaO}_{0.5}}^{\text{SiO}_{2}}\right) + 6.89\frac{X_{\text{Al}}^{\text{Al}}}{X_{\text{Al}}^{\text{Al}}} \]

\[ T(\text{K}) = \frac{93100 + 544P(\text{kbar})}{61.1 + 36.6\left(X_{\text{TiO}}^{\text{Clpx}}\right) + 10.9\left(X_{\text{Clpx}}^{\text{Clpx}}\right) - 0.95\left(X_{\text{Al}}^{\text{Clpx}} + X_{\text{Clpx}}^{\text{Clpx}} - X_{\text{Na}}^{\text{Clpx}} - X_{\text{K}}^{\text{Clpx}}\right) + 0.395\left[\ln\left(X_{\text{EnF}}^{\text{EnF}}\right)\right]^2 \]

\[ \frac{10^4}{T(K)} = 7.53 - 0.14\ln\left(\frac{X_{\text{Clpx}}^{\text{Jd}} X_{\text{Clpx}}^{\text{EnF}} X_{\text{Clpx}}^{\text{EnF}}}{X_{\text{Clpx}}^{\text{DiHd}} X_{\text{Al}}^{\text{Al}} X_{\text{Al}}^{\text{Al}}}\right) + 0.07\left(H_2O^{\text{liq}}\right) - 14.9\left(X_{\text{Clpx}}^{\text{Clpx}} X_{\text{Clpx}}^{\text{Clpx}}\right) - 0.08\ln\left(X_{\text{TiO}_{2}}^{\text{TiO}_{2}}\right) - 3.62\left(X_{\text{NaO}_{0.5}}^{\text{Clpx}} + X_{\text{KO}_{0.5}}^{\text{Clpx}}\right) - 1.1\left(Mg\#^{\text{liq}}\right) - 0.18\ln\left(X_{\text{Clpx}}^{\text{EnF}}\right) - 0.027P(\text{kbar}) \]

\[ \frac{10^4}{T(K)} = 6.39 + 0.076\left(H_2O^{\text{liq}}\right) - 5.55\left(X_{\text{Clpx}}^{\text{Clpx}} X_{\text{SiO}_{2}}^{\text{SiO}_{2}}\right) - 0.386\ln\left(X_{\text{Clpx}}^{\text{Clpx}}\right) - 0.046P(\text{kbar}) + 2.2 \times 10^{-4}\left[\ln\left(P(\text{kbar})\right)\right]^2 \]

Equation 16 - Clinopyroxene-Liquid thermobarometers from the calibrations of Putirka (2008). Equation (A) recovers T to ± 42°C and Equation (B) is based on liquid composition only and recovers T to ± 45°C for experimental data (Putirka, 2008).
Olivine – Liquid Thermometry

For volcanic rocks with olivine crystals in equilibrium with a liquid component, a temperature of equilibrium can be calculated based on the exchange of components such as MgO, FeO, MnO, and/or NiO (Roeder & Emslie, 1970; Arndt, 1977; Sisson & Grove, 1992; Beattie, 1993; Putirka et al., 2007; Putirka, 2008). When in equilibrium, the coefficient for Fe and Mg exchange between olivine and its surroundings, \( K_{D(Fe-Mg)}^{ol-liq} = \frac{(X_{FeO}/X_{MgO})^{olv}}{(X_{FeO}/X_{MgO})^{liq}} \), will be 0.30, independent of pressure or temperature. Experimental data indicates a range of 0.30 ± 0.03 (Roeder & Emslie, 1970; Putirka, 2008). This can be portrayed graphically in a “Rhodes Diagram” (Rhodes et al., 1979), shown here for rims and cores of olivine phenocrysts from Cerro Overo maar and the Puntas Negras – El Laco mafic lava in Figure 78. In most cases, analytical measurements from the cores of olivine phenocrysts will be in equilibrium with whole-rock compositions from which they have crystallized, as bulk compositions include the chemistry of the crystals themselves as well as the melt. Olivine rims, on the other hand, will more likely be in equilibrium with compositional measurements of the glass immediately adjacent to the phenocryst, representing the melt composition from which the most recent olivine directly crystallized. Most models require an input of crystal and liquid composition, pressure, and H\(_2\)O content of the liquid. The model of Beattie (1993) does not include an H\(_2\)O content component and can thus be used as a check against the water input of the other models.

Two sets of temperature calculations were carried out for olivine phenocrysts from Cerro Overo maar, La Albóndiga dome, and the Puntas Negras mafic lava. Whole-rock and olivine phenocryst core compositions display Fe-Mg exchange equilibrium with no corrections for all three lavas. Olivine-liquid thermometry calculations yielded very similar results (Table 21) despite significant differences in both whole-rock and olivine compositions. This suggests similar magmatic histories and conditions between the centers, which is unsurprising considering both lavas appear to have been dominantly controlled by the same deep-cutting transverse lineament crossing the Andean arc at around 23° S. Similar olivine phenocryst morphology despite differences in crystal chemistry in the different lavas is further support for similar thermal histories, particularly as olivine morphology is dominantly a function of temperature of crystallization and cooling rate (Donaldson, 1976; Milman-Barris et al., 2008). Modeled temperatures cover a range of ~ 100° C, which is broader than the precision of the modeling itself (± 27° C) (Putirka, 2008), almost entirely dependent on the composition of the
olivine and not the whole-rock component. These results suggest a range of crystallization temperatures have been recorded by the phenocryst cores, as would be expected of a magma crystallizing as it cools. Diffusion of Fe and Mg through the lattice will have led to a certain degree of olivine composition homogenization, and thus the modelled temperatures can be interpreted to represent a minimum range of crystallization temperature.

Liquid compositions in equilibrium with olivine rims were calculated by subtracting olivine composition from whole rock values until the $K_{D}(\text{Fe-Mg})_{\text{ol-liq}}$ showed equilibrium Fe-Mg exchange, and then re-normalizing to 100 wt %. The whole rock composition of Cerro Overo required the removal of 14.6 % olivine to reach equilibrium with the crystal rims and Puntas Negras required 13.8 % olivine removal. Direct measurements of groundmass glass compositions showed highly localized variability ranging from basaltic to dacitic and were thus not used for calculations (Figure 137). Re-calculated liquid compositions and the resultant Olivine-liquid temperature estimates are shown in Table 20. The olivine rim crystallization temperatures for both lavas ranged from 970 – 1040° C, which encompasses a range of temperatures just below those calculated for groundmass plagioclase (Table 17). Compared with olivine core crystallization temperatures of 1150 - 1255° C calculated using whole-rock compositions as the liquid, these rim temperatures support a sequential high temperature core growth and a low temperature crystal rim growth. This interpretation is also backed by the petrographic observation that phenocrysts tend to show a euhedral olivine core with skeletal or hopper overgrowth. Compositional mapping of phenocrysts also shows that olivine crystals from both Cerro Overo and Puntas Negras display a high Ni, low Mn core and a low Ni, high Mn rim with less-diffuse boundaries than Fe-Mg zoning (Figure 139 - Figure 155). Greater Ni content (and lower Mn) in olivine represents crystal growth at higher temperatures (Arndt, 1977), and these two elements do not re-equilibrate by diffusion as easily as Fe and Mg (Milman-Barris et al., 2008). Ni and Mn content do, however, display a region of compositional gradient around the core before rapidly increasing or decreasing, respectively, immediately adjacent to the phenocryt rims. This pattern suggests a crystallization history of high temperature core growth, a period of intermediate-high temperature growth of a mantle around the core as the magma cooled, and a period of sudden, low temperature olivine growth at the rim, representing approximately syn-eruptive and post-eruptive crystallization.
Olivine-liquid thermometry could also be applied to the compositions of melt inclusions and their olivine hosts. The meaning of the modeled temperatures is not as clear in this case, as the trapped melt may represent a composition other than that from which the olivine was crystallizing (e.g. Kent et al., 2008). Additionally, Fe-Mg diffusion through the olivine lattice will have shifted the crystal composition toward lower forsterite content as the host magma differentiated, and thus melt inclusion thermometry calculations employing the olivine host composition must be considered minimum estimates of entrapment temperature. The results of thermometry calculations for eight melt inclusions (Table 21) gave an average value of 1269°C with a relatively small spread in values, suggesting trapping of melt at higher temperatures than the majority of olivine crystallization. As most large, glassy, and isolated melt inclusions (i.e. those which make suitable analytical targets) are located at or near the centers of their olivine hosts, this result is unsurprising. However, calculated temperatures using liquid-only thermometry with the compositions of the included melt resulted in temperatures averaging 1205°C, similar to phenocryst core – whole rock calculations. These results are technically within error of each-other and may simply indicate liquid-only thermometers provide low estimates of temperature while olivine-liquid calculations provide upper estimates for temperature. Another interpretation is that diffusion has reduced the forsterite content of the olivine host, which drives temperature estimates higher for constant liquid calculations, resulting in an over-estimate. A third interpretation is that trapping by crystallization occurred over a temperature range, from which the olivine-liquid thermometer captures a high temperature start to crystallization and the liquid-only calculation represents the last temperature of the melt while it was still in contact (i.e. able to exchange chemical constituents) with the bulk magma. Ultimately, geothermometry results are best compared with calculations from the same model, calibrated to the same data to avoid any systematic errors inherent to either the theory, calibration, or application of each specific thermometer.
Table 20 – Average liquid compositions in equilibrium ($K_{D(Mg-Fe)} = 0.30 \pm 0.03$) with the crystal rims and cores of olivine phenocrysts from Cerro Overo maar (C. Overo) and the Puntas Negras – El Laco mafic lava (P. Negras). For both lavas, the compositions in equilibrium with olivine cores was measured analytically (whole rock) and the compositions in equilibrium with olivine rims was calculated by removing olivine from the starting composition and then re-normalizing. To achieve equilibrium, 14.6 % and 13.8 % olivine was removed from Cerro Overo and Puntas Negras, respectively.

<table>
<thead>
<tr>
<th>Composition (wt %):</th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>FeO*</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>$T_{olv-liq}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. Overo Cores (Fo87)</td>
<td>53.4</td>
<td>7.35</td>
<td>7.07</td>
<td>0.90</td>
<td>15.9</td>
<td>8.06</td>
<td>3.26</td>
<td>1.28</td>
<td>1207</td>
</tr>
<tr>
<td>C. Overo Rims (Fo75)</td>
<td>57.6</td>
<td>2.24</td>
<td>4.51</td>
<td>1.08</td>
<td>19.2</td>
<td>9.68</td>
<td>3.93</td>
<td>1.54</td>
<td>1022</td>
</tr>
<tr>
<td>P. Negras Cores (Fo84)</td>
<td>53.6</td>
<td>6.98</td>
<td>8.29</td>
<td>1.28</td>
<td>15.9</td>
<td>8.32</td>
<td>3.12</td>
<td>1.40</td>
<td>1193</td>
</tr>
<tr>
<td>P. Negras Rims (Fo67)</td>
<td>56.5</td>
<td>2.09</td>
<td>6.01</td>
<td>1.50</td>
<td>18.5</td>
<td>9.68</td>
<td>3.64</td>
<td>1.63</td>
<td>1015</td>
</tr>
</tbody>
</table>

Table 21 – Basic statistics for olivine crystallization temperature modeled from elemental partitioning between phenocryst cores and whole-rock compositions from Cerro Overo (n=14), Olivine-hosted melt inclusions from Cerro Overo maar (n=8), La Albóndiga Grande (n=3), and Puntas Negras – El Laco (n=11) basaltic andesites. This summary includes the results for four different olivine-liquid thermometers (Sisson & Grove, 1992; Beattie, 1993; Putirka et al., 2007; Putirka, 2008) with the updated calibrations of Putirka (2008). The precision for the updated thermometers is ± 27°C, or less. The results for all three centers suggest the majority of olivine was crystallized over a 100°C range.

<table>
<thead>
<tr>
<th>$T_{olv-liq}$</th>
<th>Cerro Overo (°C)</th>
<th>CO Melt Inclusions</th>
<th>La Albóndiga (°C)</th>
<th>Puntas Negras (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average $T_{olv-liq}$</td>
<td>1207</td>
<td>1269</td>
<td>1199</td>
<td>1208</td>
</tr>
<tr>
<td>Std Deviation</td>
<td>36.9</td>
<td>17.1</td>
<td>34.6</td>
<td>20.7</td>
</tr>
<tr>
<td>Minimum $T_{olv-liq}$</td>
<td>1150</td>
<td>1229</td>
<td>1159</td>
<td>1165</td>
</tr>
<tr>
<td>Maximum $T_{olv-liq}$</td>
<td>1256</td>
<td>1293</td>
<td>1240</td>
<td>1244</td>
</tr>
</tbody>
</table>

Mantle Potential Temperature Estimates

The mantle potential temperature ($T_p$) is an approximation of the temperature the (solid) mantle would be if it were adiabatically brought to the surface. An estimate for $T_p$ derived from a magma composition essentially represents a broad estimate of the temperature of the mantle with which the parental magma(s) last reached equilibrium. Input is a mantle mineral-liquid equilibrium temperature (olivine-liquid equilibration temperature) and pressure at which this temperature of equilibration occurred (Putirka, 2008). Using the Olivine-liquid thermometer results as T-input and the pressure calculated by the silica activity barometer for
Olivine-spinel thermometry

Wan et al. (2008) developed an igneous geothermometer based on the Cr# ($Y_{Cr}$) of spinel inclusions in olivine and the partitioning coefficient ($K_D$) of $Al_2O_3$ between co-crystallized forsteritic olivine and Cr-spinel (Equation 17). An updated calibration encompassing a wider range of conditions and comparisons with results from natural samples was put forth by Coogan et al. in 2014. This olivine-spinel thermometer is based on the temperature-dependent $Al$ partitioning of co-crystallizing forsteritic olivine and Cr-spinel, recording conditions of crystallization for mineral phases which develop in primitive magma. The calculated temperature represents the last temperature at which olivine-spinel pairs achieved equilibrium $Al$ exchange. Given that $Al^{3+}$ does not readily diffuse through the olivine lattice (Milman-Barris et al., 2008), temperatures estimated from the $Al$-in-olivine-spinel could represent minimum estimates for the earliest onset of olivine crystallization, shortly following melt extraction from the mantle (Coogan et al., 2014). Additionally, unlike other olivine thermometers, temperature estimates are not significantly influenced by $fO_2$, $H_2O$ content, or pressure variations (Wan et al., 2008; Coogan et al., 2014), reducing potential error from base assumptions and providing an independent check on the input values for these parameters for other geothermometers. The $Al$-in-olivine-spinel thermometer has been precisely calibrated to ± 22°C for experimental data sets, making it one of the most precise thermometers for igneous systems (Wan et al., 2008). However, only one publication addressing the application of spinel-olivine thermometry to natural sample has been published (Coogan et al., 2014), so the dependability of this model is not fully verified.
The olivine-spinel aluminum partitioning thermometer was originally calibrated for spinel with low Fe\textsuperscript{3+} and Ti\textsuperscript{4+} in equilibrium with Fo\textsubscript{90±3} olivine at 100 kPa (~ 1 atm) in reducing conditions over a temperature range of 1250 – 1450 °C (Wan et al., 2008). The choice of calibration under reducing conditions by Wan et al. (2008) was to eliminate the possibility of a coupled substitution involving Fe\textsuperscript{3+} along with Al\textsuperscript{3+} at the olivine tetrahedral site [\textsuperscript{VI}Al\textsuperscript{VI}Fe\textsuperscript{3+} ↔ (MgFe)Si] instead of solely aluminum [\textsuperscript{VI}Al\textsuperscript{VI}Al ↔ (MgFe)Si], skewing results toward lower temperature estimates. The updated calibration of Coogan et al. (2014) considers a wider range of temperatures (1100 – 1500 °C) and spinel and olivine compositions with overall relatively minor adjustments to the thermometry model (Equation 17). The updated calibration also included experimental variation in oxidation state and silica activity (\(a_{SiO_2}\)), both of which produced variations in calculated temperature that were less than the thermometer uncertainty of ± 22° C (Coogan et al., 2014). Experiments in more oxidizing environments produced spinel with a high Fe\textsuperscript{3+} content, avoided in the original calibration for fear that Fe\textsuperscript{3+} substitutions would interfere with Al\textsuperscript{3+} inclusion, found that even for experimental spinel with Fe\textsuperscript{3+} consisting of up to 35% of the total Fe content, temperature estimates only increased by ≤ 11 °C (Wan et al., 20080; Coogan et al., 2014). The updated calibration of this thermometer extend its usefulness (or, at least, calibration) to the conditions experienced in the oxidizing, calc-alkaline environment of the central Andean subduction zone. High forsterite olivine phenocrysts from Cerro Overo maar and La Albóndiga dome (average of Fo\textsubscript{86}) and the Puntas Negras-El Laco flow (average Fo\textsubscript{83}) contain abundant Cr-spinel inclusions and are thus ideal subjects for applying the Al-exchange thermometer.

Table 22 - Calculated olivine equilibrium temperatures (° C) average, standard deviation, and range for \(n\) analyses using the spinel-olivine Al-partitioning thermometer of Wan et al. (2008) updated with the calibrations of Coogan et al. (2014). These results are calculated using the average aluminum content of each olivine phenocryst, compiled from multiple EPMA spot analyses.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sample</th>
<th>Average T (°C)</th>
<th>StdDev (±σ)</th>
<th>Min T (°C)</th>
<th>Max T (°C)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo</td>
<td>CO-43</td>
<td>1135</td>
<td>48.7</td>
<td>1048</td>
<td>1269</td>
<td>38</td>
</tr>
<tr>
<td>Cerro Overo</td>
<td>CO-42</td>
<td>1163</td>
<td>53.2</td>
<td>1098</td>
<td>1324</td>
<td>71</td>
</tr>
<tr>
<td>La Albóndiga</td>
<td>CO-56</td>
<td>1206</td>
<td>55.8</td>
<td>1080</td>
<td>1262</td>
<td>9</td>
</tr>
<tr>
<td>Puntas Negras</td>
<td>PN-12</td>
<td>1129</td>
<td>26.3</td>
<td>1091</td>
<td>1224</td>
<td>36</td>
</tr>
</tbody>
</table>
Targeting aluminum partitioning between olivine and Cr-spinel inclusions presents several analytical difficulties. Foremost, the Al content of olivine crystals is extremely low, in the 10s to 100s ppm range, as it is not readily incorporated into the olivine lattice (Milman-Barris et al., 2008). Electron microprobe measurements of Al$_2$O$_3$ content in olivine ranged 0.012 – 0.044 wt % Al$_2$O$_3$ (60 – 220 ppm Al) for samples of this study, requiring well-calibrated electron beam analyses with long dwell times (120 seconds on-peak and half as long background measurements). Fine-tuned calibration with natural and synthetic standards ultimately yielded a 2σ precision of ± 0.004 wt % (± 20 ppm Al). Higher measured Al content in the host olivine ultimately leads to a higher calculated T (Equation 17). An increase in Al$_2$O$_3$ as small as 0.003 wt % can increase calculated T by around 23 °C for the T range of the mafic rocks being considered, essentially equivalent to the uncertainty in the thermometer calibration itself. As an example of the general reproducibility, five analyses of the same point in a Puntas Negras-El Laco olivine crystal produced values of 0.0170 ± 0.0018 wt % Al$_2$O$_3$ (1σ). Another testament to analytical reproducibility are the similarities in measured compositions, and thus the calculated temperature values for similar Cerro Overo basaltic andesite samples CO-43 and CO-42, which were acquired during separate microprobe sessions almost one month apart (Table 22).

Wan et al. (2008):

\[ T(°C) = \frac{10,000}{0.512 + 0.873Y_{Cr} - 0.91 \ln(K_D)} - 273 \]

Coogan et al. (2014):

\[ T(°C) = \frac{10,000}{0.575 + 0.884Y_{Cr} - 0.897 \ln(K_D)} - 273 \]

*Equation 17 – Top:* The geothermometer of Wan et al. (2008) based on aluminum partitioning between olivine and spinel where \( Y_{Cr} = \text{Cr/(Cr+Al)} \) in atomic proportions and \( K_D = \text{Al}_2\text{O}_3^{sp}/\text{Al}_2\text{O}_3^{ol} \) in wt %. *Bottom:* the updated model calibration of Coogan et al. (2014) which covers a broader range of magmatic conditions and has been checked against natural samples.
One way to reduce temperature estimate variability due to analytical uncertainty is to use Al₂O₃ contents averaged from several analyses of the same phenocryst. In the recalibration of Coogan et al. (2014), the authors tested how much temperature estimates varied when strictly linking Cr-spinel inclusion locations with adjacent olivine composition versus using a spatially arbitrary analytical point within the olivine for the thermometer. The authors found little to no difference in thermometry results, even when comparing Al exchange between Cr-spinel grown at olivine rims and olivine measurements from the crystal cores or vice versa (Coogan et al., 2014). These results are unsurprising as Al is generally evenly-distributed in olivine crystals, negligibly affected by diffusion, and any growth-related zoning is nearly indistinguishable from the background concentration (e.g. Milman-Barris et al., 2008). Using averaged Al₂O₃ content for each olivine phenocryst in thermometry calculations not only resulted in less spread in temperature estimates, but also largely eliminated outlier results which were likely related to analyses of olivine which included, in-part, unnoticed micro-inclusions or other such aberrations. Boundary layers form around growing crystals, enriched in elements not included in the lattice, eventually forming sub-micrometer compositional variations which can significantly alter the interpretations of magmatic history based on nano-beam analyses (Milman-Barris et al., 2008; Zellmer et al., 2016). Averaging multiple electron probe analyses for each phenocryst aids in eliminating such effects.

Measurements of Cr-spinel inclusions by EPMA are more straightforward as the elements of interest (Ca, Al) are major crystalline components. However, the inclusions in all samples were in the 10 -20 μm range, with outliers < 5 μm and up to ~ 35 μm. As a result, analyses must be considered average values for each spinel and cannot be spatially correlated with core/rim crystal domains, mainly due to limitations in electron beam targeting. Much care is also required in reviewing measured values, as the beam (spot size = 1 μm) interacts with a larger volume at the higher beam current used (200 nA, 20 keV) and the imprecision of the targeting software and human eye make accidental measurements of surrounding olivine possible. Also, since only two dimensions are visible in thin section, spinel caught near corners or edges may be thin enough the electron beam interaction volume could extend to the underlying olivine. Elevated measured MgO, relative to other spinel from the same crystal/sample, is the most obvious indicator of a “spill-over” analysis. Another issue is the difficulty in distinguishing Cr-spinel from other oxide phases, such as magnetite, both by petrographic scope (all opaque) and electron probe (all bright white) (Figure 157). However,
high TiO₂ and FeO accompanied by low Al₂O₃ and Cr₂O₃ values makes identification of accidentally targeted Fe-Ti oxides relatively simple.

No immediately obvious correlation exists between olivine-spinel temperature calculations and the structure of the host olivine (Figure 157 - Figure 161). A core-to-rim progression of decreasing temperatures may not be obviously recorded for olivine as recent studies have found olivine first rapidly crystallizes in a skeletal form before more gradual infilling of the structure gives the final form (e.g. Shea et al., 2015). Spinel inclusions are most commonly found between the rapid-growth regions defined by high P content, suggesting the spinel grows during the slower olivine growth periods or is, perhaps, trapped by the rapid bursts of skeletal crystal growth. In a review of P zoning in igneous, plutonic, and experimental olivine, Welsch et al. (2014) remarked on a similar pattern in which melt inclusions and crystal embayments were found almost exclusively in between the high phosphorous zones. The complete relationship between olivine structure and spinel inclusions cannot be ascertained in only two dimensions. Clustered temperature values, however (e.g. Figure 161) indicate the capturing or inclusion of spinel occurs at certain thermal moments in magmatic history, and not so much as a continual process. Maximum calculated T values correspond to what might be expected from the upper asthenosphere and may represent rare cases of preserved spinel from near the time of olivine’s initial inception. The lower temperatures correlate well with values calculated from plagioclase-liquid thermometry (Table 22) and represent the final bursts of olivine crystallization near eruption.
Discussion

Sources of Monogenetic Volcanism within the Central Andes

Instances of minor volcanism across the subduction arc of the Altiplano-Puna region of the central Andes are generated from at least three different partial melting mechanisms: melting of depleted meta-mafic rocks at depth (e.g. Defant & Drummond, 1990), fluid flux melting of the asthenosphere above the subducting slab, and decompression melting of upwelling hot asthenosphere following removal of the lithospheric root. Respectively, this manifests as adakite-signature, aphyric intermediate lava before (west of) the arc, mantle-derived calc-alkaline lavas mixed with variable degrees of crust within the arc, and intraplate-signature mantle-derived volcanism in the back-arc. Complicated lithospheric structure and geodynamic events have led to volcanism composed of variable mixtures of any of the above magmas, plus or minus contamination from crustal components (e.g. Matteini et al., 2002; Mamani et al., 2010).

Parental Melts of the Arc and Back-Arc

There is general agreement that primary magmas generated in subduction zones from melting of the peridotitic asthenospheric wedge are hydrous and oxidized high-Mg basalts (≥ 10 % MgO) or picrites (≥ 18 % MgO) (Richards & Kerrich, 2007, and references therein). Clearly, even the most primitive Neogene lavas within the arc of the Altiplano – Puna region, the 7.4 wt % MgO Cerro Overo maar and the 6.7 wt % MgO Puntas Negras - El Laco basaltic andesites have yet experienced significant magmatic differentiation. The most mafic rocks of the entire Central Andes, including the only recorded instance of an erupted picritic basalt (Davidson & De Silva, 1992), are pre-Miocene, high-K monogenetic tholeiitic (i.e. shoshonite basalt) eruptions in the back-arc, intraplate regime (De Silva & Francis, 1991; Davidson & De Silva, 1992; Kay et al., 1994; Davidson & De Silva, 1995; Matteini et al., 2002; Hoke & Lamb, 2007; Kay et al., 2012). At this time, monogenetic eruptions of arc-derived basaltic andesite along lithosphere-cutting lineaments are the best surficial evidence as to the nature of parental arc magma being delivered to the base of the lithosphere beneath the central Andean arc. Volcanic rocks derived from melting in the asthenosphere mitigated by slab-derived fluids are uniquely identifiable by
enrichment relative to the mantle in Large Ion Lithophile Elements (LILE: K, Cs, Ba, Rb, Sr), Li, B, Pb, As, Sb, and S while displaying depletion (or non-enrichments) in insoluble High Field Strength Elements (HFSE; Nb, Ta, Zr, Hf), Ti, and P (Coira & Kay, 1993; Brenan et al., 1994; Kay et al., 1994; Pearce & Peate, 1995; Richards & Kerrich, 2007).

Olivine-hosted melt inclusions often trap parental melts within the early-formed minerals (e.g. Kent et al., 2008), and single-crystal isotopic analyses certainly suggest a more primitive melt is trapped within olivine crystals erupted at Cerro Overo maar (Figure 75). Major and trace element characteristics of these inclusions, such as depletion in Ba, enrichment in P and Ti, and high Sr/Y and Ti/Zr ratio values place the inclusions within compositional fields for back-arc volcanism, but La/Nb and Ba/Nb ratios indicate melting in the presence of a high-pressure rutile phase, associating the inclusions with subduction arc magmatism (Figure 108). A direct parental relationship between the trapped mafic melt and the basaltic andesite erupted at Cerro Overo maar is however not entirely clear. The magmatic characteristics of Cerro Overo bulk rock could potentially be derived from crustal assimilation and fractional crystallization of the trapped melt, but the required degree of each process varies wildly depending on the mixing variable (i.e. element, oxide, or isotope) considered. The most likely scenario is the olivine-hosted inclusions (49.7 wt % SiO2; 7.3 wt % MgO; 4.9 wt % K2O + Na2O) represent one of several melt compositions derived from the mantle above the slab and delivered to the base of the lithosphere/lower crust where they experienced Mixing, Assimilation, Storage, and (re) Homogenization (MASH); a process common to igneous petrogenesis in the CVZ (Thorpe et al., 1984; Davidson et al., 1991; Stern, 2004; Mattioli et al., 2006; Blundy, 2009; Delph et al., 2017).

Geophysical evidence suggests a widespread MASH zone exists at the crust-mantle transition beneath the southern Puna plateau where mantle-derived melts interact with the lithosphere and undergo differentiation until the melt density becomes low enough for magma batches to propagate upward (Delph et al., 2017). Interactions (mixing) between different mafic melts delivered to the lower have the potential to induce rapid olivine crystallization by creating a thermal (and/or compositional) gradient, trapping portions of the unrelated melt near crystal cores (e.g. Faure et al., 2003). The majority of large, glassy melt inclusions suitable as analytical targets in Cerro Overo olivine are located at crystal cores, indicating trapping during early stages of olivine crystallization. Many of the inclusions not found at crystal cores show compositions more reflective of the basaltic andesite host at the time of eruption (i.e. they have re-
equilibrated with the surrounding melt) or of more silicic material, potentially formed when sudden cooling introduced by wall-rock assimilation initiated rapid olivine growth, trapping surrounding melt.

Table 23 – Hypothetical major element and isotopic composition of Cerro Overo magma preceding the 10 – 15 % crustal contamination modeled by Rosner et al. (2003) using Sr-Nd-B isotopic systematics with the Atana Ignimbrite representing a typical middle-upper crustal dacitic composition.

<table>
<thead>
<tr>
<th></th>
<th>Cerro Overo</th>
<th>Atana Ignimbrite</th>
<th>CO - 10 % crust</th>
<th>CO - 15 % crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52.7</td>
<td>65.5</td>
<td>51.3</td>
<td>50.4</td>
</tr>
<tr>
<td>MgO</td>
<td>7.83</td>
<td>1.47</td>
<td>8.53</td>
<td>8.95</td>
</tr>
<tr>
<td>FeO*</td>
<td>8.24</td>
<td>4.23</td>
<td>8.68</td>
<td>8.94</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.93</td>
<td>0.61</td>
<td>0.96</td>
<td>0.99</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.5</td>
<td>16.6</td>
<td>16.4</td>
<td>16.4</td>
</tr>
<tr>
<td>CaO</td>
<td>8.70</td>
<td>3.86</td>
<td>9.24</td>
<td>9.56</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.38</td>
<td>3.70</td>
<td>3.34</td>
<td>3.32</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.29</td>
<td>3.81</td>
<td>1.01</td>
<td>0.84</td>
</tr>
<tr>
<td>La/Ta</td>
<td>36.0</td>
<td>27.5</td>
<td>36.9</td>
<td>37.5</td>
</tr>
<tr>
<td>87Sr/86Sr</td>
<td>0.70617</td>
<td>0.70950</td>
<td>0.70579</td>
<td>0.70558</td>
</tr>
<tr>
<td>εNd</td>
<td>-4.27</td>
<td>-8.02</td>
<td>-3.86</td>
<td>-3.61</td>
</tr>
<tr>
<td>206Pb/204Pb</td>
<td>18.76</td>
<td>18.98</td>
<td>18.74</td>
<td>18.73</td>
</tr>
<tr>
<td>207Pb/204Pb</td>
<td>15.63</td>
<td>15.65</td>
<td>15.62</td>
<td>15.62</td>
</tr>
<tr>
<td>208Pb/204Pb</td>
<td>38.72</td>
<td>38.98</td>
<td>38.69</td>
<td>38.67</td>
</tr>
</tbody>
</table>

The behind-arc magmatic regime of the central Andes has been widely attributed to a combination of slab steepening, lithospheric delamination, mantle corner flow, and upwelling-induced asthenospheric melting combined with arc-related magmatism and melting of portions of the overriding continental crust (Coira & Kay, 1993; Kay & Kay, 1994; Davidson & De Silva, 1995; Matteini et al., 2002; Hoke & Lamb, 2007; Risse et al., 2008; Acocella et al., 2011; Kay et al., 2012). Geochronological evidence from behind-arc rocks suggest they have been dominantly produced in the Oligo-Miocene or in the Plio-Pleistocene (Hoke & Lamb, 2007; Risse et al., 2008). The composition of volcanic rocks from the back-arc display intraplate characteristics of high K₂O content compared with the main arc, enrichment in Ti, Nb, and Zr, and diagnostically low La/Ta (< 25) compared to arc ratios (La/Ta > 30) (this study; Kay et al., 1994; Hoke & Lamb, 2007). Low values for La/Ta ratios (Figure 106) and enrichments in Nb
(Figure 107) and Ti (Figure 109) are a result of magma generation without significant high-pressure Fe-Ti oxide phases in the residual mineral assembly, itself an aspect of slab-dehydration melting associated with subduction arc magmatism (Brenan et al., 1994; Pearce & Peate, 1995). The olivine-clinopyroxene-phyric basaltic andesite erupted in the Cordón de Puntas Negras, near the eastern margin of the main arc of the central Andes displays characteristics of a transitional compositional (e.g. 25 < La/Ta < 30) between arc and back-arc magmatism. These results indicate a hybrid of both intraplate and arc melting occurs within (at least) the eastern portion arc system. Puntas Negras mafic lava composition could not be reproduced from models of basic mixing (and fractionation) of end-member compositions from Cerro Overo basaltic andesite or Cerro Overo basaltic melt inclusions and mafic-intermediate back-arc intraplate (La/Ta < 25) lavas or shoshonitic compositions.

This suggests the Puntas Negras endmember does not represent a hybrid composition produced from magma mixing, but rather a magma derived from parental melt(s) generated in a hybrid arc-intraplate transitional melting regime. The implication is arc magmatism composition, timing, and mineralogy can be affected by geodynamic events occurring behind the arc itself, such as steepening subduction and delamination of the lithospheric root. While this may seem readily apparent, the compositional variability of magmas across the CVZ arc is widely attributed to variable AFC processes and mixing within the crust (e.g. Davidson et al., 1991; Richards & Villeneuve, 2002; Mamani et al., 2010), without considering melts of multiple origins reaching the lower crust. K content, in particular, has been observed to increase eastward across the arc (Rogers & Hawkesworth, 1989; Mamani et al., 2010; Salisbury, 2011), broadly attributed to increasing depth to the Wadati-Benioff Zone (WBZ) and progressive dehydration of the slab accompanied by generation of smaller melt fractions (e.g. Matteini et al., 2002). Increasing K-content, among other attributes, may be in part also controlled by the amount of intraplate melt being generated in the back-arc and being delivered to lower crustal MASH zones along the arc’s margin.

The Adakite-Like Signature of Tilocálar Group Magmatism

Intermediate lavas erupted west of the main arc at Tilocálar Norte y Sur and Cerro Tujle maar in the Lomas de Tilocálar area (The Tilocálar Group) display compositional features suggesting magma generation from a small amount of partial melting of depleted meta-mafic
rocks, possibly the eclogitic lithospheric root or material introduced into the mantle by fore-arc subduction erosion (e.g. Kay, 1978; Kay et al., 2010). Distinguishing characteristics include high Sr/Y and La/Yb ratios (Figure 135; Figure 110), high Sr content (Figure 127), heavy REE and Y depletion (Figure 82), relatively low concentrations of fluid-mobile incompatible element (Cs, Rb, Th, U), and lower-than-expected ratios of radiogenic to non-radiogenic Sr and Pb and higher Nd ratios (Figure 25; Figure 29 - Figure 31) (e.g. Kay, 1978; Defant & Drummond, 1990; Rudnick & Fountain, 1995; Martin et al., 2005; Moyen, 2009). Depletions in HREEs relative to LREEs (high La/Yb and Dy/Yb ratios) (Figure 111) and a deep Nb-Ta trough in normalized trace element patterns (Figure 82) indicate the primary melt(s) were generated with garnet and rutile in the residual mineralogy (e.g. Brenan et al., 1994; Pearce & Peate, 1995; Martin et al., 2005). Depletion in HREEs relative to LREEs and high Zn/Fe* ratios require clinopyroxene and garnet to be the dominant phases in the melt source (Murray et al., 2015), but the intermediate MgO and SiO₂ compositions of the lavas suggest an eclogitic (mafic) rather than pyroxenitic (ultramafic) source (Moyen, 2009). The major element compositions of Tilocálar Group lavas follow most trends defined by the mantle-derived lavas of the main subduction arc of the Central Volcanic Zone (Figure 8), although Na₂O, TiO₂, and Al₂O₃ content are high. The chemical characteristics of the Tilocálar Group monogenetic lavas fulfill the description of Adakite signature as defined by Defant & Drummond (1990), including: SiO₂ greater than 56 wt %, Al₂O₃ greater than or equal to 15 wt %, Sr greater than 400 ppm, Y less than 18 ppm, and Yb less than 1.9 ppm. The one exception being ⁸⁷Sr/⁸⁶Sr, generalized to be ≤ ~ 0.7045 for adakite magma derived from melting of the oceanic slab (Defant & Drummond, 1990), which ranges 0.705 – 0.707 for lavas of the Tilocálar Group. This one discrepancy suggests the Tilocálar Group lavas were derived from a meta-mafic material with greater amounts of radiogenic Sr than typical oceanic crust (i.e. the Nazca Plate). The most likely sources in this case are delaminated lithospheric root or material introduced into the asthenosphere by fore-arc subduction erosion.

Andesites and dacites with Adakite-like signatures have been proposed to be directly derived from partial melting of subducted lithosphere or mafic lower crust, and are not generated from fractional crystallization or contamination of a basaltic parental melt (Kay, 1978; Defant & Drummond, 1990; Rudnick & Fountain, 1995; Defant & Drummond, 1999; Xu et al., 2002; Rollison & Tarney, 2005; Moyen, 2009). Additional interaction of these low-degree, relatively felsic melts with mantle peridotite can potentially produce an even larger range of compositions (Moyen, 2009). For example, while the original classification of Adakite-like
magnas by Defant & Drummond (1990) called for MgO content less than 3%, re-equilibration with asthenosphere could raise the Mg content of the melt (Kay, 1978; Moyen, 2009). Subsequent melting of asthenospheric peridotite altered by interactions with slab melt has been implicated as the source of so-called High-Magnesium Andesites (HMAs) (Richards & Kerrich, 2007 and references therein). However, some authors contend key features of Adakite-like signatures, such as low Y and Yb content and high Sr/Y and La/Yb ratios could be derived from asthenosphere-derived arc magmas by interaction with the overriding plate and crystal fractionation (Figure 124) (e.g. Richards & Kerrich, 2007). Melting of gravitationally unstable lithospheric pyroxenite has been proposed as the source of some minor basaltic eruptions in the back-arc of the Central Andes which display wide ranges in La/Yb, La/Ta, and $^{87}$Sr/$^{86}$Sr (Murray et al., 2015). However, the Tilocálar Group intermediate lavas do not show elemental trends suggestive of mineral fractionation (e.g. Ni and Sr is enriched relative to MgO, SiO$_2$, etc., indicating, respectively, little to no removal of olivine or plagioclase) or crustal assimilation ($\epsilon$Nd = -4.9 to -4.4; $^{87}$Sr/$^{86}$Sr = 0.70647 – 0.70702 (Figure 32; Figure 28). These traits are evidence that the Tilocálar Group are relatively un-differentiated lavas, despite displaying intermediate composition, derived from partial melting of a mafic source (e.g. Martin et al., 2005) and not an ultramafic asthenospheric source.

In the central Andes, some back-arc compositions argued to result from intraplate decompression melting of the asthenosphere interacting with the overriding continental lithosphere (Kay et al., 1994; Kay et al., 2012) fall within the broadest definitions of adakites, such as fulfilling the Sr/Y versus Y distinction laid out by Defant & Drummond (1990; 1993; 1999) (Figure 124). However, the high Mg and low Si content of the majority of these back-arc rocks precludes them from being defined as Adakites sensu stricto (i.e. derived directly from melting of the slab), and several compositional features distinguish them from the Lomas de Tilocálar lavas (e.g. Kay, 1978; Kay et al., 1994; Moyen, 2009). Tilocálar Group adakite-like lavas are distinct from low silica, high Sr/Y lavas of the back arc as they display much higher La/Ta (> 60), Ba/Nb, and La/Yb (>35), indicating melting with both garnet and rutile residual phases, and larger La/Sm ratios with respect to La content than even the high-K basaltic shoshonites of the back-arc, indicating a very minor degree of partial melting. The high Sr/Y back-arc rocks also do not display the sodic nature (> 3.5 wt % Na$_2$O) which is also part of the Adakite definition (Defant & Drummond, 1990; Martin et al., 2005). Of all these distinctions, the most striking is the La/Ta ratio. The lower ratio range (La/Ta = 10 – 50) (Kay et al., 1994; Murray et al., 2015) for
all calc-alkaline, transitional, and intraplate magmatism behind the frontal arc reflects the influence of adiabatically melted ascending asthenosphere compared with the Tilocálar Group signature (La/Ta = 60 – 70 for Cerro Tujle; La/Ta = 90 – 120 for the Tilocálars), which reflects a source with significant rutile in the residual mineralogy (e.g. the slab or eclogitic lithosphere).

Adakite compositions of the restricted definition of Defant & Drummond (1990) can undoubtedly be formed by partial melting of mafic rocks in the garnet stability field, as shown in a large number of experimental studies (Rapp & Watson, 1995; Martin et al., 2005 and references therein). Naturally-occurring Adakites and those produced experimentally from melting of metabasaltic oceanic material display characteristic high degrees of LREE/HREE fractionation and high La/Ta ratios along with the high Sr/Y ratio which is perhaps over-used in diagnosis of Adakite origin (Martin et al., 2005; Moyen, 2009). Experiments in adakite production by melting of metabasalts found residual mineral assemblages of plagioclase ± amphibole ± orthopyroxene ± ilmenite at low pressure (8 kbar), and garnet + amphibole ± plagioclase ± clinopyroxene ± ilmenite at intermediate pressure (16 kbar), and garnet ± clinopyroxene ± rutile at higher pressure > 16 kbar (corresponding to depths of > ~ 60 km) (Martin et al., 2005 and references therein). The depth to the Moho of the central Andes is variable, ranging ~ 55 -65 km in the Altiplano – Puna region (Cahill & Isacks, 1992; Beck et al., 1996; Yuan et al., 2002; McGlashan et al., 2008), and melting of the slab should produce trace element compositions indicative of a garnet, clinopyroxene, and rutile residue.

The source of andesitic to dacitic lava at the Tilocálars and Cerro Tujle could be small amounts of partial melt derived from three possible sources: underplating of the eclogitized root of the thickened lithosphere of the central Andes (~ 50 – 65 km depth) (Zandt et al., 2003; McGlashan et al., 2008), melting of the eclogite-facies lithospheric root within the asthenosphere after its removal by delamination or convection (≥ 55 km depth) (e.g. Coira & Kay, 1993), or melting of relatively young and warm oceanic meta-basalt (now eclogite) of the subducted slab (80 – 90 km depth) (e.g. Cahill & Isacks, 1992). Depletion in HREE (high La/Yb) and Y indicate melt formation in the presence of garnet, which preferentially includes these elements over LREE, and high Sr concentrations reflect the absence of plagioclase, which preferentially partitions Sr, in the source. Additionally, the Tilocálar Group lavas display very minor negative Europium anomalies which diverge from the SiO₂ – Eu/Eu* inverse correlation that persists across arc and back-arc lavas (Figure 130). The small negative europium anomaly
of the Lomas de Tilocálar Adakite-like rocks indicates both melt generation from a source without residual plagioclase and subsequent suppression of plagioclase crystallization and fractionation. At high pressures, plagioclase is replaced by garnet and jadeitic pyroxene (e.g. Richards & Kerrich, 2007). The high Ni and Cr contents (Figure 133) for andesites of the region suggest initial formation at higher temperatures than intermediate rocks of the arc itself.

The Tilocálar Group lavas display MgO up to 4.5 wt % (high relative to SiO₂ for arc rocks of the region), Ba enrichment, and typical arc-signature Nb and Ta depletion, suggesting a significant component of the primary melt(s) was derived with participation of fluids derived from dehydration of the subducting slab (e.g. Rollinson & Taney, 2005). An initially hydrous melt could be the reason plagioclase crystallization was suppressed in Tilocálar and Cerro Tujle rocks. Water content estimated from groundmass plagioclase composition (i.e. a minimum estimate) is around 2.0 – 3.0 wt % H₂O (Table 17), suggesting the magma could reasonably have hosted the H₂O content > 5% required to prevent plagioclase crystallization (e.g. Lange et al., 2005). Additionally, the Tilocálar and Cerro Tujle lavas do not show amphibole crystallization, indicating they reached the surface at temperatures exceeding 1000° C (e.g. Mattioli et al., 2006 and references therein), a relatively high temperature for andesite, further supported by geothermometer calculations indicating an eruptive temperature ranging 1040 – 1100 ° C (Table 17). However, the exact source of the Adakite-signature of these melts is much more difficult to discern. Melting involving slab-derived fluids could have occurred in the slab itself or in an encounter between asthenospheric melt and lithospheric material.

Melting caused by underplating of the lithosphere within the amphibolite or granulite facies would produce lavas with low aluminum (Al₂O₃ ≤ 12 wt %) and significant negative Europium anomalies (Defant & Drummond, 1990). The Tilocálar and Cerro Tujle lavas, however, display Al₂O₃ ≥ 15.7 wt % and very minor negative Europium anomalies (Eu/Eu* ≥ 0.91), suggesting they were derived at eclogite-facies depths. A large degree of HREE depletion (i.e. high LREE/HREE ratios, such as La/Yb = 35 - 66) indicates melting with a garnet residue (Figure 110). The garnet stability field is at approximately > 40 km depth, at pressures greater than 10–12 kbar (e.g. Moyen, 2009 and references therein). This includes the amphibolite-facies lithosphere as well as the eclogitized root, but trace element patterns do not show the MREE depletion indicative of melting with a significant amount of amphibole in the residue (Figure 82). Adakite production by melting of the subducted oceanic slab has been postulated...
to require the subducted material is still relatively hot, having been produced by rift volcanism < 25 Ma (Defant & Drummond, 1990; Martin, 1999). The temperature of subducted oceanic lithosphere does not normally reach high enough temperatures to melt, and progressive dehydration renders the oceanic material increasingly infusible. Geophysical modeling suggests downgoing oceanic crust will be nearly completely dehydrated by the time it reaches depths of 90 to 110 km (Forneris & Holloway, 2003), the approximate depth to the WBZ beneath the Tilocálar and Cerro Tujle (Cahill & Isacks, 1992; Rosner et al., 2003). The Central Volcanic Zone of the Andes, however, is notable for being the point at which the oldest portion (50 – 60 Ma) of the Nazca plate is currently being subducted (e.g. Stern, 2004 and references therein). The temperatures required for direct melting of the subducted, dehydrated, eclogitized oceanic slab are unlikely to be encountered in the region, and other geodynamic forces must be invoked.

The most likely source for the Adakite-signature lavas of the Tilocálar Group is a small degree of partial melt derived from mafic lower crust. The isotopic signatures of Tilocálar Group lavas are more evolved \((^{87}\text{Sr}/^{86}\text{Sr} = 0.705 – 0.707; \varepsilon\text{Nd} = -4.86 – -4.37)\) than would be expected for parental melts derived from direct melting of oceanic crust. The Nazca plate has an average \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of \(~0.7035\) near the subduction trench west of the central Andes, and similar andesitic magma generated from melting of metaoceanic slab material would be expected to display \(^{87}\text{Sr}/^{86}\text{Sr} \leq 0.7045\) (Defant & Drummond, 1990; Martin, 1999; Xu et al., 2002; Richards & Kerrich, 2007; Moyen, 2009). Much of the lower crust and lithospheric root of the central Andes is believed to consist of meta-mafic material derived from sources such as accreted ocean island arcs, various mafic igneous rocks from buried pre-Miocene magmatism, and repeated injections of basaltic melt generated from the mantle (e.g. Lindsay et al., 2010 and references therein). However, the exact nature of the source material for the Tilocálar Group is difficult to discern. The location of melt generation can reasonably be assumed to have been approximately beneath the SE corner of the Salar de Atacama, as this is where the Tilocálar Group lavas were erupted. The most likely sources of parental material are delaminated lithospheric root sinking into the asthenosphere or material eroded from the base of the lithosphere by the subducting slab (i.e., fore-arc subduction erosion) (e.g. Kay et al., 1994; Kay & Coira, 2009; Kay et al., 2010).

Lithospheric delamination and associated mafic volcanism and crustal melting has been well documented in the back-arc of the southern Puna in NW Argentina, associated with
steepening of the subducting Nazca slab (Coira & Kay, 1993; Coira et al., 1993; Kay et al., 1994; Trumbull et al., 2006; Risse et al., 2008; Kay & Coira, 2009; Acocella et al., 2011; Kay et al., 2012; Risse et al., 2013; Mahlburg & Sandvol, 2014), and has been suggested as a magma-generation mechanism in the back-arc of the northern Puna, in SW Bolivia (Davidson & De Silva, 1995; Hoke & Lamb, 2007). Delamination-induced magmatism is constrained to < 7 Ma in the southern Puna, began by the Late Miocene, reached a maximum in the early Pliocene (6 – 4 Ma), and has persisted into the Quaternary (Risse et al., 2006). The Late Pleistocene ages for the Tilocálar volcanoes (Gardeweg & Ramirez, 1982; Gonzalez et al., 2009) places them within the proper time frame. Asthenospheric flow following delamination is by far the most likely cause of the adakite-signature volcanism west of the arc. However, the question remains as to what material these magmas were derived from. The majority of studies of natural adakites at subduction origins implicate direct melting of the slab (Kay, 1978; Defant & Drummond, 1990; Defant & Kepezhinskas, 2001; Martin et al., 2005; Richards & Kerrich, 2007; Moyen, 2009). However, the old and cold nature of the Nazca plate in the Central Andes is contrary to the findings of previous studies addressing adakite magmatism and its correlation with young, ‘hot’ slabs in other volcanic zones of the Andes (Defant & Drummond, 1990; Stern & Killian, 1996; Moyen, 2009). Studies of adakitic intrusive rocks in purely continental settings from central and eastern China provide evidence for production of adakite-signature melts from the partial melting and delamination of the eclogitic root of thickened crust (Xu et al., 2002; Wang et al., 2007).

The depth to the Moho is approximately 50 – 65 km over most of the Altiplano-Puna region of the central Andes (Zandt et al., 2003; Schurr & Rietbrock), shallower than the Moho in the Altiplano of the northern portion of the central Andes (17° – 20° S) due to loss of the eclogitic lithospheric root due to density-driven delamination and/or convective removal, which has imbued the CVZ at large with substantial Moho topography (Coira & Kay, 1993; Kay et al., 1994; Yuan et al., 2002; Schurr & Rietbrock, 2004; Hoke & Lamb, 2007; Kay et al., 2009; Kay et al., 2012). The delaminated material, as imaged by geophysics (e.g. Kay et al., 2012) has the density of eclogite-facies mafic material. The trace element composition of the Tilocálars and Cerro Tujle display significant depletions in the fluid-mobile incompatible elements (Cs, Rb, Th, U), indicating derivation from a depleted and/or dehydrated source (e.g. Rollinson & Tarney, 2005). A subset of the Plio-Pleistocene behind-arc mafic rocks in SW Bolivia (i.e. at the northeastern margin of the Puna) show similar depletions. However, certain compositional differences distinguishes the Bolivian behind-arc rocks from those of the Lomas de Tilocálar, and
the Adakite signature (parentheses) in general: the back-arc rocks commonly display SiO$_2$ < 54 % (≥ 56 %), Y > 20 ppm (≤ 18 ppm), Yb > 2 ppm (≤ 1.9 ppm), and $^{87}$Sr/$^{86}$Sr > 0.7060 (≤ 0.7045), indicating they are so-called low-silica adakites, derived from depleted mantle (Defant & Drummond, 1990; Richards & Kerrich, 2007).

Hoke & Lamb (2007) modeled a situation in which the Bolivian behind-arc lavas were derived from long-lived melting of a peridotitic, MORB-like source. They suggest upwelling in the mantle corner flow controlled by lithospheric thickness variations caused advection of depleted mantle into the melt zone beneath the arc, generating trace element signatures depleted in fluid-mobile compatible elements and still showing the Nb-Ta trough indicative of slab-metasomatism influenced arc melting (Hoke & Lamb, 2007). However, there is not geophysical evidence for large-scale corner flow concentrating depleted mantle beneath the arc of the CVZ, and corner flow reaching as far west as the Tilocálar, considering the Salar de Atacama lithospheric block appears to be potentially coupled to the subducted slab and blocks mantle flow in the region (Schurr & Rietbrock, 2004; Riller et al., 2006). Seismic studies, however, do indicate the depth to the Moho under the Lomas de Tilocálar is less (48 – 65 km) than the thicker lithosphere (70 – 80 + km) of the Altiplano to the north of the Salar de Atacama (Yuan et al., 2002; Zandt et al., 2003). This indicates loss of the lithospheric root has affected this portion of the Altiplano-Puna region, as well. Seismic data has provided ample evidence for nearly complete delamination of the eclogitic lithospheric root centered beneath the Cerro Galan ignimbrite center (25.92° S, 66.93° W)) (Kay et al., 2012) and periodic removal of the lithospheric root following steepening in the slab at ~ 16 Ma has been suggested for the majority of the Altiplano-Puna plateau (Kay & Coira, 2009).

Melt contribution from deep crustal material will be characterized by high Sr/Y, Ba/Rb, and La/Yb due to generation with garnet as a residual phase and incompatible behavior of Sr (e.g. Davidson et al., 1991). The mafic lower crust has high Ba content (Hildreth & Moorbath, 1988) and a high Rb/Cs ratio. Taylor & McLennan (1985) proposed a Rb/Cs ratio of ~53 for mafic lower crust. The mantle-derived lavas of Cerro Overo, Puntas Negras – El Laco, and El País lava display Rb/Cs values ranging 13 – 30, with an average Rb/Cs of ~ 22. The Tilocálar Group lavas display a Rb/Cs range of 41 – 61, with an average value of ~ 51. Not only is this evidence for a lower crustal origin for Tilocálar Group lavas, but also suggests relatively minimal upper crustal contamination or sediment involvement, which could lower this ratio.

People use MASH model at base of crust to account for lower crustal signatures seen in the back-arc (Wörner et al., 1994). Needs high T introduction or dehydration from below, e.g. transition from amphibole-bearing gabbros to anhydrous lithologies (i.e. granulite-eclogite).
Eruption of Adakite-Signature Lavas at Arc Stratovolcanoes

Tilocálar Norte y Sur and Cerro Tujle show a significantly stronger Rare Earth Element (REE) fractionation pattern (La/Yb > 35, Dy/Yb > 2.5) than frontal arc rocks, including the other centers addressed in this study (Arc: La/Yb < 30, Dy/Yb ≤ 2.7; Mafic: La/Yb < 17, Dy/Yb < 2.3), displaying depletion in Heavy REEs (HREEs) and/or enrichment in Light REEs (LREEs) (Figure 110). This compositional distinction is one feature which distinguishes these three volcanoes as a separate group from the other minor volcanism of the Altiplano-Puna, along with a spatial correlation and similar nearly-aphyric, andesitic petrography. Other compositional features which distinguish the Tilocálers and Cerro Tujle from major arc trends include enrichments in Ba and Sr, and weak Eu depletions with respect to silica content. These strongly-fractionated lavas erupted at arc stratovolcanoes show similar Adakite-like signatures to the lavas of the Tilocálers and Cerro Tujle, indicating a potential component of melted meta-mafic material mixed into certain instances of arc magmatism itself. Similar Late Pleistocene timing of anomalous dacites with such characteristics erupted at Llullaillaco stratovolcano (Richards & Villeneuve, 2001; 2002) and the Tilocálar Group monogenetic centers is certainly intriguing and hints at a widespread derivation of a small melt fraction from a foundering eclogitic component (e.g. Xu et al., 2002), although further research is required to confirm this possibility.

A review of published values from the GEOROC database and the compiled dataset of Mamani et al. (2010) reveals a sparsely-populated, but distinguishable subset of volcanism with strong LREE/HREE fractionation and other Adakite-like characteristics (e.g. high Sr/Y) in the CVZ main arc. Within the latitudinal range of this work (20-25° S), encompassing the Altiplano-Puna Volcanic Complex and the full potential extent of the Altiplano-Puna Magma Body (De Silva et al., 2006; Perkins et al., 2016), there are at least five other recorded instances of lava compositions with highly fractionated REEs (La/Yb > 35). North to south these are Sairecábur (-22.72, -67.90), Licancabur (-22.87, -67.89), Tul-Tul – Del Medio (-24.15, -67.15), Socompa (-24.40, -68.36), and Llullaillaco (-24.72, -68.54) (Matteini et al., 2002; Richards & Villeneuve, 2001; Mamani et al., 2010; GEOROC, accessed 2015). Of these, the best-described samples are from a set of Pleistocene dacitic flows at Cerro Llullaillaco (Richards & Villeneuve, 2001; 2002).

Cerro Llullaillaco is a quaternary stratovolcano along the border of Chile and Argentina (24.720 S, 68.538 W), approximately 90 km south-southwest of the Tilocálers. Llullaillaco marks
the westernmost extent of a chain of Late Miocene–Quaternary subduction-related volcanism erupted along the NW-SE trending *Archibarca* transverse lineament (Richards & Villeneuve, 2002). Volcanic deposits along the ~50 km section where the Archibarca lineament intersects the arc range from olivine-bearing high-K basaltic andesite (54 – 56 wt % SiO$_2$, 3.5 – 4.5 wt % MgO) to dacitic ignimbrites (69 wt % SiO$_2$, 0.9 wt % MgO), spanning the Miocene up to the Quaternary (Richards & Villeneuve, 2002). Lavas along this lineament represent compositions standard to and common within the central Andean frontal arc, including within REE fractionation (e.g. La/Yb = 17 - 30) patterns, which are relatively consistent from the Pleistocene to the late Neogene (Richards & Villeneuve, 2002). In contrast, Llullaillaco lavas from the Pleistocene (0.40 – 0.05 Ma, most ~ 0.16 Ma) display distinctive highly fractionated (HREE-depleted) patterns, very high Sr/Y (~ 78) absence of significant negative Eu anomalies (Eu/Eu*≈0.84–0.90), low Rb/Sr (~0.10), and lower enrichments in certain incompatible elements (Richards & Villeneuve, 2001; 2002).

Several distinguishing features are shared between the Tilocálar volcanoes and Cerro Tujle maar and Cerro Llullaillaco stratovolcano which separate them from the main body of arc rocks. These rocks are all intermediate lavas with microcrystic plagioclase in a glassy groundmass, with or without phenocrystic plagioclase. Notably, Eu depletion is nearly absent, suggesting no extensive plagioclase fractionation has taken place despite the occurrence of plagioclase phenocrysts or microphenocrysts in some of the lava. Minimal plagioclase fractionation, which preferentially removes Sr, is also supported by low Rb/Sr values for Llullaillaco (~0.10), Tilocálar Norte (~0.06), Tilocálar Sur (~0.02), and Cerro Tujle (~0.05) which generally ranges 0.05 – 0.70 for the CVZ arc suite (Richards & Villeneuve, 2001). In whole rock compositions, Heavy REEs are depleted and/or Light REEs are enriched, visible in normalized REE patterns or charts of trace element ratios, such as La/Yb, Sr/Y, La/Sm, or Dy/Yb. The patterns of distinct fractionation of HREEs without shallowing of the Middle REE patterns suggest these magmas were generated with garnet as a residual phase, which preferentially retains HREEs over LREEs (e.g. Kay et al., 1991). La/Sm ratios are high with respect the arc suite, suggesting relatively low degrees of melting in magma generation.

Along with petrologic associations, the REE-fractionated lavas of the CVZ also show correlations in space and time. All of the volcanoes selected from the literature based on elevated Dy/Yb and La/Sm are erupted along a longitudinal trend, following the larger trend in
the main arc. This is notable as the frontal arc bends some 30 km eastward “around” the Salar de Atacama and surrounding region, with the exceptions of the Tilocálers and Cerro Tujle. Erupted at the SE margin of the Salar, these three volcanoes are emplaced approximately where the volcanic arc would pass through the region were it not for the eastward oroclinal bend. Lavas with strong REE fractionation are found immediately to the north (Sairecábur & Licancabur) and south (Llullaillaco) of this bend, but not within arc rocks of the eastward bend itself (excepting the three Tilocálar Group minor centers of this study). This longitude-composition correlation, ignoring the actual path of the arc at the surface suggests generation of the REE-fractionated lava is related to a deeper structure, such as slab depth (~100 - 125 km), which steadily increases west-to-east, or crustal thickness (~60 km), which slightly decreases west-to-east (Cahill & Isacks, 1992; Beck et al., 1996).

The one exception to this correlation is the Tul-Tul – Del Medio complex, from which Matteini et al. (2002) sampled lavas with strong REE fractionation some 70 km southeast of the bend in the arc. This lava is likely unrelated otherwise, as it is an east-of-the-arc regime which shows evidence for interaction with components derived from the underthrust Brazilian shield (Matteini et al., 2002). In addition, lavas from the Tul-Tul-Del Medio have been dated to 6-8 Ma, making it significantly older than the other arc volcanoes (Matteini et al., 2002). What Tul-Tul-Del Medio does have in common with other volcanoes in this grouping, however, is its orientation along the Calama-Olacapato-Del Toro (COT) transverse lineament. Llullaillaco is associated with Archibarca lineament of the southern Puna and Sairecábur & Licancabur are situated along minor NW-SE transverse lineaments immediately north (and presumably related to) where the COT lineament passes through the main arc. Minor eruptions and hydrothermal activity to the SE of Socompa at (24.5638° S, 67.8661° W) and the El Negrillar monogenetic field to the NW hint this stratovolcano is also associated with a crustal lineament.

The Tilocálers and Cerro Tujle maar are clearly associated with compression-induced faulting and folding features as the southeastern margin of the Salar de Atacama. Both the regional transverse lineaments and the SE Atacama compressional features are believed to be fundamentally controlled by basement structures at depth (Mazzuoli et al., 2008; Lin et al., 2016). Collectively, these volcanoes also show evidence for generation at depths where residual garnet is stable (> 40 km), little evidence for plagioclase fractionation, and some component of melt generation from a meta-basalt (i.e. Adakite-like signature). Age data is not specifically
available for most of the considered samples, but highly REE-fractionated samples from Tilocálar Norte y Sur and Cerro Llullaillaco have been dated to the Mid- to Late-Pleistocene (Gonzalez et al., 2009; Richards & Villeneuve, 2002). Precedent and subsequent lavas from Cerro Llullaillaco do not show any of the distinguishing compositional features discussed, such as HREE depletion or nearly absent Eu anomalies, indicating a temporal constraint for these lavas (Richards & Villeneuve, 2002). Potentially, a widespread event causing melting of meta-mafic material occurred beneath the Altiplano-Puna region in the Late Pleistocene with the magmatic evidence broadly obscured by the much greater volumetric contribution of fluid flux melting above the subducting slab in most instances. One such possibility is that in this time frame, the foundering, delaminated eclogitic lithospheric root reached temperatures high enough to produce a small degree of partial melt with a garnet residue. Fault-controlled volcanism, such as that along transverse crustal lineaments and the basement-controlled faulting that reaches the surface at the southeast margin of the Salar de Atacama, may have provided the rare opportunity for such melts to reach the surface and still be compositionally discernable.
Conclusions

Monogenetic volcanoes in the central Andes reveal a diversity of subduction-related lava compositions not observed at long-lived volcanic systems of the arc front. Magma in the arc commonly experiences processing by assimilation of crustal material, storage in the lower-crustal MASH zone, and/or extended sub-volcanic stalling or storage, during which magmas evolve by AFC processes. The double-thick crust and large mid-crustal felsic magma bodies of the Altiplano-Puna region are particularly conducive to such extensive magma processing, leading to a surficial volcanic system dominated by intermediate and felsic compositions. The olivine-bearing basaltic andesites erupted at Cerro Overo maar and the Puntas Negras – El Laco flow define endmember arc lava compositions for the region. Trace element characteristics and isotopic composition suggest Cerro Overo lava is purely sourced from fluid flux melting above the slab while Puntas Negras – El Laco lava includes a contribution from delamination-related dry melting of upwelling asthenosphere (Figure 186). The characteristics of these two mafic lavas are the best direct evidence of the nature of magmas at the base of the crust where MASH processes are dominant. Combined liquid- and mineral-based geothermometry provides evidence both basaltic andesites began crystallizing forsteritic olivine in the upper mantle and/or at the base of the crust. Thus, the compositions of basaltic olivine-hosted melt inclusions from Cerro Overo approximate the compositions of different parental melts in the arc system.

West of the arc, the Tilocálar Group of minor volcanoes define a distinct geochemical grouping (Figure 106 - Figure 111). Lava compositions display higher than expected MgO content, greatly elevated Sr/Y ratios, strong REE fractionation in general, nearly absent Sr anomalies, and thermometry results suggesting elevated eruptive temperatures for andesitic compositions. Additionally, the isotopic compositions of Tilocálar Group lavas are less-evolved than would be expected for andesite developed dominantly from AFC processes. Cumulatively, these geochemical features suggest magmas of this group originated as small melt fractions of metabasaltic material at pressures within the garnet stability field. These results suggest magmas throughout the arc may contain contributions from melting of material other than the asthenosphere (eventually producing arc andesites) or the middle-upper crust (the source felsic ignimbrites). The most likely candidates for the melt source are either delamination or forearc subduction erosion of the lower crust/lithosphere (Figure 186).
Chapter 3: Trace element zoning and morphology of igneous olivine – untangling processes of magma origin and ascent for mafic monogenetic volcanism, Chile.
Abstract

The internal structure and microchemistry of olivine phenocrysts from monogenetic lavas of the Central Andes provide evidence of the magmatic history of the most mafic lavas erupted in the region. Microzoning of Phosphorous and disparities in the concentration profiles of major and trace elements in olivine phenocrysts records information of crystallization conditions not preserved in major element zoning patterns (Milman-Barris et al., 2008). Cerro Overo maar and the Puntas Negras mafic lava in northern Chile have produced the most mafic lavas in the region, but lack crystals with easily studied zonation, such as plagioclase. Combined with whole-rock geochemistry and geothermobarometry calculations, unconventional studies of the internal zoning and concentration of trace elements in olivine phenocrysts can provide additional insight into the development of these magmas as they traversed the lithosphere (e.g. Welsch et al., 2014). Micron-scale phosphorous zoning in olivine from Cerro Overo and Puntas Negras indicate both lavas crystallized olivine by cyclical rapid skeletal growth followed by slower infilling crystallization. Experimental studies suggest a dendritic, P-rich olivine framework can rapidly develop on the order of minutes, followed by P-poor ingrowth occurring on time scales of weeks to months (Jambon et al., 1992; Welsch et al., 2014; Shea et al., 2015). The P-zoning in olivine phenocrysts from Cerro Overo are suggestive of relatively unimpeded, continuous crystallization, likely reflecting magmatic ascent from the lower crustal MASH zone with negligible stalling or magma storage. Puntas Negras olivine zoning patterns are more complicated, displaying separate core versus rim compositions and morphologies indicative of two distinct stages of crystallization. Combined with geothermometry and barometry estimates, phenocryst microstructure indicates this magma likely stalled or entered storage in the upper crust for days or weeks. Upper crustal structure may be the reason for the two disparate magmatic histories. While both eruptions occurred along the orogen-oblique Calama-Olacapato-El Toro (COT) transverse fault zone, Cerro Overo is additionally spatially correlated with an orogen-parallel antiformal feature which may be a splay of a larger thrust fault to the west (Figure 34). The additional crustal weakness presented by the intersection of the two structural features may have provided the pathway mafic lava requires to avoid stalling in or interacting with the felsic upper crust.
Olivine Growth, Zoning, and Morphology

Compositional zonation of magmatic crystals has long been recognized as a useful tool for exploring the petrogenetic history of igneous rocks (e.g. Blundy et al., 2008). Zonation studies dominantly focus on major element zoning in minerals with solid solution endmembers, such as plagioclase (anorthite: CaAl\(_2\)Si\(_2\)O\(_8\) – albite: NaAlSi\(_3\)O\(_8\)), wherein extrinsic properties, such as temperature or magma chemistry force differences in composition. At first glance, olivine ((Mg\(^{2+}\), Fe\(^{2+}\))\(_2\)SiO\(_4\)) appears to be an ideal target for studying the history of mafic or ultramafic magmatic rocks as it is a common phase with a relatively simple composition which can be described by the temperature-dependent percentage of magnesian endmember forsterite (Mg\(_2\)SiO\(_4\)) versus ferrous endmember fayalite (Fe\(_2\)SiO\(_4\)). Composition is usually reported as percent forsterite (Fo %). Changes in temperature could easily be extracted from Fe and Mg partitioning variability in the crystal if zoning in forsterite content were preserved. However, an increasing amount of recent studies have found growth-induced development of major element (Fe-Mg) gradients in olivine is rarely preserved or extremely limited and that distinguishing growth patterns from diffusion patterns is difficult and unreliable (e.g. Shea et al., 2015 and references therein). Divalent cations rapidly diffuse through the crystal lattice at magmatic temperatures, erasing evidence for all but the most recent shifts in the host magmatic environment (Jambon et al., 1992; Milman-Barris et al., 2008). As a result, Fo% zoning is not immediately useful in studying complex or early crystallization histories of olivine, and neither are the most common minor elements, also divalent cations (i.e. Mn\(^{2+}\), Ni\(^{2+}\), Ca\(^{2+}\)) which also diffuse through the lattice, although at slower rates (Milman-Barris et al., 2008). Either rapid crystallization improbably does not generate zoning in fast-diffusing elements (Fe, Mg, Ni), or zoning is rapidly erased and not well preserved (Shea et al., 2015).

As nano-beam technology (e.g. EPMA, SIMS) becomes more widely available and easier to use, olivine studies have increasingly started to focus more on mapping trace elements with very low concentration (< 0.5 wt % oxide). For example, phosphorous (P\(^{3+}\)) and aluminum (Al\(^{3+}\)) are highly incompatible cations in the olivine system, but are nevertheless incorporated into the crystal lattice at low concentrations as impurities (Milman-Barris et al., 2008). X-ray k\(\alpha\) maps acquired by EPMA, employing high beam currents (≥ 100 nA) and long dwell times (generally ≥ 200 ms), have been able to consistently discern micron-scale zonation of P content, with no correlated zoning of Fo% content (Milman-Barris et al., 2008; Shearer et al., 2013; Welsch et al.,
Phosphorous forms a highly charged (+5) cation, and thus requires high activation energy for diffusion through the olivine lattice, preserving micron-scale compositional variation even at temperatures high enough to erase or relax zoning in divalent elements. As an olivine crystal develops, the melt immediately adjacent to the growth front becomes depleted in olivine-forming elements and relatively enriched in elements incompatible in the crystal structure (Jambon et al., 1992; Zellmer et al., 2016). When crystal growth rate exceeds the rate at which incompatible elements can diffuse through the melt away from the growth front, impurities near the crystal/melt interface become incorporated into the crystal lattice at levels exceeding equilibrium expectations (Milman-Barris, 2008; Watson et al., 2015). In this way, regions high in impurities, such as P, represent stages in crystallization history where growth was rapid enough to outpace diffusion, and low impurity zones represent periods wherein olivine was growing at a slow enough pace for crystal/melt equilibrium to be maintained.

A study of trace element distribution in olivine by Milman-Barris et al. (2008) found discernable P-zoning in igneous olivine from a wide variety of sources: terrestrial basalts, andesites, dacites, komatiites, and a Martian meteorite. Microanalyses of $P_2O_5$ content ranged from below detection limits ($\leq 0.01$ wt %) to \( \sim 0.4 \) wt %, defining high and low concentration zones on the order of microns (Milman-Barris et al., 2008). The only natural olivine crystals in the study which did not display any P-zoning were from the Brenham pallasite, an extraterrestrial rock with a notably low overall P content ($0.004$ wt % $P_2O_5$) (Milman-Barris et al., 2008 and references therein). Plutonic olivine also displays dendritic P-zoning, but to a lesser degree, likely due to longer residence times at higher sub-solidus temperatures (Welsch et al., 2014). Experimentally-grown olivine crystals also show zoning in Al and Cr not seen in natural samples and equivalent to P-zoning, implying zoning of impurities with a lower charge (+3) relax relatively rapidly in contrast to the more stable compositional variations delineated by elements with greater ionic charge, i.e. P (+5) (Welsch et al., 2014). Comparison of Fe-Mg and Ni-Mn zoning in natural olivine indicates Fe enrichment occurs without a coupled depression in Ni content due to the much greater Fe-Mg interdiffusion coefficient (Nakamura, 1995).

Texture of olivine can be an important indicator of petrogenetic history, even without zoning data, as morphology is very sensitive to thermodynamic and kinetic conditions of crystallization. In a strong thermal gradient, for example, olivine will preferentially grow along
the a axis, producing elongated crystals (Welsch et al., 2012). A progression of crystallization style as a function of increasing rate of (super)cooling (euohedral – acicular – dendritic – spherulitic), is generally accepted as common knowledge amongst material scientists and metallurgists. Similar morphologic progression has been observed in experiments crystallizing natural forsteritic olivine, with crystal growth shifting from polyhedral (equant or tabular) to granular (some rounded embayments) to subequant skeletal (unfilled framework) to growth styles dominated by chain-like progression of a fine-grained, dendritic crystal mesh (Donaldson, 1976). The spinifex olivine texture seen in ancient komatiite lavas is a well-known example of crystal morphology resulting from exceptionally rapid growth. In general, however, equant and tabular olivine crystals are common, while acicular or chained growth is relatively rare (Donaldson, 1976). In most natural lavas, olivine growth can be categorized as a balance between diffusion-controlled (supersaturated) growth, which creates a skeletal framework roughly outlining the common prismatic olivine form, and interface-controlled growth, which drives infilling of the crystal body (Shea et al., 2015). It is this oscillation in crystallization style that likely drives development of complex P-zoning, although the exact thermodynamic mechanisms are still not fully understood (Welsch et al., 2014; Watson et al., 2015).

The growth rate of a crystal depends upon the diffusion rate of necessary elements (to the growth front) and the surface energy of the crystal faces. During formation, the surrounding melt is depleted in the necessary components for growth (or, enriched in elements incompatible in the lattice). New material must diffuse through the melt, cross the depleted zone, and reach the crystal surface. Small ions with low charges diffuse the most quickly. Conversely, the heat produced by crystallization and incompatible elements excluded from the lattice must diffuse away from the growth front for crystallization to continue. Theoretically, undercooling can increase viscosity and impede diffusion through the melt, encouraging growth with minimal need for diffusion, i.e. by addition to “local” pre-existing lattice structures (Welsch et al., 2012). When most of the driving force is dissipated in diffusion, the interface moves at a rate controlled by diffusion. Interface-controlled growth occurs when most of the available free energy is dissipated in the process of transferring atoms across the melt/crystal interface.

When the rate of diffusion (in either direction) is outpaced by that of crystal growth, crystals form in a radiating, dendritic shape, reaching out beyond the zone of depletion of the growth front to access the required elements for growth. Movement or perturbation of the
parental melt/crystal mixture will reduce the limiting effects of outpaced diffusion. Crystals grow more rapidly at corners or apexes (i.e. the lattice points) as there is a higher ratio of surface area to volume at these points on a crystal, meaning a relatively high availability of surface ions (atoms with unbalanced charge, due to a lack of a complete surrounding crystal lattice). Additionally, these edges and corners have access to a larger volume of melt to derive components (and dissipate heat), along with a concentration of “unsatisfied” bonds.

Undercooling and/or supersaturation causes rapid growth at these points. A crystal which begins growing with a skeletal habit, ripening to polyhedral habit, experiences a decreasing growth rate, implying the initial crystal/melt disequilibrium (thermal or compositional) reduces over time as a result of crystallization (Welsch et al., 2012). Impurities in the melt can slow growth—the oscillatory nature of P-zoning may be in part due to a cycle of growth and relaxation. Rapid crystallization will both concentrate impurities in the crystal and the growth front, eventually slowing crystallization, perhaps enough for incompatible elements to diffuse away from the expanding lattice, creating brief pauses in the dendritic growth which creates the P-rich zones observed in olivine (Welsch et al., 2014). Exsolution of water from a magma, supersaturation, or rapid cooling can also induce rapid, dendritic (or skeletal) olivine growth (Welsch et al., 2014). Diffusion-controlled growth occurs as rapidly as new crystal-building material can be encountered (i.e. collision frequency). Sudden rapid crystallization can be induced by stirring or agitating a mixture, such as during eruption, but not for the slower growth dependent on the rate at which elements cross the melt/crystal interface.

### Table 24 – Olivine morphology resulting from different crystallization conditions, determined from experimental studies in olivine growth (data from Jambon, 1992; Welsch et al., 2012). Polyhedral crystals (euhedral) form from interface-controlled growth at a low cooling rate near equilibrium. Skeletal crystals (polyhedral habit with hollow faces) and dendritic (branching) crystals form at higher cooling rates from diffusion-controlled growth.

<table>
<thead>
<tr>
<th>Crystal morphology</th>
<th>Undercooling (-\Delta T=T_{\text{liquidus}}-T_{\text{quench}})</th>
<th>Cooling Rate</th>
<th>Olivine growth rate</th>
<th>Control on crystal growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyhedral</td>
<td>&lt; 20 °C</td>
<td>&lt; 47 °C h(^{-1})</td>
<td>(10^{-8}) to (10^{-9}) m s(^{-1})</td>
<td>interface</td>
</tr>
<tr>
<td>Skeletal</td>
<td>20 – 60 °C</td>
<td>47 – 1890 °C h(^{-1})</td>
<td>(10^{-7}) m s(^{-1})</td>
<td>diffusion</td>
</tr>
<tr>
<td>Dendritic</td>
<td>&gt; 60 °C</td>
<td>47 – 1890 °C h(^{-1})</td>
<td>(10^{-6}) m s(^{-1})</td>
<td>diffusion</td>
</tr>
</tbody>
</table>
Phosphorous Zoning in Igneous Olivine

X-ray maps of trace elements, particularly phosphorous, reveal complex crystal zoning patterns which support the concept of olivine development by dendritic (or skeletal) growth followed by infilling of cavities as the crystal matures (e.g. Welsch et al., 2014; Shea et al., 2015). Micron-scale regions of increased P content, over an order of magnitude higher concentration, define polyhedral crystal faces separated by regions of low P (Milman-Barris et al., 2008). These zones are usually parallel to the final edges of the resultant phenocryst, and are not truncated by melt inclusions or crystal embayments, which appear to develop, as remarked by Welsch et al., “between struts of the P-rich dendrite architecture” (2014). In early P-zoning studies, such as that of Milman-Barris et al. (2008), crystals sectioned orthogonal to major crystallographic axes presented concentric P-rich zones, interpreted as formed during tree-ring style growth. Subsequent research considered olivine sectioned at angles oblique to primary crystallographic axes, revealing the P-rich lineations did not propagate concentrically, but extended first from the crystal center toward the vertices, followed by dendritic branching parallel to crystal faces (Welsch et al., 2014). These recent discoveries have challenged a basic assumption of zoning: when equilibrium between crystal and melt is not maintained, rims of new composition are added concentrically to the pre-existing crystal, as in the growth of a tree’s rings. Concentric zoning is often preserved in minerals, such as plagioclase feldspar, due to the strength of local bonds (the Si-O and Al-O bonds are strong enough to prevent re-equilibration by Si-Al exchange). Welsch et al. (2014) employ textural relationships and pre-established olivine growth rates to argue olivine phenocrysts first form an impurity-rich dendritic framework (diffusion controlled growth) within a few minutes of crystallization, followed by impurity-poor overgrowth (interface controlled), developed on the scale of “a few weeks.” In this way, olivine evolves from skeletal to spongy to a euhedral morphology as initial crystal embayments are filled or are sealed off as inclusions (Welsch et al., 2014; Shea et al., 2015).

These findings not only have important implications with regard to our understanding of the chemo-mechanical development of magmatic crystals, but also in our interpretation of igneous textures. For example, a common canonical assumption of igneous petrologists is that the oldest portion of a crystal is at its core, progressively younging outward to the rim. However, if olivine commonly forms with the creation of a skeletal or dendritic framework, then some parts of the crystal closer to the outermost faces will be older than “infilled” portions.
closer to the core (e.g. Welsch et al., 2014). Even the outermost rim of a crystal may not be the youngest growth stage in some cases if resorption or breakage have conspired to bring an older dendritic limb to the surface. This is an important consideration for future olivine studies, particularly those wishing to correlate multiple melt or mineral inclusion compositions with a changing magmatic environment.

Milman-Barris et al. (2008) were able to re-create P-zoning in laboratory experiments by simple linear cooling of a basaltic liquid. This finding supports rapid dendritic growth followed by gradual infilling as an intrinsic crystallization process likely motivated by crystal component availability, and not an extrinsic model wherein crystal “growth spurts” or dampening is forced by changes in the magmatic environment (Welsch et al., 2012). Zones of high P can not necessarily be considered to represent extrinsic changes, such as injection of new magma or a sudden reduction in pressure, but a dendrite-infill cycle may represent oscillations more common to crystallization than traditionally presumed. For example, Welsch et al. suggest temperature oscillations in a magma chamber may help regulate dendritic versus “ripening” growth in olivine (2012). If rapid, P-enriched growth were kick-started by injections of hot, mafic melt, one would expect to see embayments in the rims represented by high-P surfaces, however this has yet to be observed in natural or experimental samples of published studies (Welsch et al., 2014 and references therein). Pairing of skeletal P-zones and low-P ingrowth can be thought of as representing a full cycle of olivine production, with additional dendritic high-P zones representing additional periods of growth.

Compositional zoning, of course, cannot be expected to last indefinitely in igneous systems where available free energy is relatively high. Welsch et al. (2014) observed dendritic P-zoning in gabbroic olivine similar to that in volcanic olivine, but much reduced in concentration and resolution, implying a loss of zoning information to diffusion at sub-solidus temperatures over the slow-cooling history of plutonic rocks. Through forward diffusion modeling, Watson et al. concluded P-zoning in olivine on the 5 μm scale most commonly seen by Milman-Barris et al. (2008) could not be preserved for more than “a few months” at high temperature without pronounced damping of zoning features (2015). This implies only olivine phenocrysts grown relatively recently prior to eruption, or held below the olivine closure temperature (630° – 984° C) would preserve such fine-scale zoning (Watson et al., 2015 and references therein). However, Shea et al. (2015) found delicate oscillatory P zoning in Hawaiian olivine could persist
for a minimum of 4 – 5 months at magmatic temperatures, a timescale calculated from 2-D and 3-D modelling of Fe-Mg diffusion in phenocrysts displaying dendritic P zoning alongside uncorrelated Fe-Mg gradients. Heating experiments conducted by Watson et al. (2015) found no discernable (by EPMA) mobilization of P in olivine after 30 days at 1300° C. Minor elements Ca and Cr diffuse through the olivine lattice by about an order of magnitude faster than P at basaltic near-liquidus temperatures, and preservation of correlated Ca and Cr (or Al) zoning near rims can be interpreted as evidence for rapid-growth of portions of the phenocrysts immediately preceding or during eruption (Jambon et al., 1992; Milman-Barris et al., 2008; Watson et al., 2015).

Zoning and Morphology of Olivine Phenocrysts from Cerro Overo, La Albóndiga, and Puntas Negras Basaltic Andesites

The morphology, distribution, and composition of olivine crystals in lava from Cerro Overo maar and La Albóndiga dome is virtually identical. Phenocrysts range from 0.5 – 4 mm and are generally subequant with skeletal overgrowths at some, but not all, crystal apexes. Forsterite content is normally-zoned with cores ranging 84 – 88 Fo % ($\bar{\chi} = 86.3 \pm 0.9$ Fo %) and rims on the scale of 10 – 30 $\mu$m with 70 – 83 Fo % ($\bar{\chi} = 78.7 \pm 3.2$ Fo %) (Figure 72; Figure 73). The transition from high forsterite core to low forsterite rim is relatively rapid, although curved zoning profiles indicate some degree of diffusive re-equilibration has occurred (Figure 139 - Figure 145). Concentration profiles in Puntas Negras phenocrysts are less steep, indicating a greater influence of diffusion of the internal major element zoning, suggesting Puntas Negras olivine have experienced longer residence times in hot magma than Cerro Overo and La Albóndiga crystals. Compositional changes initially influenced by changing magmatic conditions has since been modified by re-equilibration as the compatible divalent elements (Mg, Fe, Ni, Mn) diffused through the crystal lattice (e.g. Costa et al., 2008). Forsterite content follows a curved profile from the maximum concentration at the core to the minimum rim concentration at the crystal boundary over an average of 15 - 45 $\mu$m for Cerro Overo and La Albóndiga and over 50 -70 $\mu$m for Puntas Negras olivine (Figure 139 - Figure 148). The diffusion gradients defined by Ni content are wider (Table 27), and the difference in core-to-rim composition much greater (e.g. Figure 140).
Wavelength-dispersive (WDS) and Energy-dispersive (EDS) X-ray intensity maps were collected by EPMA at the University of Iowa on a JEOL 8230 Superprobe for olivine phenocrysts from maar Cerro Overo, La Albóndiga lava dome, and the Puntas Negras lava flow for major (Mg, Fe, Si), minor (Mn, Ca, Ni), and trace (e.g. Cr, Co, Ti, Al, Na, P) elements. Alternatively, the mapped elements can be divided into those compatible (Fe, Mg, Si, Mn, Ni, Co) and incompatible (Ca, Al, P, Na, Ti, Cr) in the olivine lattice (e.g. Jambon et al., 1992). Maps were acquired with a 20 keV accelerating voltage, a 300 nA beam current, a pixel resolution of 1.5x1.5 μm, and 300 ms/px dwell time. As quantifiable WDS mapping required 20 -70 hours per five elements per crystal, not all elements were mapped for all target phenocrysts. Olivine crystals were chosen for chemical mapping based on the selection criteria of Shea et al. (2015): crystals with archetypal morphology, displaying clear skeletal growth, with some apparent Fe-Mg zoning, and with an orientation in the section close to crystal axes a, b, or c. Crystal orientation was approximated by the apparent shape of the phenocrysts in thin section (Table 28).

Researchers have found fine-scale zoning patterns seen in thin section can be dependent on crystal orientation, and an imperfect crystallographic axis orientation may not reveal all possible intracrystalline information (Welsch et al., 2012; Shea et al., 2015).

Phenocryst Architecture

Olivine phenocrysts from the basaltic andesite of Cerro Overo maar display subhedral habit with ubiquitous (> 90 % of crystals) skeletal overgrowth. The phenocrysts display high forsterite cores (86.3 Fo % average) which generally follow the shape of euherdal olivine crystal form (Figure 139; Figure 141; Figure 142) and 10 – 30 μm lower forsterite rims ranging 72 – 82 Fo %. Zoning is normal for Mg and Ni content and reverse for Fe and Mn throughout all crystals. The lowest forsterite content is found in the skeletal overgrowths, which display relatively unzoned element concentrations (i.e. overgrowths do not possess higher forsterite or Ni cores) (Figure 140; Figure 141). Groundmass crystals of olivine (microcrysts) display the same compositional range as the skeletal overgrowths and do not possess any high forsterite olivine growth equivalent to the phenocrysts cores. The olivine population of basaltic andesite extruded at La Albóndiga dome is nearly indistinguishable from Cerro Overo olivine in size and composition, although the dome crystals generally display more symmetric skeletal overgrowth and crystals from near the outer margins of the lavas display Fe-rich overgrowth rims developed.
from destruction and salvaging of the host olivine components (Figure 144). The majority of phenocrysts (> 60 %) from both lavas possess very thin (≤ 2 µm) rims outside of their crystal boundaries which display Mg and Ni enriched relative to the groundmass, but lower than olivine concentrations, and the inverse pattern for Fe and Mn content (Figure 139). These rims appear to be qualitatively similar in composition to groundmass microcrysts of clinopyroxene, but are too thin for their stoichiometric makeup to be confidently resolved by microprobe. Alternatively (or additionally), these rims may represent compositional boundary layers (e.g. Zellmer et al., 2016), enriched in olivine-compatible elements which have diffused through the melt toward the lattice but were left un-precipitated as the thermal window for olivine crystallization came to a close.

Concentration of Mn in olivine phenocrysts (Figure 141; Figure 145) from Cerro Overo and La Albóndiga is depleted at crystal cores (~ 0.18 wt %) and highly enriched in the of rapid skeletal overgrowths (up to 0.50 wt %), even relative to the low forsterite olivine immediately surrounding the high forsterite cores (~ 0.30 wt %). The concentration zoning of Co and Ca mirror Mn and thus were not collected for most mapping runs to reduce analytical time. Nickel content is highly enriched (0.20 – 0.45 wt %) at the crystal cores relative to the rims (below detection to 0.20 wt %, averaging ~ 0.08 wt %) and nearly completely absent from the surrounding groundmass + microcryst assemblage (Figure 140). Al₂O₃ concentration is low (~ 100 ppm), but homogenous throughout each phenocryst. Where multiple olivine crystals are joined (e.g. Figure 153), they all shown identical crystal orientation, and separate but fused (continuous) high Fo %/high Ni cores not separated by lower forsterite growth, indicating these unions are inherited from higher temperature olivine precipitation early in the magmatic history.

In some samples from La Albóndiga dome lava, the olivine phenocrysts have thin, micron-scale (reaction) rims of microcrystalline overgrowth, (possibly iddingsite or phlogopite ± magnetite) (Figure 144). The interface between the olivine and any existing rim is generally convoluted and irregular, suggesting the overgrowth material is derived from the phenocrysts themselves. These rims are more pronounced on skeletal growth features and can contain a significant portion of Fe-oxides concentrated at the inner regions of the rim. Some olivine phenocrysts from Puntas Negras, particularly those from the lower, more plagioclase and pyroxene rich flows display resorption of olivine recrystallizing as parasitic clinopyroxene (Figure
This feature is not widespread and appears to require a pre-existing microphenocrysts of clinopyroxene which begins to form from olivine components presumably when magmatic conditions have shifted from those favorable to olivine crystallization to those (lower temperature, more evolved), which preferentially promote pyroxene precipitation.

Olivine phenocrysts (0.5 – 5 mm) from the basaltic andesite of the Puntas Negras mafic lava flow display nearly euhedral and/or partially-infilled, irregular skeletal crystal habit. Smaller (0.7 – 2 mm) subhedral to euhedral phenocrysts are much more common (up to 75 % of the population) in earlier erupted Lower Flows which are also distinguished by more developed plagioclase microphenocrysts, clinopyroxene phenocrysts, and an overall more fully-crystallized groundmass. The Lower Flows also contain euhedral plagioclase crystals with sieved cores. The Upper Flows are dominated by large (1 – 6 mm) olivine phenocrysts (up to 70 % of the population) which commonly show irregular skeletal or hopper style growth which has experienced additional incomplete in-fill crystallization. However, across both flow groupings and their respective crystal morphologies, the composition of olivine is identical. The phenocrysts display high forsterite cores (79 – 83 Fo %) which generally follow the shape of the overall crystal form (Figure 146; Figure 147; Figure 148) and 25 – 50 μm lower forsterite rims ranging 68 – 70 Fo %. Zoning is normal for Mg and Ni content and reverse for Fe and Mn throughout all crystals. When present, skeletal overgrowths display zoned element concentrations (i.e. overgrowths possess higher forsterite and Ni cores) (Figure 146; Figure 148). Overgrowth rims on Puntas Negras olivine are not dominantly dendritic or skeletal, but generally follow the pre-existing morphology indicated by the high forsterite cores with only occasional skeletal development (e.g. Figure 147). Groundmass olivine crystals (0.05 – 0.5 mm) display the same compositional range as the low forsterite overgrowths and do not show any significant zoning, but are frequently mantled or intergrown with clinopyroxene. Some of the olivine phenocrysts (e.g. Figure 147) also display co-crystallization with clinopyroxene. In some cases, especially in the Lower Flows, phenocrysts are observed breaking down to contribute to adjacent clinopyroxene. The majority of phenocrysts (> 85 %) from Puntas Negras possess very thin (≤ 3 μm) rims outside of their crystal boundaries enriched in olivine components relative to the groundmass, similar to Cerro Overo and La Albóndiga.

Compositionally, there is not a continuous core to rim progression across Puntas Negras phenocrysts, as there is with Cerro Overo and La Albóndiga olivine (Figure 162 - Figure 166).
Rather, the phenocryst cores and rims of Puntas Negras appear to have grown in two separate magmatic environments, separated by an intervening period of resorption or non-crystallization. This core-rim compositional gap is visible in the forsterite content (a sharp 82 - 73 Fo % drop) (Figure 162), the concentration of divalent minor element Mn (0.18 – 0.26 wt % at the cores, 0.39 – 0.50 wt % in the rims) (Figure 164), and in trace elements such as Ca (0.13 – 0.17 wt % at the cores, 0.22 to 0.30 wt % in the rims) (Figure 165). In general, Puntas Negras phenocrysts display lower forsterite content, lower Ni concentration, and higher Mn and Ca content compared to respective core/rim locations in Cerro Overo olivine. These compositional traits indicate the Puntas Negras olivine developed from more differentiated magma.

Micron scale P-enriched zonation enriched defines internal skeletal to dendritic olivine architecture not observed in the distribution of other, more compatible elements in Cerro Overo and La Albóndiga olivine (Figure 150 - Figure 155). The fine-scale P structure indicates the phenocrysts from these lavas experienced regular cycles of diffusion-controlled growth at high supersaturation extending rapidly and diagonally from crystal corners, followed by a slower stage of interface-controlled growth and diffusive relaxation of the melt boundary layer (Milman-Barris et al., 2008; Welsch et al., 2012; Welsch et al., 2014; Shea et al., 2015). The portion of the P-enriched architecture visible in thin section varies significantly with the location and angle of the cutting plane passing through each phenocryst, producing a wide array of two-dimensional zoning patterns (Figure 167). Crystals intersected nearly oblique to the olivine c-axis display ordered, repetitive concentric zoning (Figure 151; Figure 154) (Welsch et al., 2012). Crystals intersected at an angle to crystallographic axes/planes can display relatively complex internal architecture (Figure 152). These fine scale zonations enriched in P represent periods of rapid olivine crystallization and inclusion of impurities in the lattice. The absence of P-zoning at the rims of specific phases of some phenocrysts is evidence for removal of material or suppression of late stage olivine growth.

The olivine of Puntas Negras, Cerro Overo, and La Albóndiga all display some degree of P-zoning in their crystal cores suggesting euhedral olivine morphology and a sequence of parallel zones in the outermost overgrowth rims. Cerro Overo and La Albóndiga olivine prolifically display zinging throughout the crystal body, continually from core to rim (e.g. Figure 153). Puntas Negras olivine, on the other hand, commonly shows a significant gap in P-enriched traces between the zoning at the core and the more recent zoning at the rim (e.g. Figure 155).
The reason for this is not entirely clear. Middling zonation may have partly been removed by resorption. Puntas Negras may have grown at different time scales than Cerro Overo olivine, with greater temporal and/or compositional gaps between rapid growth phases. Alternatively, phosphorous may have been less available in the parental melt, although whole rock composition is higher in P₂O₅ than Cerro Overo, suggesting this is not the case (Figure 116). It is possible that P-zoning has been dampened or partially erased in Puntas Negras olivine by diffusion while the crystals resided in a magma above the olivine closure temperature (630° – 984° C) (Watson et al., 2015 and references therein). The resorbed appearance of the high Mg/high Ni cores common to Puntas Negras olivine is in agreement with some length of high temperature storage (Figure 146). However, the time scales required for dampening of P-zoning in olivine is poorly constrained, with estimates ranging from a few weeks to over 5 months at basaltic temperatures (Watson et al., 2015; Shea et al., 2015).

Zoning patterns of P near crystal cores of complex olivine phenocrysts also reveals an architecture of several different crystal cores fusing or aligning and later growing together to form a larger conglomerate which shares more recent growth features (e.g. Figure 152). Widespread similarity in the size of the crystal cores delineated by regular P-zoning in Cerro Overo and La Albóndiga olivine of around 90 – 120 µm suggests early crystallization history of this magma involved an incipient period of cyclical rapid-slow olivine precipitation. This core-forming growth stage may represent lower crustal storage wherein the magma differentiated by olivine crystallization and MASH processes until it was re-mobilized at a density able to reach the surface. P-zone defined cores in Puntas Negras are less clear and do not commonly show cyclical banding, although they do cluster in size around 300 – 400 µm and display elongated form (e.g. Figure 154; Figure 155).

Resorption surfaces or embayments are common for all studied phenocryst populations, but usually visible on only one or two crystal faces, implying a possible chemical or thermal gradient. The increased density of asymmetric crystal forms in Cerro Overo basaltic andesite (relative to La Albóndiga and Puntas Negras) agrees with anisotropic crystallization conditions induced by magmatic gradients as it is the only sampled lava of this study displaying prolific felsic xenoliths. Destructive features in Cerro Overo olivine are visible not only as disruptions in crystal outlines, but are also discernable in forsterite content, with the lower-Fo rim missing or truncated at a crystal edge (Figure 140; Figure 142). Incomplete and altered outer crystal rims
provide another complication in interpreting diffusion profiles. Mineral (dominantly Cr-spinel, rarely Fe-Ti oxides) inclusions are common in all phenocrysts, ranging from 5 – 30 μm across, with few outlying exceptions. Spinel inclusions are frequently found in clusters or defining relict crystal faces in the interior of phenocrysts, indicative of specific periods of magmatic conditions conducive to spinel growth and/or capturing (Figure 168 - Figure 173; Figure 174). The Cr-spinel mineral inclusions in olivine are distinct from any of the microcrystic groundmass oxides, but the Fe-Ti oxides at olivine rims are similar to the widespread groundmass oxides. Melt inclusions in Cerro Overo and La Albóndiga olivine are relatively common, often taking the form of glassy inclusions near crystal centers (Figure 150). Melt inclusion are less ubiquitous in Puntas Negras olivine, much smaller (< 10 μm in most cases) and frequently turn out to be connected to the host magma (Figure 148).

Both melt and mineral inclusions are found almost exclusively in the lower-P zones in between the struts of dendritic growth (Figure 85). In the rare occasion where mineral inclusions interact with P-enriched zones, the internal structure defined by high-P is truncated by the inclusion. This relationship indicates trapping of melt and sealing of spinel inclusions within olivine phenocrysts occurs during the slower, interface-controlled growth stages (also observed in the study of Welsh et al., 2012), and the inclusions are not the result of the impurity-enriched boundary layer that forms around rapidly crystallizing minerals (e.g. Zellmer et al., 2016). As the melt inclusions are captured during the slower growth periods where the melt surrounding the precipitating olivine has time to re-equilibrate with the far-field magma composition through diffusion, inclusions remain justifiable representatives of magmatic evolution. The correlation between skeletal growth and inclusion formation also implies rapidly-forming skeletal framework may be instrumental in initial melt inclusion formation, subsequently sealed in by slower, interface-controlled growth (e.g. Welsch et al., 2014). Trapping by skeletal growth is in agreement with the morphology of many non-rounded melt inclusions which show a morphology reflective of dendritic or skeletal growth from olivine corners (Figure 150).
Modeling of Diffusion Timescales

Forward modeling from a sharp (immediate) boundary between low and high Fo % was carried out using the discretized numerical methods to analytical solutions published by Costa et al. (2008) (Figure 149). After defining boundary conditions, one attempts to match the observed diffusion profile to one of several modeled profiles with different $\Delta t$, representing the time elapsed for each crystal at temperatures high enough to incur Fe-Mg diffusion. Pressure and temperature inputs were informed by thermometry and barometry based on whole-rock and/or olivine compositions to encompass a range of potential solutions. Additional diffusion timescale approximations were carried out with the diffusion equation solution and chemical diffusion coefficients of Spandler & O’Neill (2010) (Equation 18). This model is experimentally calibrated to both trace and major elements, but unfortunately the model is calibrated to higher forsterite (~ 90 Fo %) olivine residing at 1300°C, neither of which are conditions mirroring the natural samples of this study. Regardless, the diffusion solution can be used to roughly estimate the time needed to generate the observed profiles, and has the added advantage of direct comparison of forsterite zoning with Ni/Mn zoning.

Results were highly variable for both modeling approaches, ranging from < 6 hours up to 2 weeks for Cerro Overo and from ≤ 3 days up to 3.6 weeks for Puntas Negras. Temperature and pressure inputs were based on values calculated from olivine-based and liquid-based geothermometers and barometers which define a broad range of temperatures at which diffusive re-equilibration has occurred (Table 17). Estimates from major element (Fe) versus Mn/Ni zoning produced approximately equivalent time frames from Equation 18, suggesting that the variability in profile shape (Figure 141) is due to differences in diffusion coefficients and the intensity of the chemical gradient and not multiple magmatic residence stages. The change in concentration of Ni especially is much greater between the olivine core and the surrounding melt (groundmass) than the gradients for Mg, Fe, or even Mn (e.g. Figure 141). Negligible concentrations of Ni outside of the crystals with high Ni cores have created much greater chemical gradients and thus the effect of diffusion on the compositional profile is more extreme (Figure 145). Overall, even complex diffusion modeling cannot fully account for the quickly changing magmatic environment preceding eruption and is best suited for investigating timescales of magma chamber storage in relatively stable conditions (e.g. Costa et al., 2008). In addition, calibration data for these models is derived largely from experimental samples under
highly controlled conditions. Diffusion profile shape is also highly dependent on crystal orientation as elements diffuse at different rates along the [100], [010], and [001] crystallographic axes of olivine (Spandler & O’Neill, 2010; Shea et al., 2015), and the orientation of natural crystals in this study was not measured directly, but estimated based on crystal habit and the orientation of P-zoning (Table 28). As such, the above estimates indicate relatively brief periods of diffusive re-equilibration in olivine phenocrysts, precluding prolonged magma storage on the order of months, years, decades, etc. The greater estimates of residence time for Puntas Negras olivine is likely to represent a real difference in magmatic history from Cerro Overo and La Albóndiga. Not only are the measured diffusion profiles wider and more gradual for Puntas Negras olivine, but internal morphology of the high Fo % / high Ni cores suggest a period of olivine resorption before subsequent addition of lower temperature olivine, and more developed plagioclase crystals in Puntas Negras lava agree with a longer period of sub-surface cooling and crystallization than seen for Cerro Overo lava.

\[
\frac{c_i - c(x)}{c_i - c_0} = \text{erf} \left( \frac{x}{2(D_Mt)^{0.5}} \right)
\]

Equation 18 – The solution to the diffusion equation of Spandler & O’Neill (2010) for one-dimensional diffusion into a semi-infinite slab with constant melt composition maintained at the crystal interface. The chemical diffusion coefficient \(D_M\) of major and trace elements was experimentally calibrated by Spandler & O’Neill (2010) for San Carlos olivine at 1300°C. The measured values include distance \(x\), the concentration at the interface \((x = 0)\) \(c_i\), and the initial concentration \(c_0\). Time diffusing \(t\) is varied until the composition profile defined by \(c(x)\) approximately matches the measured concentration of the natural olivine. erf is the error function.

Table 25 - Summary of olivine forsterite content in basaltic andesite of the Altiplano-Puna region.

<table>
<thead>
<tr>
<th>Average Fo%</th>
<th>Core</th>
<th>(n_{\text{core}})</th>
<th>Rim</th>
<th>(n_{\text{rim}})</th>
<th>Groundmass</th>
<th>(n_{\text{GM}})</th>
<th>Liquid*</th>
<th>(n_{\text{liq}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo</td>
<td>86.3 ± 0.9</td>
<td>107</td>
<td>78.7 ± 3.2</td>
<td>89</td>
<td>79.8 ± 4.4</td>
<td>6</td>
<td>64.9 ± 0.3</td>
<td>15</td>
</tr>
<tr>
<td>La Albóndiga</td>
<td>85.8 ± 1.7</td>
<td>51</td>
<td>77.6 ± 2.0</td>
<td>58</td>
<td>78.1 ± 1.2</td>
<td>10</td>
<td>64.9 ± 0.4</td>
<td>13</td>
</tr>
<tr>
<td>Puntas Negras</td>
<td>83.1 ± 2.3</td>
<td>29</td>
<td>68.6 ± 2.4</td>
<td>23</td>
<td>67.7 ± 0.2</td>
<td>8</td>
<td>59.5 ± 1.4</td>
<td>15</td>
</tr>
</tbody>
</table>

*Liquid Fo% is calculated from whole rock (bulk) measurements of MgO and FeO\(^{\text{total}}\).
Trace Element Characteristics of Igneous Olivine

Lava from Cerro Overo maar has previously been used as a compositional representative for mafic recharge in mid to upper crustal magma chambers and for primary melts before significant crustal influence for magma batches which have risen through central Andean crust (e.g. O’Callaghan & Francis, 1986; Matthews et al., 1999; Rosner et al., 2003; Mattioli et al., 2006). Olivine phenocrysts are forsteritic (average 86.3 Fo %) and high in nickel, with microprobe measurements of phenocrysts ranging 1260 – 3500 ppm Ni at their cores (Figure 163). The high Ni content of the dominant phenocryst of Cerro Overo lava is reflected in the elevated Ni content of the bulk rock (120 ppm average), which are easily the most Ni-rich rocks in the Altiplano-Puna region (Figure 132). The olivine chemistry for Cerro Overo and La Albóndiga follow contiguous trends where forsterite content (i.e. how unevolved the parental melt was) is positively correlated with Ni content and negatively correlated with Mn, Co, and Ca content (Figure 163 - Figure 181). Charts of Ni/Co versus an indicator of evolution (e.g. Fo %) show the two elements follow a roughly exponential, coupled evolution (Figure 175). Such a trend is expected for olivine crystallizing from a mantle-derived melt which includes no contribution from plume (i.e. hotspot) activity (Sobolev et al., 2007).

Cr content of the olivine phenocrysts follows a more inscrutable trend with the majority of Cerro Overo crystal compositions ≤ 450 ppm Cr and a minority (~ 26 %) displaying greatly elevated Cr values (up to 2170 ppm) at equivalent forsterite contents (Figure 176). Only a small handful of measurements from La Albóndiga olivine cores and crystal rims from both basaltic andesites exceed 500 ppm and no olivine composition from Puntas Negras – El Laco exceed 250 ppm Cr. It is quite possible that these elevated Cr measurements do not purely represent olivine compositions, but rather represent microprobe measurements which have included Cr values from micro-inclusions of Cr-spinel. High-resolution elemental X-ray maps of individual phenocrysts reveal such micro-inclusions are indeed present in Cerro Overo and La Albóndiga olivine. Thermobarometry calculations based on Al partitioning between olivine and Cr-spinel similarly resulted in occasional illogical crystallization temperature estimates (1550 – 2300 °C for 80 – 85 Fo % olivine) due to analyses which included, in part, the high Al content of spinel micro-inclusions. Encouragingly, such anomalous results for either Cr or Al content were not measured for olivine from Puntas Negras – El Laco lava which does not display spinel micro-inclusions in elemental maps. Chromium content in olivine from mantle-derived melts is
strongly controlled by the amount of spinel and garnet in the source material (Sobolev et al., 2007; Walter et al., 1998). Olivine Cr contents of ≤ 500 ppm for crystals with forsterite content ≤ Fo91 can be interpreted as crystallized from a melt generated with significant Cr-spinel in the restite (Sobolev et al., 2007; Hauri et al., 1996). The asthenospheric source would have to have experienced high-degrees of melting to incorporate Cr-rich phases, such as spinel. A lack of relative Heavy Rare Earth Element depletion (Sm/Yb = 2.4 for Cerro Overo) supports an interpretation that these magmas were generated outside of the garnet stability field, but rather in conditions favorable to spinel-bearing asthenosphere.

Of all the parameters discerning the origin and evolution of olivine crystallization modeled by the extensive review of forsteritic olivine by Sobolev et al. (2007), the Mn/Fe ratio is the index least dependent on olivine fractionation and can be considered diagnostic of differences in the composition of the primary magma. The value of the Mn/Fe ratio is relatively invariable (Mn/Fe = 1.1 – 1.6) across the compositions of olivine cores from Cerro Overo, La Albóniga, and the olivine from Puntas Negras – El Laco, indicating all three magmas are derived from melting of similar material (Figure 177). Phenocryst rims range Fo65 to Fo84 for the three volcanic centers, yet measured Mn/Fe is similarly limited (1.5 – 2.0). The exception is olivine rims displaying reaction rims from Cerro Overo and La Albóniga, which show depletion in Fe relative to Mn (Figure 177). The work of Sobolev et al. (2007) also determined a relationship between the Mn/Fe ratios of olivine grown from mantle-derived melts and the amount of pyroxenite (versus peridotite) in the melt source. The amount of pyroxenitic endmember (Xpx) in the melt source could be described by a simple linear relationship for experimentally grown equilibrium olivine compositions (Equation 19).

Equation 19 – The fraction of pyroxenite endmember in the melt source (Xpx) is related to the Mn/Fe ratio of olivine grown from the melt by a simple linear function for experimental olivine compositions produced at high temperatures and pressures (Sobolev et al., 2007).

\[
X_{px} = 3.48 - 2.071 \times (100\frac{Mn}{Fe})
\]

This estimate of the fraction of pyroxenite-derived component was calibrated to olivine grown at high temperature and pressure and its usefulness has not been investigated for a wide range of compositions or magmatic conditions. The thick lithosphere of the Central Andes does
provide barometric conditions for the source within the calibrations of Sobolev et al. (2007) and initial attempts in applying the pyroxenite-component estimator to a wider range of magmatic settings were hopeful, but the approximation has not been widely applied to arc magma nor olivine not fully crystallized directly in the mantle. Regardless, I applied the calculation to equilibrium olivine core compositions from Cerro Overo, La Albóndiga, and Puntas Negras as a semi-quantitative investigation of the source (Figure 182 - Figure 184). These results should not necessarily be interpreted as the true fractions of pyroxenite in the melt, but rather estimates of relative source heterogeneity within magma batches and source variability between magmas. Histograms of the amount of pyroxenite-derived melt in the source calculated for 189 olivine cores from Cerro Overo (Figure 182) and 109 from La Albóndiga (Figure 184) both show wide distributions ranging from 0.0 (0 %) to 1.0 (100%) pyroxenite with peaks centered around 0.40 – 0.55. Results for Puntas Negras olivine (Figure 184) are more obtuse, but suggestive of a peak at ≤ 0.25 pyroxenite-derived fraction of the melt. The variability (i.e. standard deviation) of the calculated fractions is very high for all samples (Table 26), approaching the average calculated fraction. The applicability of the model is questionable in this context, but these numbers may actually reflect a reality of extensive mixing and re-homogenization of a wide range of mantle-derived melts in MASH zones at the mantle-crust boundary (e.g. Delph et al., 2017).

Table 26 – Summary of estimates of the fraction of pyroxene-derived component in the parental melt calculated from the Mn/Fe ratio of olivine phenocryst cores (Equation 19) after the methods of Sobolev et al. (2007).

<table>
<thead>
<tr>
<th></th>
<th>Average X_{px}</th>
<th>Standard Deviation (1σ)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Overo</td>
<td>0.377</td>
<td>± 0.263</td>
<td>189</td>
</tr>
<tr>
<td>La Albóndiga</td>
<td>0.556</td>
<td>± 0.510</td>
<td>109</td>
</tr>
<tr>
<td>Puntas Negras</td>
<td>0.354</td>
<td>± 0.244</td>
<td>52</td>
</tr>
</tbody>
</table>
Discussion

Micron-scale zoning of phosphorous in olivine phenocrysts from Cerro Overo maar/La Albóniga dome and the Puntas Negras mafic lava flow indicate a crystallization history for both lavas consisting of cyclical rapid skeletal growth followed by slower infilling crystallization (e.g. Welsch et al., 2014). Crystal growth rates determined from experimental studies suggest P-rich frameworks develop on the order of minutes of rapid growth, followed by P-poor ingrowth occurring on time scales of weeks to months (Jambon et al., 1992; Welsch et al., 2014; Shea et al., 2015), evolving from skeletal or dendritic into euhedral crystal form. Thermal exchange between a magma batch and its environment is prohibitively slow at depth and unlikely to produce the dendritic crystallization indicated by P content by rapid cooling. Rather, rhythmic enrichments of incompatible elements in olivine reflects cycles of diffusive depletion and re-enrichment at crystal growth fronts. Melt and mineral inclusions were produced as boundary layers depleted in olivine components (Mg, Fe, Si, Ni, Mn, Co, ± Ca) at the forefront of rapidly crystallizing olivine (e.g. Zellmer et al., 2016) led to the growth and/or capture of Cr-spinel and melt within the zones of interface-controlled (i.e. slow infilling) olivine development. Internal crystal architecture defined by P content suggests Cerro Overo and La Albóniga olivine experienced continuous core-rim olivine growth with a final stage of rapid skeletal crystallization generated by undercooling in the melt during or immediately preceding eruption. These patterns are evidence for relatively unimpeded magmatic ascent since processing in the lower crustal MASH zone. P zoning patterns across Puntas Negras olivine display separate core versus rim compositions and morphologies indicative of two distinct stages of crystallization. The higher forsterite cores developed complex, often skeletal morphology until the magma briefly (days to weeks) stalled or entered storage in the upper crust, and subsequently experienced partial maturation by infilling of lower forsterite olivine after an intervening period of resorption and/or non-crystallization.

Olivine Morphology and Crystallization Kinetics

Olivine phenocrysts from rare mafic monogenetic centers in the arc of the Central Andes display well-formed, high-forsterite, high Ni cores with skeletal overgrowths of low-forsterite and low-Ni olivine which display fine scale, parallel P-enriched zonation. These consistent features near crystal rims indicate a final stage of crystallization that was rapid and controlled by
diffusion of the growth front through the melt (e.g. Shea et al., 2015). Complex internal P-
zoning indicates within the olivine cores for all three lavas is evidence the earlier-formed high
forsterite olivine developed through consistent crystallization oscillating between rapid
diffusion-controlled growth and slower interface-controlled growth at relatively regular
intervals. The majority of the P-zoning patterns mirror the overall final crystal form (excluding
low forsterite overgrowth) (e.g. Figure 151). Cerro Overo maar and La Albóndiga dome lava
display this complex zoning continually from core to rim. Puntas Negras olivine displays a gap in
P-zoning indicative of resorption and/or dampening of P-zoning by prolonged residence in high
temperature magma. A smaller population of crystals displays zoning indicative of a change in
the habit, associated with the fusion of two or more crystal cores into a single crystallizing unit.
Zoning is absent at the junction of crystals and zoning in parallel between joined crystals,
indicating fusing of co-crystallizing phenocrysts occurs along identical crystal faces.

Deviations from simple core/overgrowth geometry in some phenocrysts, such as higher
forsterite olivine in direct contact with the groundmass (Figure 142), indicate variations in
localized crystallization environment (e.g. Welsch et al., 2014). Thermal gradients in the
crystallizing melt are the most likely cause of these deviant crystal geometries as the
morphology does not suggest mechanical alteration of crystal form (i.e. breakage). As the
phenocrysts of Puntas Negras and La Albóndiga do not display such forms in the same
abundance as Cerro Overo, it is likely these local effects are a result of the introduction of
relatively cold felsic xenoliths to Cerro Overo basaltic andesite immediately preceding and
during eruption and not simply crystallization near the outermost boundary of each lava. The
introduction of xenolithic material, from which felsic glass was added to the lava (Figure 137;
Figure 37), may have induce localized thermal gradients with undercooling at rates greater than
2400°C/hour (40°C/minute), impeding olivine crystallization (Jambon et al., 1992).

The outermost rims of olivine phenocrysts and the groundmass olivine
microphenocrysts in the basaltic andesite of this study represent continued crystallization of
olivine as the lavas reached the uppermost crust and eruption. Skeletal olivine growth, such as
that seen along the outer margins of Cerro Overo and La Albóndiga phenocrysts and
microphenocrysts has been estimated to develop at a rate of ~10^{-7} \text{ m s}^{-1} (0.1 \mu \text{m per second})
(Table 24). Extensions of skeletal growth extend 28 – 123 \mu \text{m amongst all the olivine examined,
but are generally closer to the average thickness of ~ 75 \mu \text{m (Table 27). Overgrowths of this size

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could have developed over 230 seconds (3.8 minutes) to 1280 seconds (21.3 minutes) with an average growth time of around 750 seconds (12.5 minutes). The low forsterite rims on Puntas Negras olivine fall within this range as well, if fine-scale P zoning is interpreted as representing rapid (i.e. skeletal) growth. These estimates are derived from the results of experimental work (Welsch et al., 2012 and references therein) under ideal crystallization conditions, and therefore represent minimum estimates as in the natural, turbulent setting of volcanic eruptions, the necessary crystal components (Fe, Mg) will not necessarily be available in abundance, as indicated by the wide range in composition for groundmass glass in the studied basaltic andesites (Figure 137). The lower forsterite content of the skeletal overgrowths (and groundmass olivine crystals) indicates they were developed under different magmatic conditions than the crystal cores, and micron-scale P-enriched zonation supports a model of rapid growth (Figure 151 - Figure 155). The low degree of diffusive relaxation of the divalent cations seen either enriched (Fe, Mn) or conversely depleted (Mg, Ni) in the outermost thin skeletal rims of the olivine is evidence these crystals did not experience prolonged residence in hot magma. Welsch et al. (2012) estimate euhedral macrocrysts (0.5 – 5 mm), such as those forming the cores of Cerro Overo phenocrysts, could be crystallized in as little as 8 min up to 58 days.

Geothermometry calculations (Chapter 2) suggest an eruptive temperature of ~ 1130-1170°C for Cerro Overo and ~ 1165-1170°C for Puntas Negras lava. Groundmass plagioclase-based thermometry indicates equilibrium crystallization at ~ 1090°C at Cerro Overo. Groundmass clinopyroxene composition in Puntas Negras suggests equilibrium crystallization at ~ 1115°C. These broad estimates of temperature range and rate of crystallization lead to an incredibly wide estimate of cooling rates for both lavas spanning approximately 200 – 1600°C per hour. Despite ranging over an entire order of magnitude, these rough approximations of cooling are well within the range of conditions for diffusion-controlled skeletal olivine growth (47 – 1890 °C h⁻¹) (Table 24). Groundmass crystallization within the gaps between branching growths of individual olivine phenocrysts in many cases encompasses the entire space with well-developed clinopyroxene or plagioclase (Figure 185), indicating the continued growth of these lower temperature phases after the cessation of olivine formation. Overgrowths of lower forsterite olivine and the development of skeletal olivine microphenocrysts in the groundmass of a lava do not necessarily imply accelerated olivine crystallization during a rapid ascent (e.g. Mattioli et al., 2006), but rather eruption of lava at temperatures high enough (and
compositions with enough available Fe and Mg) to continue crystallizing olivine. The estimated cooling rates and time required to form the observed skeletal overgrowths indicates the final growth phase of olivine did not occur during rapid quenching (e.g. quenching due to water-magma interaction), but immediately preceding, during, and following eruption in a period of agitation, gas exsolution, and cooling at a rate < 2000°C/hour (Faure & Schiano, 2004; Welsch et al., 2012).

Boundary layers enriched in olivine components are the result of a rapidly cooling and crystallizing lava (e.g. Milman-Barris et al., 2008; Zellmer et al., 2016). Very thin (< 2 µm) layers at the outermost boundaries of olivine phenocrysts show enrichment in Fe, Mn, Ni, and Mg and depletion in K, Al, and ± Ca relative to the groundmass glass. These elements are inversely enriched or depleted relative to the phenocrysts themselves. The thin boundary layers display compositional enrichments and depletions opposite to those of enclosed melt inclusions comprised of melt excluded from olivine formation (Figure 150; Figure 147; Figure 139). These thin outer boundaries do not show discernable enrichment in P, indicating the completion of the phase of rapid olivine growth, which concentrates P at the liquid/crystal contact by ~ 20 wt % (Milman-Barris et al., 2008). We propose thin boundary layer features represent small amounts of melt around each growing olivine phenocrysts enriched in the elemental components of olivine. At the final stages of olivine crystallization, as rapid skeletal growth came to a close, elements diffused through the melt either toward or away from the melt/crystal interface to provide the atoms needed for additional olivine formation. However, as the lava cooled below crystallization temperatures, a very thin layer of melt primed to produce additional olivine developed without crystallizing. These boundary layers are essentially transient zones of enrichment in olivine material (Mg, Fe, Si) which would have begun to form slower, interface-controlled euhedral olivine growth had the lava not cooled to a degree where olivine was no longer energetically favorable. In some cases, this has caused microcrystals of pyroxene (Puntas Negras) or Fe-oxides (La Albóndiga) to form.

Iddingsite results from the reaction of H₂O, other gases, and olivine at low pressure, intermediate temperature, and highly oxidizing conditions. Rims of iddingsite are present on olivine phenocrysts from La Albóndiga samples collected near the outer surface of the lava dome, but are rare for Cerro Overo maar olivine and absent from Puntas Negras lava flow phenocrysts. The reaction rims on La Albóndiga olivine (and Cerro Overo to a lesser degree)
were likely produced post- or near eruption as the lava interacted with the atmosphere and thermal gradient at the surface. This would explain why the olivine phenocrysts in most Cerro Overo thin sections do not display these reaction rims, as the lava was thick enough in many places to have insulated its crystal cargo and shield it from the oxidizing conditions of the exterior. The lava sampled at the exterior surface of La Albóndiga dome, however, is notable for its consistently higher vesicularity and the presence of this reaction rim on nearly every olivine phenocryst observed. The vesicular nature of these rocks is clear evidence of the widespread interaction between lava and volatiles as the lava dome degassed when it breached the surface (or at least came near). The rusty color of the surficial lava of La Albóndiga lava is additional evidence for widespread oxidation in the outermost lava through interaction with volatiles. Oxidized lava surfaces are present at Cerro Overo, but to a much lesser extent, and associated with lava flow exterior features, such as pahoehoe ropes.

Inclusions of melt and/or oxides are well-correlated with internal P-zoning of olivine phenocrysts, found exclusively within the more slowly grown low-P regions and not intersecting with the P-enriched dendritic zones (Figure 85). Often, spinel follows the crystal habit represented both at external faces and by internal P-zoning. Mineral inclusions in the interior of Cerro Overo and La Albóndiga olivine consists solely of Cr-spinel, although crystals of magnetite are occasionally found at phenocryst rims, in contact with the host magma (Figure 144;). Puntas Negras olivine displays both Cr-spinel and Fe-Ti-oxide inclusions in crystal interiors, likely due to the bulk Fe enrichment of the lava due to fractionation of Mg-rich phases and the corresponding crystallization of higher Fe content (lower forsterite) olivine (Table 25). Oxide and melt inclusions are commonly found together, often with a small pocket of glass at the edge of a larger spinel inclusion (Figure 170). Cr-spinel is unlikely to crystallize from trapped melt as it would require an unreasonably high concentration of Cr in the trapped liquid (Welsch et al., 2012). Melt inclusions around spinel generally do not show significant enrichment in the slow-diffusing impurity elements (Al, Cr, P) relative to the groundmass, indicating that trapped melt associated with oxides was in diffusive contact with the surrounding bulk melt composition up to the point of sealing. In fact, the melt inclusions which do display enrichment in incompatible elements do not also include spinel crystals and are dominantly (possibly exclusively) associated with enclosure in rapidly grown skeletal struts (e.g. Figure 150; Figure 151). Rather, spinel nucleation may be a result of Cr enrichment in the boundary layer developed at the growth front of diffusion-controlled, rapidly-crystallizing olivine. When olivine growth enters the
slower, interface-controlled growth stage, spinel will have been chemically encouraged to grow within the incompatible element enriched hollow hoppers of the skeletal/dendritic crystal. As slow olivine growth fills the hopper regions, oxide crystals are trapped as inclusions.

**Conclusions: Magmatic History Recorded by Olivine Growth**

Growth-induced compositional zoning in olivine extends from crystal apexes, while diffusion-generated zonation runs mutually perpendicular to crystal lattice orientations (Shea et al., 2015). Zoning of immobile impurity P preserves the growth patterns of crystals, but due to diffusive relaxation, the concentric zoning in compatible divalent elements Mg, Fe, Ni, and Mn does not necessarily preserve compositions reflective of magmatic conditions at formation (e.g. Milman-Barris et al., 2008). Broadly, Cerro Overo, La Albóndiga, and Puntas Negras olivine all display high Fo % cores and low Fo % rims with concentric, slightly smaller (70 – 80 % width) high Ni cores with complementary high Mn rims (Figure 139 - Figure 148). The boundary between high and low forsterite content (Fe, Mg) is generally sharper than the high-low Ni transitions, which are more gradual (Figure 141). However, major element zoning generally follows the growth orientation of internal skeletal P-zoning (i.e. crystal apexes), suggesting at least some of the observed Mg/Fe/Mn/Ni zoning is due to crystallization and not purely a result of diffusion, which would have created a gradient perpendicular to lattice orientation (Figure 150) (see Shea et al., 2015 for an example of the opposite case). Cerro Overo and La Albóndiga olivine major element zoning is symmetric around the crystal cores, both in morphology and in concentration profiles, following the growth directions indicated by P-zoning.

Puntas Negras olivine chemical zoning is more difficult to categorize, as the high forsterite zones display a high degree of irregularity in many of the phenocrysts (e.g. Figure 148; Figure 155). Phenocrysts with euhedral form, however (e.g. Figure 154) display more regular and symmetric profiles, quite similar to Cerro Overo olivine. As the concentration gradients of Fe-Mg and Ni zoning has been well-documented to extend more along the c axis of olivine than along the a axis (anisotropic zoning), asymmetry is considered a sign of significant diffusive re-equilibration in olivine. This does not imply these olivine have experienced no diffusive re-equilibration, but rather divalent compatible element zoning is not necessarily dominated by diffusion effects. The crystal forsterite content transitions from core values to the low forsterite at the melt/crystal boundary gradually, over an average of ~ 20-45 µm for Cerro Overo/La
Albóndiga olivine and ~ 50 -70 µm for Puntas Negras olivine (Figure 149). Modeling of diffusion profiles in forsterite and Ni content was not entirely conclusive, yielding time frames of several hours up to 2 weeks for Cerro Overo and from ≤ 3 days up to 3.6 weeks for Puntas Negras. These results, while not exact, do indicate very brief residence time at magmatic temperatures for Cerro Overo olivine, suggesting rapid ascent, while the slightly longer time frame for Puntas Negras crystals is in agreement with a brief period of stalling or storage (Figure 186).

The outer boundaries of the high Fo % and high Ni core zones in certain Puntas Negras olivine phenocrysts are highly irregular (Figure 146). This internal morphology suggests olivine which has experienced either periods of resorption or incomplete growth by infilling before addition of the lower forsterite material along its boundaries. Distinct from Cerro Overo and La Albóndiga phenocrysts, which show low forsterite overgrowth on a high forsterite core, the high Fo %/Ni regions of Puntas Negras crystals extend into the interior of skeletal growth struts (Figure 146). Additionally, while nearly all (> 90 %) of the Cerro Overo olivine displays some form of skeletal overgrowth, Puntas Negras olivine displays subhedral to euhedral morphology for up to 75 % of olivine phenocrysts in a sample. The crystals of Puntas Negras are also more likely to display skeletal/hopper morphologies if they are larger (> 1 mm) while groundmass olivine is uniformly subhedral. Cumulatively, Puntas Negras olivine appears to have experienced rapid skeletal (diffusion-controlled) growth at higher temperatures, reflected in the high Fo % of the interior of skeletal struts. Subsequently, the lower temperature/Fo % olivine was grown during slower, interface-controlled growth. Partially-infilled skeletal branches on larger phenocrysts represent incomplete maturation of crystal growth. An intervening period of olivine resorption is suggested by the rounded forms of the high Fo % cores in some of the phenocrysts (e.g. Figure 146; Figure 148), subsequently overgrown with lower temperature olivine. A petrogenetic history of rapid crystal growth, a pause in olivine crystallization, and then subsequent growth under different conditions (i.e., productive of olivine with lower forsterite content) is in agreement with the major and minor element composition of Puntas Negras olivine, which show discrete gaps in high temperature (e.g. high Ni, Fo %) and lower temperature olivine chemistry. Cerro Overo olivine, in contrast, shows unbroken continuity between core and rim/groundmass compositions, suggestive of continual olivine addition (Figure 162 - Figure 166).
Geobarometric calculations of groundmass plagioclase equilibrium for Cerro Overo yield surface pressures (-0.5 to +0.6 kbar), indicating syn-eruptive growth (Table 18). The same calculations for (the slightly larger) plagioclase from the groundmass of Puntas Negras, however, result in an average estimate of 6.9 ± 1.8 kbar, equivalent to approximately 25.5 ± 6.7 km depth. Whole rock barometry yields a similar pressure of 7.1 ± 2.9 kbar for Puntas Negras basaltic andesite. The greater depth of plagioclase crystallization at Puntas Negras over Cerro Overo is also reflected in plagioclase-based thermometry, estimated at ~1095°C for Cerro Overo and ~1170°C for Puntas Negras. Taken together, these results suggest Puntas Negras experienced a minor degree of storage, crystallization, and olivine resorption around the ductile-brittle transition (Prezzi et al., 2009). A depth of around 15 – 30 km has been broadly implicated in the CVZ as a density (and/or viscosity) barrier leading magma storage and the development of long-lived partial melt zones (e.g. Davidson et al., 1991; Zandt et al., 2003; Mattioli et al., 2006; Prezzi et al., 2009; Del Potro et al., 2013; Delph et al., 2017). Alternatively, or perhaps in addition to storage, the Puntas Negras magma may have experienced interaction with and assimilation with the widespread (>500,000 km³) partial melt zone known as the Altiplano Puna Magma Body (Perkins et al., 2016 and references therein). Plagioclase phenocrysts with sieved cores found only in the stratigraphically lower (i.e. first erupted) lavas of the Puntas Negras flows may represent a crystal cargo, despite having achieved equilibrium with the basaltic andesite magma at their rims. The difference in the later stages of magmatic history between the two lavas may be a result of the local tectonics of the upper crust (Figure 186). While both monogenetic volcanoes were erupted along the orogen-oblique Calama-Olcapato-El Toro (COT) transverse fault zone, Cerro Overo is additionally spatially correlated with an orogen-parallel antiformal feature which may be a splay of a larger thrust fault to the west (Figure 34). The additional crustal weakness presented by the intersection of the two structural features may have provided the pathway mafic lava requires to avoid stalling in or interacting with the felsic upper crust.
## Olivine Measurement Tables

Table 27 - Measurements of features from archetypical olivine from Cerro Overo (CO43), La Albóndiga (CO56), and Puntas Negras-El Laco (PN12). “Long axis” and “short axis” refer to the length of the widest and narrowest measurements across a given crystal, taken perpendicular to each other, and do not necessarily correspond to specific crystallographic orientations. The compositional rim measurements are averages derived from high resolution EPMA x-ray maps of phenocrysts. The “Min. rim” column represents the smallest measurement from the high Fo%/high Ni/low Mn crystal core to the groundmass. Composition of which rim is not specified as when the measured rim is thin, it is equal width for all three.

<table>
<thead>
<tr>
<th></th>
<th>Xtal long axis</th>
<th>Short axis</th>
<th>Low Fo% rim</th>
<th>Low Ni rim</th>
<th>High Mn rim</th>
<th>Min. rim</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO43-olv01</td>
<td>440 μm</td>
<td>240 μm</td>
<td>17 μm</td>
<td>34 μm</td>
<td>14 μm</td>
<td>7 μm</td>
</tr>
<tr>
<td>CO43-olv03</td>
<td>402 μm</td>
<td>202 μm</td>
<td>19 μm</td>
<td>62 μm</td>
<td>15 μm</td>
<td>12 μm</td>
</tr>
<tr>
<td>CO43-olv07</td>
<td>373 μm</td>
<td>246 μm</td>
<td>13 μm</td>
<td>54 μm</td>
<td>13 μm</td>
<td>6 μm</td>
</tr>
<tr>
<td>CO43-olv08</td>
<td>405 μm</td>
<td>223 μm</td>
<td>17 μm</td>
<td>24 μm</td>
<td>8 μm</td>
<td>3 μm</td>
</tr>
<tr>
<td>CO56-olv03</td>
<td>415 μm</td>
<td>240 μm</td>
<td>30 μm</td>
<td>39 μm</td>
<td>7 μm</td>
<td>3 μm</td>
</tr>
<tr>
<td>PN12-olv05</td>
<td>666 μm</td>
<td>255 μm</td>
<td>28 μm</td>
<td>45 μm</td>
<td>6 μm</td>
<td>4 μm</td>
</tr>
<tr>
<td>PN12-olv06</td>
<td>1271 μm</td>
<td>1111 μm</td>
<td>42 μm</td>
<td>167 μm</td>
<td>29 μm</td>
<td>14 μm</td>
</tr>
<tr>
<td>PN12-olv08</td>
<td>1056 μm</td>
<td>459 μm</td>
<td>28 μm</td>
<td>102 μm</td>
<td>N/A</td>
<td>6 μm</td>
</tr>
</tbody>
</table>

Table 28 – Descriptions and measurement of crystal features for specific archetypical olivine phenocrysts from Cerro Overo maar (sample CO43), La Albóndiga dome (sample CO56), and the Puntas Negras mafic lava (sample PN12). The descriptions of crystal (xtal) morphology employ the vocabulary of Donaldson (1976) and descriptions of P-zoning employ the designations of Welsch et al. (2012). Inclusions include oxides (ox), dominantly Cr-spinel with a subordinate Fe-Mg-oxide population, and melt (mlt).

<table>
<thead>
<tr>
<th></th>
<th>Dominant xtal morphology</th>
<th>Maximum skeletal overgrowth</th>
<th>P-zoning thickness range</th>
<th>P-zoning dominant style</th>
<th>Approx. cut*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO43-olv01</td>
<td>Equant</td>
<td>62 μm</td>
<td>5-10 μm</td>
<td>Herring-bone</td>
<td>D</td>
</tr>
<tr>
<td>CO43-olv03</td>
<td>Subequant</td>
<td>77 μm</td>
<td>2-7 μm</td>
<td>Concentric</td>
<td>C1</td>
</tr>
<tr>
<td>CO43-olv07</td>
<td>Equant</td>
<td>73 μm</td>
<td>3-6 μm</td>
<td>Concentric</td>
<td>C1</td>
</tr>
<tr>
<td>CO43-olv08</td>
<td>Skeletal</td>
<td>111 μm</td>
<td>3-6 μm</td>
<td>Parallel</td>
<td>C2</td>
</tr>
<tr>
<td>CO56-olv03</td>
<td>Subequant</td>
<td>57 μm</td>
<td>3-8 μm</td>
<td>Herring-bone</td>
<td>D</td>
</tr>
<tr>
<td>PN12-olv05</td>
<td>Equant</td>
<td>123 μm</td>
<td>3-9 μm</td>
<td>Concentric</td>
<td>C1 (A?)</td>
</tr>
<tr>
<td>PN12-olv06</td>
<td>Blocky/Equant</td>
<td>28 μm</td>
<td>2-11 μm</td>
<td>Parallel</td>
<td>C1</td>
</tr>
<tr>
<td>PN12-olv08</td>
<td>Blocky/skeletal</td>
<td>93 μm</td>
<td>3-8 μm</td>
<td>Partial concentric</td>
<td>C2</td>
</tr>
</tbody>
</table>

Note: measurements are derived from BSE or WDS microprobe imagery and converted from pixel length.

*Approximated from the categorization of Welsch et al. (2012) (Figure 167).
Conclusions: Diverse Monogenetic Volcanism across the Main Arc of the Central Andes, Northern Chile.
Conclusions

The magmatic production of new crust at convergent margins is a complex process involving the generation of silicate partial melts under a variety of pressure, temperature, and chemical conditions. In some arcs, the variety of magma generation mechanisms and conditions are reflected in the compositional variety of erupted lavas. In the arc front of the central Andes, particularly the Altiplano-Puna high plateau region, lavas display a restricted, bimodal compositional distribution of andesite to dacite versus rhyolite, representing arc front stratovolcanoes and crust-derived ignimbrites, respectively (Figure 7; De Silva et al., 2006; Stern, 2004; Kay et al., 2010; Mamani et al., 2010; Blum-Oeste & Wörner, 2016). Post-Miocene (i.e., modern Andes) mafic volcanism is rare. The predominance of evolved lava compositions can largely be attributed to the double-thickened crust and large stores of mid-crustal dacitic magma, both of which function as density and viscosity barriers to dense, mafic magmas (Ochs & Lange, 1999; Zandt et al., 2003; Prezzi et al., 2009; Del Potro et al., 2013; Ward et al., 2014; Perkins et al., 2016). Weaknesses in the crust of the central Andes, however, provide alternative magmatic pathways to the surface (Figure 186). Monogenetic mafic centers located along these structural features may represent diverse, subduction-generated magmatic compositions not seen in the dominant main arc and caldera volcanism of the central Andes (Figure 6; Figure 8). Mafic, olivine-bearing lavas erupted at Cerro Overo maar and the Cordón de Puntas Negras provide evidence on the nature and source of parental magmas within the arc. Olivine-hosted melt inclusions from Cerro Overo provide additional evidence for a basaltic parent melt with $^{87}\text{Sr}/^{86}\text{Sr} < 0.705$, indicating the highly radiogenic isotopic compositions of central Andean volcanic rocks is dominantly due to interaction with the crust and not source region (i.e. upper asthenosphere) contamination.

Mafic volcanism within the arc

Cerro Overo maar and the Cordón de Puntas Negras have erupted olivine-bearing mafic lavas. Their locations along the Calama-Olacapato-El Toro crustal lineament, where it crosses the arc front, represent a large-scale zone of crustal weakness that may extend as deep as the base of the lithosphere (Figure 5; Figure 16; Zeil, 1964; De Silva & Francis, 1989; Gonzalez-
Ferrán, 1995; Matteini et al., 2002; Mazzuoli et al., 2008; Acocella et al., 2011; Norini et al., 2013). The lava of Cerro Overo maar is basaltic andesite (54.6 wt% SiO₂, 7.35 wt% MgO, 0.70628 ⁸⁷Sr/⁸⁶Sr) with major and trace element characteristics indicating an association with lavas of the arc front (i.e. produced by fluid flux melting above the subducting slab), and not intraplate magmatism (Figure 102). This lava has experienced relatively little evolution (compared to the central Andes arc at large) from crystal fractionation, with chemical and petrographic evidence indicating assimilation of 8 – 15% crustal material (Rosner et al., 2003; this study). The compositions of olivine-hosted melt inclusions (Figure 8; Figure 75) suggest that Cerro Overo magma originated as basaltic melt(s) at the base of the crust (i.e., the MASH zone; Delph et al., 2017) before rapidly ascending with little to no subvolcanic storage or stalling, as indicated by the continuous zoning and skeletal morphology of olivine phenocrysts (Figure 150 - Figure 162; Figure 186). For example, modeling of olivine diffusion profiles (forsterite and Ni content) yielded time frames of several hours up to 2 weeks of residence time at magmatic temperatures for Cerro Overo phenocrysts (Figure 149). In addition, the whole-rock composition of Cerro Overo represents the predicted “basaltic andesite” endmember of Blum-Oeste & Wörner (2016) for a parental (baseline) magma generated from the lower crustal MASH zone (Delph et al., 2017) during steady-state magmatism (as opposed to flare-up events).

Basaltic andesite from Cerro Overo maar displays low ⁸⁷Sr/⁸⁶Sr (0.7062-0.7065) and high ¹⁴³Nd/¹⁴⁴Nd (average 0.51244; -3.89 εNd) ratios indicating a low degree of crustal involvement relative to Altiplano-Puna arc lavas. However, the least-evolved whole rock isotopic compositions reported for the region are found in certain intermediate lavas from Lascar stratovolcano (⁸⁷Sr/⁸⁶Sr = 0.70550; Mamani et al., 2010), an active arc volcano adjacent to Cerro Overo. The local occurrence of less-evolved isotopic compositions within the central Andean arc at around 23° S is likely a result of the zone of weakness represented by the Calama-Olacapato-El Toro lineament which passes through the arc beneath these volcanoes (Matthews & Vita-Finzi, 1993; Matteini et al., 2002; Norini et al., 2013). Felsic xenoliths are common in Cerro Overo lava, however, indicating some interaction with upper crustal material (⁸⁷Sr/⁸⁶Sr ≥ 0.709; De Silva & Francis, 1989; Mamani et al., 2010; this study). Isotopic compositions measured for single, olivine-hosted melt inclusions reveal an isotopically less-evolved population (⁸⁷Sr/⁸⁶Sr = 0.70376 – 0.70432), indicating the preservation of potential parental material trapped within olivine phenocrysts (Figure 75). These values are within the range of the least-evolved isotopic composition in the entire central Andes: the pre-Miocene Chiar Kkollu intraplate picro-basalt
(44.85 wt% SiO₂; 9.26 wt% MgO; 0.704052 $^{87}$Sr/$^{86}$Sr) found deep in the Bolivian back-arc (Thorpe et al., 1984; Davidson & De Silva, 1992), the frequently-cited hypothetical (calculated) mafic endmember ($^{87}$Sr/$^{86}$Sr = 0.7045, SiO₂ = 48%) of Kay et al., (1994), and other published modeling efforts (e.g. Davidson et al., 1990; Burns et al., 2015). The composition of Chiar Kkollu basalt is commonly used as a stand-in for mantle chemistry throughout the central Andes (e.g. Davidson & De Silva, 1995; Hoke & Lamb, 2007; Mazzuoli et al., 2008; McLeod et al., 2012; Blum-Oeste & Wörner, 2016), and thus a better understanding of Cerro Overo chemistry will potentially improve petrologic models of the region.

The olivine- and clinopyroxene-bearing basaltic andesite (52.8 wt% SiO₂, 6.71 wt% MgO, 0.70590 $^{87}$Sr/$^{86}$Sr) of the Cordón de Puntas Negras, on the other hand, can be classified as a transitional arc/back-arc (i.e., intraplate) lava by the geochemical indices (e.g. La/Ta and K₂O content) first established by Kay et al. (1994). The zoning and morphology of olivine phenocrysts from Puntas Negras show evidence for a period of resorption prior to subsequent crystal growth and shortly before eruption, supported by diffusion modelling and geothermobarometry, suggesting the magma briefly stalled around the mid crust (~ 25 km depth). Modeling of olivine diffusion profiles (forsterite and Ni content) yielded time frames for diffusion at magmatic temperatures of ≤ 3 days up to 3.6 weeks for Puntas Negras olivine phenocrysts. The major and trace element characteristics of the Puntas Negras lava suggest the magma was initially formed with contributions from both fluid-flux arc melting and decompression-induced melting behind the arc following delamination of the base of the lithosphere and upwelling of hot asthenosphere (Figure 102; Figure 103; Figure 106). It is unclear whether transitional arc/back-arc magmas originate from mixing of melts formed in both fluid-flux and decompression melting regimes or as single parental melts formed under the concurrent influence of both melting mechanisms. Additional studies focused on the trace element content of olivine-hosted melt inclusions from the Puntas Negras mafic lava could potentially shed light on this origin question. The basaltic andesites of Cerro Overo maar and the Cordón de Puntas Negras, separated by only 32 km (Figure 6), reflect the diversity of parental melts generated at the convergent margin which can contribute to the eventual formation of the ubiquitous andesite-dacite compositions of the region.
Minor volcanism west of the arc front

West of the arc, the Tilocálar Group is a series of minor volcanoes emplaced along compressive structural features at the southeast corner of the Salar de Atacama basin (Figure 19; Figure 186). The minor Tilocálar Norte and Tilocálar Sur volcanoes and the Cerro Tujle maar which form the Tilocálar Group are distinct from the main arc by geography, their occurrence as fault-controlled volcanism in a compressive setting, and by their highly fractionated and adakite-like compositions. These volcanoes have erupted high temperature, aphyric andesites (58.7 – 63.4 wt% SiO₂, 2.44 – 3.56 wt% MgO) at points of highly localized extension developed from asymmetry in the indenter-driven compressive deformation of the Atacama basin (Flint et al., 1993; Kuhn et al., 2002; Gonzalez et al., 2009; Aaron et al., 2010). The Tilocálar Group intermediate lavas do not show major or trace elemental trends suggestive of mineral fractionation or significant crustal assimilation, suggesting rapid magmatic ascent. The magmatic pathways follow compressive faulting seen at the surface which likely cuts the brittle upper ~25 km of the crust (Kuhn, 2002; Lin et al., 2016). One possible magmatic route through the lower crust is the boundary between distinct sub-Andean, pre-Mesozoic basement blocks which rotate independently of each other due to the compressive stresses in the area caused by the eastward migration and counterclockwise rotation of the anomalously dense Salar de Atacama crustal block (Kuhn, 2002; Schurr & Rietbrock, 2004; Reutter et al., 2006; Gonzalez et al., 2009; Lin et al., 2016).

Trace element patterns for Tilocálar Group lavas (e.g. a significant Nb-Ta trough) indicate they originated from fluid-flux melting above the slab (i.e. subduction arc melting) (Figure 82). However, these lavas also display significant REE fractionation (high Sr/Y, La/Yb, Dy/Yb, etc.), low concentrations of fluid-mobile incompatible element (Cs, Rb, Th, U), only minor negative Europium anomalies (Eu/Eu* ≥ 0.91), and less-evolved isotopic compositions (i.e. higher ⁸⁷Sr/⁸⁶Sr and high and lower εNd) than would be expected relative to other indices of magmatic evolution, such as MgO and SiO₂ (Figure 82; Figure 106; Figure 111; Figure 130; Figure 135). Taken together, the distinct chemistry of the Tilocálar Group is evidence these magmas originated as very small melt fractions of meta-basaltic material within the high pressure garnet stability field (e.g. Xu et al., 2002; Schurr & Rietbrock, 2004; Martin et al., 2005; Rollinson & Tarney, 2005; Richards & Kerrich, 2007). The most likely sources from which such parental melts could be generated are either the eclogitic root of the lithosphere, which may be sinking.
into the asthenosphere due to delamination, or mafic lower crustal material delivered to the upper mantle by the mechanisms of forearc subduction erosion (e.g. Kay & Kay, 1993; Stern & Kilian, 1996; Xu et al., 2002; Kay & Coira, 2009; Kay et al., 2012). Unfortunately, the Pb isotopic compositions of the Tilocálar Group could be attributable to either source and their origin cannot be definitively characterized at this point.

Geophysical studies of the Altiplano-Puna region have not focused on features of the lower lithosphere or upper asthenosphere beneath the Tilocálar Group (e.g. Cahill & Isacks, 1992; Beck et al., 1996; Yuan et al., 2002; McGlashan et al., 2008; Kay et al., 2012) and thus it is unknown if lithospheric delamination has occurred this far west. Delamination is, however, well-documented in the back-arc of the region, centered beneath the Cerro Galan caldera (Kay & Kay, 1993; Kay et al., 1994; Kay et al., 2009; Kay et al., 2012; Mahlburg Kay & Sandvol, 2014). Fore-arc subduction erosion has been proposed as a possible mechanism influencing magmatic compositions in the Chilean Andes, particularly in the back-arc of the southern Puna (Kay et al., 2005; Goss & Kay, 2006; Kukowski & Oncken, 2006; Stern, 2011; Kay et al., 2012; Goss et al., 2013). Both potential interpretations of the source of the Tilocálar Group magmas extends our understanding of the scope and extent large-scale geodynamic mechanisms can contribute to localized magma chemistry and volcano formation. The anomalously dense crustal block beneath the Salar de Atacama is a significant regional feature which controls crustal faulting and deformation, volcano emplacement, and even magma chemistry as the eastward, counterclockwise movement and rotation of this block deforms both the arc and its basement (e.g. Niemeyer et al., 1984; Muñoz et al., 2002; Schurr & Rietbrock, 2004; Reutter et al., 2006; Jordan et al., 2007).

Summary

The central Andean subduction arc is a complex tectono-magmatic system and those complexities are best revealed in the variety of volumetrically minor and compositionally diverse lavas of the region (Figure 186). It is notable that all of the fault-controlled, monogenetic volcanism in this region lies just outside the boundaries of the mid-crustal, dacitic Altiplano-Puna Magma Body (Perkins et al., 2016), suggesting this may be correlated with the ability to
deliver small-batch magmas to the surface. Within the arc front, monogenetic mafic lava and olivine-hosted melt inclusions provide insights into the generation of the relatively restricted intermediate compositions that dominate the stratovolcanoes of the central Andes. Cerro Overo maar and Puntas Negras lavas are both spatially associated with tectonic features in the crust and lithosphere, and show petrographic and geochemical signs of rapid ascent with relatively minimal crustal contamination or evolution by crystal fractionation. This allows us a window into the composition of magmas close to the lower crustal baseline, potentially derived directly from the MASH zone.

The Tilocálar Group of minor volcanic centers erupted west of the arc front provide another example of a magma generation mechanism in the arc system. Here, magmas derived from very small melt fractions of meta-basaltic rocks at high pressure have been erupted along regionally compressive structural features. These lavas may represent connections between the lower lithosphere and upper crust along the margins of independently rotating basement blocks, highlighting the potential for Paleozoic geology to influence Quaternary volcanism. The chemistry of the Tilocálar Group is also suggestive of melt generation in the arc from melting of mafic crustal or lithospheric material, possibly delivered to the asthenosphere by delamination or forearc subduction erosion. Such magmatic compositions are likely common within the arc, but uncommonly reach the surface without being substantially modified or assimilated.

Recent comprehensive geophysical imaging of the lithosphere beneath the Altiplano-Puna region of the central Andes (Delph et al., 2017) have confirmed the existence of a widespread MASH zone at the base of the lithosphere (Figure 186). It can be reasonably assumed that all mantle-derived melts generated within the range of this MASH zone must pass through it during ascent. The relatively uncontaminated lava of Cerro Overo may represent mafic magmas as they are extracted from the deep MASH region (Figure 186). The chemistry of the Puntas Negras mafic lava is transitional between arc magmas representing melting due to slab dehydration and back-arc lavas representing melts generated from upwelling hot asthenosphere (Figure 104 - Figure 106). This Puntas Negras lava is evidence for a continuous connection between arc front and back-arc melt generation mechanisms, suggesting that subduction-generated arc magmas and intraplate-generated magmas are endmembers, rather than distinct products (Figure 186; Kay et al., 2012; Delph et al., 2017). The Tilocálar Group lavas were emplaced west of the arc front, and apparently west of the limits of the deep, persistent
MASH zone (Figure 186; Delph et al., 2017). Upper-crustal compressive structures, and potentially the boundaries between distinct basement blocks (Lin et al., 2016) in the middle to lower crust have allowed for the ascent of minor magma batches derived from remelting of lithospheric material beneath the Salar de Atacama. These unique, adakite-like lavas are representative of melt compositions which contribute to the volumetrically abundant volcanic products of the region, but which are generally not recognized in models of magmatism at the Andean margin due to their small volume and possible spatial restriction. The trace element patterns of the Tilocálar group (Figure 82) are evidence that slab dehydration is an important factor in the generation of these melts, affecting a meta-basaltic source material at high pressure, potentially lower crustal material eroded in the forearc and delivered to the upper asthenosphere by the subduction mechanism (Figure 186). The widespread, bimodal intermediate – felsic compositions of central Andes volcanism have been studied extensively, leading to the production of many models of magmatism in the region (e.g. Zeil, 1964; Baker, 1981; Coira et al., 1982; Thorpe et al., 1984; Rogers & Hawkesworth, 1989; Davidson et al., 1991; De Silva & Francis, 1991; Kay et al., 1991; Davidson & De Silva, 1992; Kay et al., 1992; Wörner et al., 1992; Coira et al., 1993; Davidson & De Silva, 1995; Lindsay et al., 2001; Schmidt et al., 2001; Babeyko et al., 2002; Kay & Kay, 2002; Rosner et al., 2003; Stern, 2004; Kay et al., 2005; Goss & Kay, 2006; Kukowski & Oncken, 2006; Mattioli et al., 2006; Petrinovic et al., 2006; Trumbull et al., 2006; Hoke & Lamb, 2007; Mamani et al., 2008; Mazzuoli et al., 2008; Kay & Coira, 2009; Kay et al., 2010; Litvak & Poma, 2010; Mamani et al., 2010; Salisbury, 2011; Kay et al., 2012; Tassara & Echaurren, 2012; Goss et al., 2013; McLeod et al., 2013; Mitchfelder et al., 2013; Burns et al., 2015; Murray et al., 2015; Blum-Oeste & Wörner, 2016; Delph et al., 2017). However, all of these models depend on hypothetical mantle compositions inferred from back-calculations or the use of intraplate lavas as stand-ins, and assume relatively simple parental melt generation scenarios. Monogenetic volcanoes across the Altiplano-Puna arc front have produced a diversity of lava compositions hinting at a greater complexity to central Andean subduction magmatism than has been recognized.
Figures

Introduction & Background

Figure 1 – Map of South America showing volcanic zones and plate tectonics of the South American continent and the oceanic Pacific plates showing the segmented Andean arc. Depth to the Wadati-Benioff Zone is indicated by isolines, highlighting the variable steep and shallow zones of subduction. Arrows show convergence rate and direction. Age of the oceanic plates near the Peru-Chile subduction trench are shown, as well. (Stern, 2004).
Figure 2 - Simplified geologic map of the Central Volcanic Zone (CVZ). Inset shows location of CVZ at the continental scale in relation to plate boundaries and the Northern and Southern Volcanic Zones (NVZ and SVZ, respectively). The CVZ cuts across four countries (Peru, Bolivia, Chile, and Argentina), and two major geomorphic features: the northern Altiplano and southern Puna high plateaus (extent marked by dashed lines). The range of the Altiplano-Puna Volcanic Complex is marked on both the main map and the inset. Late Neogene to contemporary volcanism encompasses both the frontal arc and back-arc volcanism. The Altiplano-Puna Magma Body, a low-density region of the middle crust modeled as a dacitic mush, is shown in dark grey. Volcanism has migrated eastward (24° - 26° S) along two major transcurrent fault systems, the Archibarca and the Calama-Olacapato-El Toro (COT). Minor eruptions of less-evolved lava, potentially defining a regional mafic compositional endmember, have been erupted along structural controls where the COT lineament intersects with a series of contractional features related to the eastward migration of an anomalously strong crustal block underlyng the Salar de Atacama. Sampling localities of minor volcanic centers included in this study are marked with circles. At this scale, not all sampling localities are visible due to overlap. Inset and basemap: de Silva, 1989 & Mattioli et al., 2006. Nazca Ridge: Stern, 2004. Transcurrent Lineaments: Matteini et al., 2002. Altiplano-Puna Magma Body: Zandt et al., 2003. Plate motion: Horton et al., 2001.
Figure 3 - Central Volcanic Zone (CVZ), after deSilva (1989). Inset depicts the CVZ in relation to other volcanic segments and general subduction geometry. Shaded region is the active volcanic front, which can be seen bending eastward around the Salar de Atacama. Rectangle indicates the approximate extent of the Altiplano-Puna Volcanic Complex (APVC). The location of Cerro Overo (23°32' S, 67°40' W) is marked with a star.
Figure 4 - The basement beneath the Salar de Atacama is recognized as colder, denser, and stronger than the surrounding lithospheric material by its high attenuation and p-wave velocity. This rheologically strong lithospheric unit blocks asthenospheric flow and deflects the volcanic arc eastward. From Schurr & Rietbrock (2004).
Figure 5 – Major structural and volcanic features of the central Andes from 19° S to 27° S. Potentially active arc volcanoes are shown as dark gray triangles. Back-arc volcanism (white circles) is mainly found to the north and south of the Altiplano-Puna Volcanic Complex (gray field), associated with structural lineaments (Davidson & De Silva, 1992; Kay et al., 1994). Salars (stippled) mark areas of local depression. The location of the study area (Figure 6) is outlined with a black rectangle.
Figure 6 - Simplified map of structural and volcanic features around the Salar de Atacama showing minor volcanism addressed in this study in relation to crustal structural features, the Salar de Atacama (stippled), the frontal subduction arc (brown), and the mid-crustal Altiplano Puna Magma Body (pink crosses). The spine (center trace) of the subduction arc is shown as a solid brown line. The approximate path of the center of the Calama-Olacapato-El Toro fault zone is shown as a gray dashed line. Inset shows study area location (yellow dot) in relation to volcanic zones of the Andes. Map includes data conglomerated from De Silva (1989a), Matteini et al. (2002), Reutter et al. (2006), Zandt et al. (2003), Reutter et al. (2006), and Gonzalez et al. (2009).
Figure 7 – Abundance of volcanic SiO₂ content in the central Andes compared against the compositions of melt inclusions from oceanic arc lavas, from Blum-Oeste & Wörner (2016). The three proposed end-member compositions of Blum-Oeste & Wörner (2016) are shown as arrows, indicating the modeled SiO₂ content for the primary Enriched Basalt (EB; green), Basaltic Andesite (BA; red), and the Rhyodacite (RD; blue). The compositions of the BA and RD end-members are controlled, respectively, by a density barrier and a viscosity barrier. Compositions denser than the BA or more viscous than the RD are unlikely to successfully traverse > 65 km of crust.
Figure 8 - Total Alkali - Silica (TAS) classification of volcanic rocks of the arc and back-arc of the central Andes. Basaltic andesites sampled from Cerro Overo maar and in the Cordon de Puntas Negras are regional compositional endmembers for arc-related rocks. The Puntas Negras lavas, however, are a transitional arc to back-arc composition. Data for Main Arc rocks (the Neogene – Recent frontal arc) and Ignimbrites are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010). Back arc data is compiled from the works of Davidson & De Silva (1992; 1995), Kay et al. (1994) and Hoke & Lamb (2007). The high-alkali, undifferentiated Shoshonites are Oligo-Miocene lavas from back-arc monogenetic fields at the eastern margins of the Puna Plateau in SW Bolivia (Davidson & De Silva, 1992; Kay et al., 1994). Classification scheme from Le Maitre et al. (1989).
Figure 9 – CVZ minor volcanism trace element patterns normalized to primitive mantle superimposed on the range of trace element patterns for the main arc of the Central Volcanic Zone of the Andes (Gray field). The Atana ignimbrite, derived from upper-crustal magma is shown as a dashed line. Primitive mantle values from McDonough & Sun (1995). Main arc compositional data from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 10 - Trace element patterns normalized to primitive mantle for felsic xenoliths (dark gray field) from Cerro Overo maar superimposed on the range of trace element patterns for the main arc of the Central Volcanic Zone of the Andes (Gray field). Note that the Atana ignimbrite trace element pattern plots within the “Ignimbrite Xenoliths” field, but is not shown to reduce visual clutter. The dotted line is the pattern of a singular andesitic composition xenolith. The pattern shows trends indicative of the arc-derived upper crust, including: a present but relatively diminished Nb-Ta trough; relative enrichment in incompatible Large-Ion Lithophile Elements (LILEs), such as Cs, Rb and Ba; enrichment in Th, U, and Pb, which are concentrated in the crust; depletion in Zr due to zircon fractionation; depletion in Sr and Ba (relative to other LILEs) due to plagioclase fractionation; a noticeable negative Europium anomaly; and a high concentration of the heavy REEs (Gd – Lu). Primitive mantle values from McDonough & Sun (1995). Main arc compositional data from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 11 - \( \text{SiO}_2 \) vs. \( \text{MgO} \) variation for Altiplano-Puna volcanic rocks including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Classification as “West-of-Arc” or “Within-arc” minor volcanism is a geographic designation further supported by differences in trace element characteristics (see text). Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 12 - Tholeiitic - calc-alkaline classification of volcanic rocks of the central Andes based on FeO*/MgO vs. SiO₂ as a proxy for redox condition (tholeiitic = reducing, calc-alkaline = oxidizing), based on the classification scheme of Miyashiro (1974). All rocks of the Central Volcanic Zone (CVZ) plot as calc-alkaline, with the exception of the Oligo-Miocene Shoshonitic basalts (Kay et al., 1994; Davidson & De Silva, 1992) and the Late Cretaceous mafic lavas (unspecified) (Hoke & Lamb, 2007) found in back-arc monogenetic fields.
Figure 13 - Topography of the study area (from Google Earth, accessed 2016) with locations of monogenetic volcanism in the Altiplano-Puna indicated.
Figure 14 - View of Cerro Overo and local andesitic-dacitic stratovolcanoes, looking south from Lascar volcano (Ukstins Peate, 2008). The maar crater is approximately 600m across. Cerro Overo sits atop a topographic rise known as the Cordón Altos de Toro Blanco, an east-vergent anticline composed of folded ignimbrite (dashed hingline). The maar is associated with a small, nearby basaltic plug, La Albóndiga Grande, which comprised of petrologically and compositionally indistinguishable lava. Gray in the foreground is pumice fall from a recent eruption of Lascar. Scale bar applies to the field of view with Cerro Overo.
Figure 15 – Schematic cartoon (not to scale) of “by-pass” mechanisms producing less-evolved magmas (SC2, La Porunita) at the flanks of Ollagüe stratovolcano. Deep faulting is the most likely mechanism for allowing more primitive magmas to reach the surface while avoiding extensive intra-crustal contamination and evolution in storage chambers. BA = basaltic andesite; PB = primary basalt; S(BA) = superheated (basaltic andesite). From Mattioli et al. (2006).
Figure 16 - Major crustal lineaments cutting the central Andes. Major morphologic and tectonic divisions of the Andes are shown (see legend). The regional lineaments cut across these divisions as they extend into the sub-Andean basement. The rectangle highlights a region of volcanism associated with the Calama-Olacapato-El Toro (COT) lineament. From Matteini (2002). Location of the Puntas Negras – El Laco mafic lava flow is indicated by a yellow star.
Figure 17 - Geologic map of the Salar de Atacama and surroundings, from Reutter et al. (2006) with locations of monogenetic volcanism of this study indicated. Isolines (gray) show the residual isostatic gravity field. Dark brown represents the frontal arc. Dashed red line marks the international boundary between Chile and Argentina.
Figure 18 – Cross section of the lithosphere and upper asthenosphere of the Altiplano-Puna region of the central Andes (at 22.28° S) from Prezzi et al. (2009) showing proposed (i.e. modeled) subsurface structure with density values in Mg/m$^3$. Black triangles show the location of active arc and back-arc volcanism. CC: Coastal Cordillera, PC: Chilean Precordillera, WC: Western Cordillera, AP: Altiplano-Puna, EC: Eastern Cordillera, SA: Subandean Ranges, A: Atacama block, B: Altiplano-Puna partial melting zone (origin of the APMB).
Figure 19 - Map summary of structural features at the southwest margin of the Salar de Atacama showing the relationship between tectonic features and minor volcanism. Centers studied in this work are Tilocálar Norte y Sur, Cerro Tujle maar, and El País lava flow. Structural data from González-Ferrán (1995), Kuhn (2002), Reutter et al. (2006), González et al. (2009), and Lin et al. (2016), and Google Earth (accessed 2016).
Figure 20 - Diagram of how differential displacement of the thrust sheet over a variably oblique-frontal ramp-flat geometry ridge can lead to the production of localized areas of extension or shortening. From Kuhn (2002).

Figure 21 - Cartoon of the flowlines of hanging wall transport across the Tilocálar and Tilomonte ridges relative to the minor Tilocálar volcanoes. Anticlines and normal faults are indicated as per standard notation.
Figure 22 - Satellite view of Tilocálar Norte y Sur. Scale bar is 3100 m. Image from Google Earth, accessed 2015.
Figure 23 - Illustration of the Tilocálar volcanoes in planform from Gonzalez-Ferrán (1995).
Figure 24 - The location of Cerro Overo maar in relation to major salars, volcanic centers, and the inferred extent of the most recent ignimbrite deposits from La Pacana caldera complex, which underlie post-Miocene volcanism in the region. Both ignimbrites are sourced from La Pacana caldera, whose crater is now occupied by the Salar de Aguas Calientes from approximately latitudes 23° 00' – 23 ° 30'. These two ignimbrites have a combined total volume of approximately 2700 km³ and distinct compositions (Lindsay et al., 2001 a). The crystal-rich, pumice-bearing dacitic tuff of the Atana ignimbrite supplied the majority of the silicic xenoliths hosted in the lava of Cerro Overo maar. Other notable volcanic centers of the region are shown as triangles. The Chascón dome and the Puntas Negras – El Laco flow, included in this study, are located within the Purica Complex and Cordón de Puntas Negras, respectively. Ignimbrite extent and volcano locations from Lindsay et al. (2001 a, b) and Gardeweg and Ramirez (1987).
Figure 25 - $\varepsilon$Nd versus SiO$_2$ content for Quaternary arc rocks (gray field) and monogenetic volcanism of the Altiplano-Puna region. The field for Lascar stratovolcano (purple) is included as it is adjacent to Cerro Overo maar and has erupted some of the isotopically least evolved (i.e. least negative $\varepsilon$Nd) intermediate lavas along the frontal arc (Mamani et al., 2010). The broad negative correlation between silica content and Nd isotopes reflects magmatic differentiation involving fractionation of mafic minerals (removal of Sm) and crustal contamination (relative enrichment in non-radiogenic Nd). The Atana Ignimbrite reflects one of the most evolved compositions of this trend. The departure from this trend in the Tilocálar Group minor volcanism reflects their origin from melting of a metabasaltic source, producing melts with relatively high silica, but less-differentiated Nd isotopic composition (Martin et al., 2005 and references therein). Data for the Quaternary main arc field is from the compilation of Mamani et al. (2010).
Figure 26 - $\varepsilon$Nd versus SiO$_2$ content for Quaternary arc rocks (gray field), back-arc volcanism (blue field), and monogenetic volcanism of the Altiplano-Puna region. The Atana Ignimbrite reflects one of the most evolved compositions of this trend, representative of the upper crust domain. Chiar Kkollu, is a c. 25 Ma picritic basalt from the back-arc in SW Bolivia is the least evolved rock (9.2 wt % MgO, $^{87}$Sr/$^{86}$Sr = 0.7041) yet described across the entire Central Volcanic Zone (Davidson & DeSilva, 1992; 1995), and is potentially representative approximates a composition similar to the mantle source. Data for the Quaternary main arc field is from the compilation of Mamani et al. (2010) and data for the back arc is from Kay et al. (1994) and Kay et al. (2012).
Figure 27 - $\varepsilon$Nd versus MgO content for Quaternary arc rocks (gray field), back-arc volcanism (blue field), and monogenetic volcanism of the Altiplano-Puna region. The broad positive correlation between Mg content and Nd isotopes reflects magmatic differentiation involving fractionation of mafic minerals (removal of Sm) and crustal contamination (relative enrichment in non-radiogenic Nd). The Atana Ignimbrite reflects one of the most evolved compositions of this trend, representative of the upper crust domain. Chiar Kkollu, a c. 25 Ma picritic basalt from the back-arc in SW Bolivia is the least evolved rock (9.2 wt % MgO, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7041$) yet described across the entire Central Volcanic Zone (Davidson & DeSilva, 1992; 1995), and is potentially representative approximates a composition similar to the mantle source. Data for the Quaternary main arc field is from the compilation of Mamani et al. (2010) and data for the back arc is from Kay et al. (1994) and Kay et al. (2012).
Figure 28 – Th/Nb vs. Nd isotopic composition for rocks of the Altiplano-Puna region indicating the degree of crustal contamination for various volcanic rocks of the arc system. Th is concentrated in the crust above subduction zones relative to Nb as Th is fluid mobile and carried by slab fluids toward the surface during slab dehydration and subsequent fluid flux melting. Nb is depleted in arc-related crustal material as it remains stationary during slab dehydration, concentrated in the relatively stable rutile phases (e.g. Pearce & Peate, 1995). The notation $\varepsilon_{\text{Nd}}$ describes the deviation in the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio from the Chondritic Uniform Reservoir (CHUR). More negative $\varepsilon_{\text{Nd}}$ values represent a greater accumulation of $^{143}\text{Nd}$ from the radioactive decay of Sm. Felsic (i.e. crustal) rocks have greater concentrations of (non-radiogenic) Nd than Sm, which is fractionated into mafic mineral phases, and thus display lower Sm/Nd ratios than mafic rocks and, as a result, lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (more negative $\varepsilon_{\text{Nd}}$ values). The effects of crustal contamination are apparent in the composition of Cerro Chascón (yellow square), a lava produced from mixing of mafic arc magma with upper-crustal dacite (Burns et al., 2015).
Figure 29 – $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic ratios for monogenetic volcanism of this study and Quaternary CVZ volcanism in the (21° - 24° S) Altiplano – Puna region (arc data from Mamani et al., 2010).
Figure 30 - $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ isotopic ratios for monogenetic volcanism of this study and Quaternary CVZ volcanism in the (21° - 24° S) Altiplano – Puna region (arc data from Mamani et al., 2010).
Figure 31 - $^{208}$Pb/$^{204}$Pb versus $\epsilon$Nd isotopic ratios for monogenetic volcanism of this study and Quaternary CVZ volcanism in the (21° - 24° S) Altiplano – Puna region (arc data from Mamani et al., 2010).
Figure 32 – $\varepsilon$Nd versus $^{87}$Sr/$^{86}$Sr for volcanic rocks of the Central Andes. CVZ main arc data from Mamani et al. (2010) and data for the back-arc field is from Kay et al. (1994) and Hoke & Lamb (2007).
Cerro Overo maar

Figure 33 - Field view of Cerro Overo crater from the northeast. The black material is the basaltic-andesite from the maar eruption and the tan is the country-rock Atana ignimbrite. Stratovolcanoes are, from left to right: Cenizos, Chilies, and Lejia.
Figure 34 – Cartoon of local structure and volcanic features around maar Cerro Overo. The maar (crater) is located at the hinge-zone of the Cordón Altos de Toro Blanco east-vergent anticline, which is probably a fault-propagation fold of a blind fault splay from the major Miscanti thrust fault to the west (Figure 17). The main body of the semi-continuous ejecta ring is shown, although scattered deposits of scoria in the surrounding area indicate its pre-erosional extent was greater. La Albóndiga Grande, an olivine-bearing basaltic-andesite lava dome is located at the edge of the anticline, at the precipice of a small basin (delineated with a thin dashed line). The hypersaline Laguna Lejía is located in a basin (delineated with a thin dashed line), the local low area, just west of the limb of the anticline. Background image from Google Earth, accessed 2016.
Figure 35 - Flow textures in lava from the crater rim of Cerro Overo maar. Hammer is ~ 40 cm long.
Figure 36 – Tumultuous tight folding of glassy lava bands separated by more vesicular lava bands. The different bands are mineralogically and compositionally identical, varying only in vesicularity. The surface of this block is flow-textured and shows slight oxidation. The right portion in this image appears to be a flow front. Hammer is approximately 40 cm long.
Figure 37 - Qualitative WDS element map of Si concentration showing a typical boundary between felsic xenolith (left) and mafic host (right). Note that, despite the crenulated border indicative of active mingling, no diffusion halo is discernable. This pattern holds true for Al, K, Fe, and Mg, as well. While both materials were apparently semi-molten and plastic, the temperature and viscosity differences were great enough for them to remain largely immiscible. Small but coherent blebs of glassy mafic material are visible within the xenolith. Olivine in the basaltic andesite is visible as low-silica areas. Black regions are vesicles (voids).
Figure 38 - Representative thin section of Cerro Overo lava displaying olivine phenocrysts of variable morphology, low vesiculality, and a groundmass with microcrysts of olivine, clinopyroxene, and plagioclase in a glassy matrix. Plane-polarized light. Feldspar lathes show a weak flow orientation and are heterogeneously distributed. A triangular glassy melt inclusion is visible at the core of an olivine crystal in the upper right.
Figure 39 - Photomicrograph of Cerro Overo basaltic andesite in crossed-polarized light. Olivine phenocrysts display a range of size and morphology. Fractured and/or resorbed xenocrysts are included in the groundmass.
Figure 40 - Morphologies of olivine phenocryst from Cerro Overo maar. a) Euhedral phenocryst (XPL) with internal morphology suggesting multiple pulses of growth. b) Skeletal phenocryst (XPL) indicative of rapid cooling. c,d,e) Glassy silicate melt (brown) and mineral inclusions (black, Cr-spinel) in euhedral phenocrysts. Yellow-brown clinopyroxene is visible and groundmass plagioclase shows weak flow orientation. f) Large, subhedral olivine phenocryst with
resorption texture, host to several melt inclusions. Heterogeneity of groundmass plagioclase distribution is evident. g) Glomerocrystic olivine with reaction rims indicative of disequilibrium with the host melt. h) Intergrown euhedral olivine phenocrysts with melt inclusions and reaction rims.

Figure 41 - Moderately vesicular olivine-phryic basaltic-andesite from Cerro Overo maar with a silicic xenolith of quartz, plagioclase, and opaque Fe-Ti oxide phases in a matrix of clear, vesiculated glass. The boundary between mafic and felsic material is sharp, showing little interaction between the two materials. The basaltic-andesite groundmass is made of a mafic glass with microcrystic olivine and plagioclase lather with occasional clinopyroxene microcrysts. The edge of another felsic xenolith is visible in the lower left corner. a) Plane polarized light. b) Crossed-polars. Olv. = olivine, qtz. = quartz, p. = plagioclase.
Figure 42 - The appearance of a typical large felsic xenolith, shown here at its boundary with the mafic host (lower left). Plagioclase phenocrysts in the xenolith are brecciated, likely xenocrysts themselves derived from the mid-crustal APMB. The dark-colored oxides visible in PPL (bottom) are, based on morphologies, breakdown of amphibole and/or biotite and can be seen melting into the surrounding clear glass. Sample CIUP 08-017.
Figure 43 - A collection of "loose" xenocrysts from sample CIUP 08-017. Plagioclase and quartz crystals are fractured and/or resorbed in the source, the Atana ignimbrite. Not the halo of reduced crystallinity around the xenocryst region.
Figure 44 - The sole quartz xenocryst with a pyroxene reaction rim, which may have been incorporated into the magma batch at some time before the introduction of massive amounts of xenolithic material just prior to and during eruption. It is unlikely this crystal was simply insulated from cooling after eruption as this texture is not see elsewhere among the abundance of xenocrysts.
Figure 45 - In places where wind has removed sediment beneath larger deposits, some volcanic stratigraphy is visible. Cerro Overo’s initial phase was dominated by 1-10 cm pieces of scoria, intercalated with tongues of glassy lava before the eruption of the thick deposits of lava around the crater rim. Scoria from the early stage is visible now beneath some deposits, cemented with desert caliche. Hammer is 80 cm long.
Figure 46 - Simplified map view of Cerro Overo maar showing the distribution and shape of the main components. The circular feature at center marks the rim of the crater. The partially-eroded ejecta blanket is shown in dark grey. A discontinuous ring of ignimbrite (white) outcrops along the crater walls, the massive basal section of the Atana ignimbrite and dominant source of xenoliths. Deposits of lava rich in xenoliths (>1%) are unevenly distributed, summarized here with medium-grey circles marking where concentrations of xenoliths were observed and/or sampled. Note that many overlapping sample locations were omitted to reduce visual clutter. Also shown are the locations of large, shattered bombs in the ejecta blanket, which are restricted to the southwestern side of the crater and represent the only coherent lava deposits away from the crater rim. Dashed line represents the apex of Cordon Altos de Toro Blanco.
Figure 47 - The largest and thickest portion of the lava deposits at the rim of Cerro Overo.
Figure 48 - View of Cerro Overo maar's typical ejecta blanket composition. Black to dark-grey material is glassy, juvenile lava from the maar eruption, olivine-bearing and sub-rounded to sub-angular. Note the general lack of vesicularity and almost complete absence of scoria. Buff-colored, irregular clasts are derived from the Atana ignimbrite, which forms the maar's substrate. Green-grey pumice is from the 1993 eruption of Lascar stratovolcano. Boot for scale is a women's size 7.
Figure 49 - View of the crater wall from the floor showing outcropping of the underlying Atana ignimbrite (tan) and the thin layer of mafic lava at the crater rim. A person is standing at the crater edge near the center of the picture.
Figure 50 - Photomicrograph of the Toconao Ignimbrite, plane-polarized with pore space stained blue. This Ignimbrite is a crystal-poor dacitic tuff with filiform pumice clasts set in the ash matrix. The Toconao ignimbrite is particularly susceptible to weathering and breaks down to a pumice rubble. Image from geo.fu-berlin.de, accessed 2015.

Figure 51 – Composite photomicrograph of the Atana Ignimbrite, the groundmass is plane-polarized and phenocrysts are shown under crossed-polarizers. Pore spaces are stained blue and highlights the frothy nature of the groundmass glass. Phenocrysts are plagioclase fragments (P), partially-resorbed quartz (Q), and biotite (B). Image from geo.fu-berlin.de, accessed 2015.
Figure 52 - "Baked" ignimbrite at the southwest of Cerro Overo’s crater showing stretched lithic clasts (Fiamme). Probably originally pumice, these clasts are now a non-vesiculated black glass with feldspar crystals.

Figure 53 - Highly glassy, homogenous lava from the rim of Cerro Overo maar. The small, mm-scale olivine phenocrysts are visible as light specks on the exposed surface. Black and white squares are 1 cm x 1 cm.
Figure 54 - A portion of Cerro Overo lava composed of agglomerated basaltic-andesite breccia. Large sledge hammer is 80 cm long.
Figure 55 - A felsic xenolith bearing plagioclase, biotite, oxides, and quartz hosted in the mafic, olivine-phyric glassy basaltic andesite from the maar Cerro Overo. Silicic xenoliths are common in lava from Cerro Overo maar, displaying a broad range in degree of incorporation/assimilation and coherency (togetherness). Here, we see a vesicular, glassy ignimbrite xenolith with a contact profile that shows mixing (bottom & left of xenolith) with the host lava as well as fracturing and dissemination near the top of the xenolith. Note the pahoehoe-like flow form at the upper-right of the basaltic andesite sample. The 'background' material in this image is representative of the majority of Cerro Overo’s ejecta blanket, consisting dominantly of sub-rounded olivine-bearing scoria mixed with pieces of (various) ignimbrite, glassy breccia, and bits of grey pumice from a recent eruption of the proximal Lascar stratovolcano. Short-sledge is 40 cm long.
Figure 56 - Grey, dacitic xenolith in Cerro Overo lava.

Figure 57 - Example of an ignimbrite xenolith partially disaggregated into the surrounding mafic lava. While the felsic glass is mostly incorporated, white plagioclase phenocrysts remain relatively intact. Black and white squares are 1 cm x 1 cm.
Figure 58 – A rare, olivine-bearing mafic xenolith with a glassy chilled-rim entrained in Cerro Overo lava. Hammer is 40 cm long. The composition of the mafic xenolith is identical to the host lava, suggesting it is a bomb re-captured by the maar eruption.
Figure 59 - Disaggregated felsic xenoliths in Cerro Overo basaltic-andesite showing flow orientation. Grass tuft is approximately 20 cm tall.
La Albóndiga Grande Dome

*Figure 60* - La Albóndiga Grande is an olivine-phyric basaltic andesite dome associated with Cerro Overo maar (77 ka), a potential regional mafic end-member ($\text{SiO}_2$ 54.4 wt%, MgO 7.4 wt %). Abundant upper-crustal silicic xenoliths and xenocrysts are present in lava from the maar, but are absent at the dome.
Figure 61 - View of La Albóndiga dome from the south with annotations of volcanological features.

Figure 62 - View of La Albóndiga dome from the northeast showing the crease structures at the dome’s apex.
Figure 63 - Major element differences between basaltic andesite from Cerro Overo maar and La Albóndiga dome are relatively minor, although the dome does show relative enrichment in silica with respect to MgO content.
The Puntas Negras – El Laco Mafic Lava Flow

Figure 64 - Interpretive field map of the Puntas Negras-El Laco lava flow showing sampling locations and the approximate divide between the "upper" and "lower" lavas (dotted line). This divide is marked by minor changes in lava textures seen in the field, differences in mineral modality, and more apparent divisions in composition, particularly minor and trace elements (e.g. Ni, Sr). Potentially, there are two vents from which the two separate lavas issued, although more extensive field mapping is needed and the current supposed vent location is indicated from observed flow directions. The Cerro Overo Stratovolcano to the east of the flow(s) is unrelated to the basaltic andesitic Cerro Overo maar included in this study, located some 35 km to the N-NW.
Figure 65 - Field photos of the olivine- and clinopyroxene-bearing Puntas Negras – El Laco lava flow near the Chile-Argentina border. A part of the relatively unstudied Cordon de Puntas Negras, this lava flow headed SE toward Salar El Laco (white area at the upper-left of this image) is rich in phenocrysts of olivine and clinopyroxene and represents an additional candidate for central Andes mafic end-member (SiO₂ 53.8 wt%, MgO 7.0 wt%). Cordón de Puntas Negras and the El Laco volcanic complex are adjacent to each other; this flow originates in the Cordón de Puntas Negras (dark-colored hills in upper-right of image) and ends in the domain of the El Laco Complex (red-tan set of hills at image center). For scale, the tussocks of golden grass are approximately grapefruit sized.
Figure 66 – Pyroxene phenocryst compositions from El País lava flow.
**Figure 67** - Here, the easternmost extent of "avalanche of basaltic-andesite" lava of Tilocálar Sur abuts the steep western limb of the Tilocálar Ridge anticline, a fault-propagation fold of the 3.2 Ma Tucúcaro-Patao ignimbrite. Boulders of ignimbrite have tumbled down the limb slope of the actively growing anticline. The interface between lava and fold-limb indicates the anticline was a pre-existing topographic feature at the time of eruption, dated to $730 \pm 50$ ka via $^{40}$Ar/$^{39}$Ar by Gonzalez et al. (2009). The rise seen at right of this image has also been described as an active fault scarp due to the ignimbrite detritus in the form of large boulders and fine sediment (Gardeweg & Ramirez, 1982).

**Cerro Tujle Maar**

**Figure 68** – Panorama of Cerro Tujle maar viewed from the northwest. The peak visible at center-right is Tolonchar stratovolcano, which sits to the south at the hinge of the same antiform, Tolonchar Ridge, as Cerro Tujle. Photographs and stitching by Ingrid Uksins Peate, 2014.
Figure 69 - A view of typical lava deposits of Cerro Tujle maar. The crater rim is marked with a dashed line. Geologist for scale, at right, is approximately 1.9 m.
Figure 70 – Chipped and flaked glassy black aphyric andesite at the rim of Cerro Tujle maar is evidence for human tool-making.
Figure 71 - Core vs. rim forsterite content (Fo %) of olivine phenocrysts from basaltic andesites erupted at Cerro Overo maar and the Puntas Negras - El Laco lava flow.

Figure 72 - Histogram of forsterite content in cores and rims of olivine phenocrysts from Cerro Overo basaltic andesite from 202 measurements by electron microprobe. Groundmass olivine is compositionally indistinguishable from phenocryst rims.
Figure 73 - Histogram of forsterite content in cores and rims of olivine phenocrysts from La Albondiga basaltic andesite from 109 measurements by electron microprobe. Groundmass olivine is compositionally indistinguishable from phenocryst rims.
Figure 74 - Histogram of forsterite content in cores and rims of olivine phenocrysts from La Albóndiga basaltic andesite from 60 measurements by electron microprobe. Groundmass olivine is compositionally indistinguishable from phenocryst rims.
Figure 75 -  Single crystal olivine $^{87}\text{Sr}/^{86}\text{Sr}$ from Cerro Overo (~0.7038 - 0.7071) define a broader range than whole rock (0.7062-0.7065). Measured isotopic values for the inclusions form three separate clusters, broadly indicating three different “classes” of trapped melt. Those with values similar to the host rock (plotted on or near the dashed gray $y=x$ line) captured melt equivalent to the erupted whole-rock, likely during ascent of the magma batch. Alternatively, these inclusions may be somehow connected to the surrounding melt and were able to re-equilibrate with the whole-rock. Points plotting well above the 1:1 line indicate trapping of more evolved melt. Assimilation of silicic crustal material would lead to portions of cooler, more evolved melt which would induce crystallization, potentially trapping the hybrid melt. The points plotting below the 1:1 line indicate preservation of juvenile magma in the olivine-hosted melt inclusions, which is lost at the whole rock scale. These less-evolved $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70376-0.70432) are the lowest yet reported for the Altiplano-Puna region of the central Andes and may represent the isotopic composition of primary arc magma(s) being delivered to the lower crust.
Figure 76 – COBA-062: basaltic andesite from the interior of the dome
Figure 77 - Photomicrograph of a Puntas Negras basaltic andesite thin section in crossed-polarized light (XPL) from the Upper Flow, displaying phenocrysts of olivine and clinopyroxene in a matrix of glass and plagioclase microphenocrysts. A glomerocrysts of fractured crystals of plagioclase (plag) intergrown with clinopyroxene (cpx) and is also visible near the center of the image. Scale bar is 1 mm.
Figure 78 – Rhode’s diagrams graphic representation of the equilibrium exchange relationship between olivine phenocrysts and the parental liquid (in this case, bulk magmatic chemistry). When in equilibrium, the coefficient for Fe and Mg exchange between olivine and its surroundings, \( K_D(\text{Fe-Mg})_{\text{ol-liq}} = \frac{X_{\text{FeO}}/X_{\text{MgO}}^{\text{ol}}}{X_{\text{FeO}}/X_{\text{MgO}}^{\text{liq}}} \), will be 0.30 ± 0.03, independent of pressure or temperature. The equilibrium exchange curve is represented by a solid line and the error range by dashed lines. Filled shapes represent measurements from crystal cores and open shapes represent measurements from rims of skeletal overgrowth and groundmass olivine microphenocrysts, which are indistinguishable in composition. Arrows indicate the manner in which different magmatic processes can be visualized as deviation from equilibrium crystal – liquid exchange.
Figure 79 - Thin section scan of two-pyroxene basaltic andesitic El País lava flow in plane-polarized light. The entire image is 45 mm across.
Figure 80 – Photomicrographs of typical El País lava taken in PPL (top) and XPL (bottom). The mineralogy consists of glomerocrysts of clinopyroxene (PPL: light green, XPL: high birefringence) and orthopyroxene (PPL: yellow-brown, XPL: gray) with subordinate plagioclase (white-gray), subhedral plagioclase phenocrysts with irregular boundaries and sieved cores, and a groundmass with lathes of plagioclase microcrysts in a dark glass.
Figure 81 - Sample TU-01 seen in plane-polarized light. Note slight flow alignment of microcrysts and the flow-oriented separation cracks. The orthopyroxene at upper left of the near-center glomerocrysts can be seen consuming plagioclase (white).
Figure 82 – Tilocalar Group volcanism trace element patterns normalized to primitive mantle, representing erupted at monogenetic centers west of the main arc (colored lines), at the southeast margin of the Salar de Atacama, superimposed on the range of trace element patterns for the main arc of the Central Volcanic Zone of the Andes (Gray field). Notably, Ba and Sr are enriched and the negative Eu anomaly is very low due to the suppression of plagioclase crystallization. Heavy REEs are greatly depleted with respect to LREEs and MREEs, indicating these magmas were generated with garnet persisting in the solid fraction. Overall enrichment in incompatible elements suggests magma generation from a relatively small melt fraction. The deep Nb-Ta trough is evidence melting occurred with high pressure Fe-Ti oxides (rutile) in the residual assemblage. Depletion in the fluid-mobile elements Cs, Rb, Th, and U reflect melt generation from a depleted source – possibly either dehydrated eclogitic lower crust and/or melt derived from the subducted metabasaltic slab itself (adakite) and mixed with asthenospheric peridotite (e.g. Defant & Drummond, 1990; Rollinson & Tarney, 2005). Primitive mantle values from McDonough & Sun (1995). Main arc compositional data from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 83 - Photomicrographs of lava from Cerro Tujle maar seen in plane-polarized (top) and cross-polarized (bottom) light. The lava is mildly vesicular with microphenocrysts of plagioclase (white-gray) and pyroxene (yellow-brown) in a groundmass of dark glass. An uncommon fragment of ignimbrite country rock is visible as a xenolith near the center of these images. This xenolith consists of fractured quartz, plagioclase, and altered biotite in a groundmass of devitrified felsic glass.
Figure 84 - Microcrystic orthopyroxene (yellow-brown) and plagioclase (white, rectangular) in the groundmass of Cerro Tujle lava
Figure 85 - Cartoon of the crystal architecture of an olivine phenocryst from Cerro Overo maar overlaid on a BSE image of the phenocryst. Dark pink schematically represents the high forsterite, high Ni core. Dark green lines illustrate the shape and distribution of fine-scale P-enriched zones. White are inclusions of Cr-spinel.

Figure 86 – Normal Mg-zoning in an olivine phenocryst with skeletal overgrowth from La Albóndiga Dome.
Figure 87 - Ternary diagram classification of pyroxenes from A. Cerro Overo maar and B. La Albóniga dome (groundmass crystals), C. the Puntas Negras-El Laco flow (groundmass and phenocryst), and D. El País lava flow (phenocrysts). All analyzed pyroxenes are clinopyroxenes except for the brown orthopyroxene phenocrysts found in El País lava, so called due to their coloring in plane-polarized light.

Figure 88 - Pyroxene chemistry for groundmass crystals from Cerro Overo maar, La Albóniga dome, and the Puntas Negras – El Laco mafic lava flow and from core and rim analyses for Puntas Negras pyroxene phenocrysts. Data is from EPMA.
Figure 89 – FeO* vs. MgO variations within Altiplano-Puna volcanic rocks, including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010). Back arc data is compiled from the works of Davidson & De Silva (1992; 1995), Kay et al. (1994) and Hoke & Lamb (2007). The high-FeO*, relatively undifferentiated Shoshonites are Oligo-Miocene lavas from back-arc monogenetic fields at the eastern margins of the Puna Plateau in SW Bolivia (Kay et al., 1994; Hoke & Lamb, 2007).
Figure 90 - WDS X-ray maps of intergrown clinopyroxene (diopside), orthopyroxene (enstatite) and plagioclase feldspar from El País lava flow, a mafic andesite. White insets indicate the targeted element for each map, all of which focus on the same area. Abbreviations are as follows: plg = plagioclase, dpsd = diopside, en = enstatite. Pyroxene compositions and classification are shown in Figure 66.

Figure 91 - Internal zoning in Al content of diopside phenocrysts from El País lava (Figure 90) shows little to no correlation in other major cations in the clinopyroxene, such as Ca, Mg, Fe, and Na. Al$_2$O$_3$ ranges 2.6 – 4.5 wt % across all clinopyroxene phenocrysts measured by EPMA EDS spot analyses (n = 13).
Figure 92 – Classification of groundmass pyroxene compositions for andesitic Tilocálar Group monogenetic volcanic centers.  
A. Tilocálar Norte,  
B. Cerro Tujle maar,  
C. dense lava from a flank flow of Tilocálar Sur,  
D. vesicular lava from the explosion crater on the south slope of Tilocálar Sur.
Figure 93 - Aerial photograph of the Chilean Puna taken from approximately (23.46° S, 67.62° W), looking southwest. 
The dark ejecta halo and crater of Cerro Overo maar are visible in the lower right of the image, at the apex of the 
Cordon de Toro Blanco. Chiliques stratovolcano (foreground, right) is immediately south of Cerro Overo. The partially-
eroded volcanic edifice to the east of Chiliques (left in this image) marks the most northwestern extension of the 
Cordon de Puntas Negras. The lakes in the upper left of the image are Laguna Miscanti (larger) and Laguna Miñiques 
(smaller). Immediately west (right) of the two lakes is the fault scarp of the Miscanti Thrust (dashed line), which is 
related to the contractional deformation caused by the Salar de Atacama lithospheric block indenter. The dark colored 
El País lava flow is barely visible in the distance. Altered from a photograph by Dick Culbert of Gibsons, B.C., Canada 
(2007), copyright CC BY 2.0.
Figure 94 – The proposed “Tumisa Line.” Ariel view of Cerro Overo maar (bottom) and surroundings viewed from the northeast, from the book “Volcanes de Chile” by Gonzalez-Ferrán (1994). In the upper right is the eastern extent of Cerro Tumisa and the dome (dark) Negro de Barriales. Cerro Tumisa is a c. 2 Ma series of domes and vents that is “in-line” with Cerro Overo maar and La Albóndiga Dome along a NW-SE lineament which passes along the southern margin of Laguna Lejía (Matthews & Vita-Finzi, 1993).
Figure 95 - Normalized trace element diagram for rocks from La Albóndiga dome (light grey, squares) and Cerro Overo maar lava, both glassy/fully juvenile (medium gray, circles) and xenolith-bearing maar lava. Elements concentrated in the crust, such as U, Pb, and the incompatible light elements are clearly enriched in the lavas with even minor crustal addition (xenoliths), but not for the dome, which hosts no coherent crustal material.

Figure 96 - The Ratio of Mg to Fe forms a continuous trend for lavas of Cerro Overo maar (circles) and La Albóndiga Grande dome (squares). Labels are brief descriptions of the plotted samples, highlighting the compositional distinction between fully juvenile Cerro Overo lava and those samples which contained some degree of contaminant material. The dome lavas plot more similarly to maar samples with obvious signs of upper crustal contamination (i.e. xenoliths), despite not containing xenolithic material themselves. Samples closer to the dome exterior plot further along the juvenile-contaminated trend defined by the maar samples, indicating interactions with surrounding country rock may have influenced the compositional spread.
Figure 97 - Samples of basaltic andesite from La Albóndiga dome (squares) show an elevated silica content w.r.t. MgO, relative to the similar basaltic andesite sampled at the nearby Cerro Overo maar. Nearly identical patterns are distinguished for SiO₂ versus FeO⁷, Al₂O₃, TiO₂, CaO, and MnO.

Figure 98 – Sr content per silica in whole-rock measurements for Cerro Overo maar (circles) and La Albóndiga dome (squares) generally distinguish samples with some upper crustal contamination or from the dome from the entirely juvenile maar lava. Lower Sr content is reflective of the Sr-depleted nature of the felsic crust contaminant.
Figure 99 - Chart of Ca vs. Mg content for the olivine-bearing lavas of this study. Olivine-hosted melt inclusions from Cerro Overo are included, highlighting their relative Ca enrichment.

Figure 100 – Ni content vs. SiO2 for monogenetic volcanism across the arc.
Figure 101 - Elevated Ti in melt inclusions, similar to that of Puntas Negras - El Laco
Figure 102 – Within-arc monogenetic mafic lava trace element patterns normalized to primitive mantle, showing the characteristics of the small-volume basaltic andesites sampled from (geographically) within the main arc. The relatively small dip in normalized Nb & Ta concentration for the Puntas Negras lava is indicative of a magmatic origin not entirely controlled by fluid flux melting above the subducting slab, but also intraplate melting. The patterns of all three mafic within-arc lavas are relatively flat and do not show depletion of Heavy REEs, which are concentrated in the garnet phase at depth. The lack of garnet residue associated with the melting origin of these lavas is not related to shallow melt generation as the lithosphere in the Altiplano-Puna region exceeds 55 km (e.g. Zandt et al., 2003), but rather due to removal of the ultramafic lithospheric root (Kay et al., 1994). Main arc compositional data from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010). Primitive mantle values from McDonough & Sun (1995).
Figure 103 - Puntas Negras mafic lava trace element patterns normalized to primitive mantle, compared with the range of patterns for the main arc (light gray) and the back-arc (dark gray) of the Altiplano-Puna region. The normalized trace element pattern for a high-K, intraplate shoshonite (black line) is also shown for comparison (Pb & Cs data not available). Primitive mantle values from McDonough & Sun (1995). Main arc compositional data from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010). Back-arc and shoshonite data from Kay et al. (1994) and Hoke & Lamb (2007).
Figure 104 – $K_2O$ vs. $SiO_2$ trends of different volcanic regimes of the central Andes, including the Quaternary – Recent main arc (dark gray field, data from Mamani et al., 2010), the southern Puna back-arc (light blue field, data from Kay et al., 1994), the northern Puna back-arc in SW Bolivia (light yellow field, data from Davidson & De Silva, 1992; Hoke & Lamb, 2007), and upper crustal ignimbrites (light gray field, data from GEOROC, accessed 2015). The compositional fields for back-arc, intraplate shoshonite basalts are colored according to their sampling location (Blue: NW Argentina, Kay et al., 1994, Yellow: SW Bolivia, Hoke & Lamb, 2007). $K$ content with respect to silica, along with $La/Ta$ ratios < 25, has been recognized as an indicator for intraplate magma generation in the region (Kay et al., 1994; Hoke & Lamb, 2007).
Figure 105 – Magnified view of K2O vs. SiO2 trends (Figure 104) showing the compositional features for basaltic–andesitic rocks of the Altiplano-Puna region. The Puntas Negras lava both falls within the back-arc high K field and displays a La/Ta ratio < 30, indicating it is a transitional back-arc to arc lava (Kay et al., 1994). Tilocálars Group lava from the Tilocálars and Cerro Tujle may be relatively elevated in K content, but with La/Ta > 60, they form their own subdivision of central Andean volcanism. Unfortunately, La/Ta data is not available for olivine-hosted melt inclusions from Cerro Overo (“C. Overo MIs,” orange field) and any association of these melts with intraplate melting remains unclear.
Figure 106 – La/Ta versus La/Yb trace element diagram showing compositional fields for different components of Central Volcanic Zone (CVZ) volcanism. The horizontal dashed lines indicate the bounding La/Ta ratio between intraplate and arc magmas (Kay et al., 1994). Compositions in the gap between the two lines are considered transitional (Kay et al., 1994; Mazzuoli et al., 2008). Compositional field for the active CVZ main arc (gray) from Mamani et al. (2010). Pliocene – Recent intraplate (orange), shoshonitic (green), and calc-alkaline (blue) volcanism from the back arc of the Puna are from Kay et al. (1994) and Mazzuoli et al. (2008). The outline for all reported CVZ back-arc volcanism (dark blue line) includes data from Davidson & De Silva (1992), Kay et al. (1994), and Hoke & Lamb (2007). Colored symbols are data from this study. Tilocálar Group minor volcanism (dotted blue outline) is designated by spatial relationship to the main arc.
Figure 107 – Ba/Nb versus Nb trace element diagram showing compositional fields for different components of Central Volcanic Zone (CVZ) volcanism. Compositional field for the active CVZ main arc (gray) from Mamani et al. (2010). CVZ back-arc volcanism (dark blue line) includes data from Davidson & De Silva (1992), Kay et al. (1994), and Hoke & Lamb (2007). The field for Miocene rocks erupted along the Calama – Olacapato – El Toro (COT) fault zone (orange) is from Mazzuoli et al. (2008) and references therein. Colored symbols are data from this study, including monogenetic volcanism, ignimbrites and xenoliths, and olivine-hosted melt inclusions. Black Xs are Oligo-Miocene shoshonitic basalts from Hoke & Lamb (2007). Tilocálar Group minor volcanism (dashed blue outline) is designated by spatial relationship to the main arc.
Figure 108 - La/Nb versus La trace element diagram showing compositional fields for the active CVZ main arc (gray) and the CVZ back-arc volcanism (dark blue field). Main arc field from Mamani et al. (2010) and back-arc field includes data from Davidson & De Silva (1992), Kay et al. (1994), and Hoke & Lamb (2007). Colored symbols are data from this study, including monogenetic volcanism, ignimbrites and xenoliths, and olivine-hosted melt inclusions. Black Xs are Oligo-Miocene shoshonitic basalts from Hoke & Lamb (2007). Tilocálar Group minor volcanism (dashed blue outline) is designated by spatial relationship to the main arc.
Figure 109 – TiO₂ vs. Zr content of volcanic rocks in the central Andes broadly distinguished arc rocks (gray field) generated from fluid flux melting above the subducted slab and back-arc lavas (blue field) generated from intraplate melting caused by upwelling of hot asthenosphere following removal of the lithospheric root (Coira & Kay, 1993; Kay et al., 1994; Davidson & De Silva, 1995). Compositions of minor volcanic centers are displayed as colored symbols. Purely intraplate, high-K shoshonitic basalts from the back arc are displayed as black Xs (Kay et al., 1994; Hoke & Lamb, 2007). Chiar Kkollu (blue circle) is a mafic dike in SW Bolivia with the least-differentiated igneous composition in all of the central Andes (Davidson & De Silva, 1992). Interestingly, the compositions of Cerro Tujle maar (orange circles) and the two Tilocálar volcanoes (blue triangles) plot within the Back-arc field, despite being erupted west of (before) the main arc and showing clear evidence for fluid-mitigated melt generation (e.g. Nb-Ta depletion, Error! Reference source not found.), indicating these lavas may be partially derived from a remelted crustal component. Data for the back-arc intraplate field (blue) is from Davidson & De Silva (1992), Kay et al. (1994) and Hoke & Lamb (2007). Data for arc volcanism composition (gray field) is from Mamani et al. (2010).
La/Sm represents Light to Medium (LREE/MREE) fractionation and La/Yb represents Light to Heavy (LREE/HREE) fractionation. Melting with amphibole in the residue will fractionate LREE from MREE while melting in the presence of stable garnet will fractionate LREE/HREE. Mafic monogenetic lavas from Cerro Overo maar (red circles), Puntas Negras (green diamonds), and El País lava (orange diamond) were erupted within the frontal arc and display REE fractionation characteristics similar to Lascar stratovolcano, the closest, currently active arc volcano. Tilocálar Group monogenetic volcanism at Cerro Tujle maar (light orange circles) and the Tilocálar volcanoes (blue triangles) show distinctly high REE fractionation patterns. In the Altiplano-Puna region of the central Andes, lavas displaying similar high fractionation patterns have been recorded in short-lived, anomalous dacitic volcanism in the late Pleistocene at Llullaillaco stratovolcano (24.71° S, 68.53° W) (Richards & Villeneuve, 2001; 2002) and two basaltic andesite flank eruptions at Ollagüe stratovolcano (23.31° S, 68.17° W) (Mattioli et al., 2006). Data for the compositional range of Quaternary – Recent lavas from the Central Volcanic Zone (CVZ) main arc field, Lascar, and Ollagüe stratovolcanoes are from compilation of Mamani et al. (2010). The field for All CVZ volcanics, including ignimbrite, back-arc volcanics, minor centers, and pre-Miocene volcanism is from GEOROC (accessed 2015). Data for the heavily-fractionated Llullaillaco Pleistocene lavas is from Richards & Villeneuve (2001; 2002). Black line represents simple mixing between a mafic intraplate sample and a high-K dacite.
Figure 111 - Chart of whole-rock LREE/HREE ratios for volcanic rocks of this study shown in relationship to broader regional chemistry. The “modern arc” field highlights the range of post-Miocene subduction (flux-melting) arc volcanism and the “all CVZ volcanics” field encompasses all other reported values for the Andean Central Volcanic Zone, including ignimbrites, intrusive complexes, and back-arc volcanism. Rare Earth Element (REE) ratios, effectively independent of magmatic differentiation processes, distinguish groupings within the suite of minor volcanic centers. This separation is likely due to differences in magmatic source. Higher Dy/Yb and La/Yb represents either Heavy REE depletion or Light REE enrichment, indicative of more crustal influence (LREEs are enriched in the crust, and HREEs concentrate in early-formed mafic products). Trace and REE data was collected for bulk samples at the University of Iowa by ICP-MS. Central Andes chemical range data from GEOROC (accessed November, 2015) and Mamani et al. (2010).
Figure 112 - $K_2O$ vs. $SiO_2$ classification diagram for rocks of the Altiplano-Puna region of the Andes. Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010). High-, Medium-, and Low-K classification divisions from Le Maitre et al. (1989).
Figure 113 – FeO* vs. MgO variations for frontal arc rocks of the Altiplano-Puna including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. The colored fields indicate compositional trends defined by specific, recently-active frontal arc stratovolcanoes of the region, highlighting the spread in Fe content trends with Cerro Overo and Puntas Negras as potential mafic endmembers. Volcanic composition data for the Central Volcanic Zone arc volcanoes are from compilation of Mamani et al. (2010).
Figure 114 - TiO$_2$ vs. MgO content variations within Altiplano - Puna volcanic rocks, including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Gray field represents the range of Quaternary arc volcanism composition. Arrow indicates the direction crystallization and fractionation of magnetite will drive composition. Data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 115 – Mg# vs. SiO$_2$ vs. variation for Altiplano-Puna volcanic rocks including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Classification as “West-of-Arc” or “Within-arc” minor volcanism is a geographic designation further supported by differences in trace element characteristics (see text). Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 116 - P$_2$O$_5$ vs. MgO content variations within Altiplano - Puna volcanic rocks, including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Arrow represents the direction in composition space that apatite crystallization and fraction will drive the bulk rock composition. Two gray fields are marked for the compositional trends of the frontal arc as a minor, P$_2$O$_5$-enriched trend is present in rocks from several different stratovolcanoes. Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 117 - $Na_2O$ vs. MgO content variations within Altiplano - Puna volcanic rocks, including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 118 – CaO vs. SiO₂ variation for Altiplano-Puna volcanic rocks including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 119 – MnO vs. MgO content variations within Altiplano - Puna volcanic rocks, including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 120 - $\text{Al}_2\text{O}_3$ vs. $\text{MgO}$ content variations within Altiplano - Puna volcanic rocks, including the minor volcanism of this study and olivine-hosted melt inclusions from Cerro Overo maar. Arrow indicates the direction crystallization and fractionation of plagioclase will drive composition. Volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc (gray field) are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 121 - Simple mixing and olivine fraction model for a consanguineous relationship between Cerro Overo average bulk composition and the composition of olivine-hosted melt inclusions.
Figure 122 - Simple mixing and olivine fraction model for a consanguineous relationship between the least-evolved Cerro Overo bulk composition and the composition of olivine-hosted melt inclusions.
Figure 123 – La/Sm ratio vs. La content for rocks erupted at minor volcanic centers of the Altiplano-Puna region of the central Andes. Olivine-hosted melt inclusions (pink circles) from Cerro Overo maar are included. La and Sm are both incompatible elements with similar chemical characteristics, but La is slightly more incompatible and is thus more enriched in smaller degrees of partial melt relative to Sm. Thus, the La/Sm ratio should increase linearly with La content for magmas derived from smaller fractions of partial melt. Since La and Sm have similar elemental characteristics otherwise (e.g. charge, size), they are similarly excluded from crystallization of most major phases. In this way, crystal fractionation seen in increasing concentration of La will also not affect Sm, driving La/Sm vs. La trends laterally away from the partial melting trend.
Figure 124 - Sr/Y vs. Y content for minor volcanic centers, arc rocks, back-arc volcanism, and ignimbrites of the central Andes. The outlines designating the Tiocâlar Group and Within-arc minor volcanism are based on spatial relationships between monogenetic volcanism and the active modern arc; designation only applies to the colored symbols within each outline. Fractionation and partial melting trends are from Richards & Kerrich (2007) and Wang et al. (2009). The gray dashed line indicates the adakite vs. arc affinity designation boundary described by Defant & Drummond (1990). Data for the compositional fields are from the following sources: Arc (Mamani et al., 2010; GEOROC, accessed 2015), Back-arc (Davidson & De Silva, 1992; Kay et al., 1994; Hoke & Lamb, 2007), Ignimbrites (this study; Lindsay et al., 2001b; GEOROC, accessed 2015). Data for Oligo-Miocene shoshonite basalts and mafic dike Chiar Kkollu are from Hoke & Lamb (2007).
Figure 125 – Ba vs. Si content. Compositional field for the Central Volcanic Zone (CVZ) main arc from Mamani et al. (2010).
Figure 126 – TiO$_2$ vs. Al$_2$O$_3$ characteristics for volcanic rocks of the Altiplano-Puna region. Data for the compositional range of Quaternary – Recent lavas from the Central Volcanic Zone (CVZ) main arc (gray field) are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 127 – Sr vs. SiO₂ content variations within Altiplano-Puna volcanic rocks, including the minor volcanism of this study. Dashed lines outline groupings of minor volcanism both within the main arc itself and to the west of the arc, at the southeast margin of the Salar de Atacama. Greatly elevated Sr content is one of the compositional features which distinguishes the Tilocálar Group rocks from the arc trend itself (gray field). Also shown are olivine-hosted melt inclusions from Cerro Overo maar (“Melt Inclusions”). Arrow represents the direction plagioclase fractionation will drive composition. Quaternary – Recent volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc (gray field) are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010). The yellow field denotes the range of crust-derived ignimbrite compositions (Lindsay et al., 2003; GEOROC, 2015; this study).
Figure 128 - The Rb/Sr ratio vs. MgO content for Altiplano-Puna volcanic rocks. Dashed lines outline groupings of minor volcanism both within the main arc itself and to the west of the arc, at the southeast margin of the Salar de Atacama. Quaternary – Recent volcanic composition data for the Central Volcanic Zone (CVZ) Main Arc (gray field) are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010). The yellow field denotes the range of crust-derived ignimbrite compositions (Lindsay et al., 2001; GEOROC, 2015; this study). If plagioclase is fractionated during magmatic differentiation, then Rb will be concentrated in the lava respective to Sr, striving the Rb/Sr ratio up with decreasing MgO content. The low Rb/Sr of the west-of-the-arc Tilocálar Group of minor volcanism is a result of plagioclase suppression despite extensive differentiation of these andesites.
Figure 129 – Europium anomaly (Eu/Eu*) vs. MgO characteristics for volcanic rocks of the Altiplano-Puna region. Data for the compositional range of Quaternary – Recent lavas from the Central Volcanic Zone (CVZ) main arc (gray field) are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 130 – SiO2 vs. Eu/Eu* correlation across different volcanic regimes of the central Andes. Gray fields are, from left to right: felsic ignimbrites, the main arc, back arc calc-alkaline mafic rocks, and intraplate high-K Shoshonites from the back-arc. Average values for these field are marked with circles. Rocks across the multiple regimes form a generally linear inverse correlation related to increasing plagioclase fractionation with magmatic differentiation. The high Eu/Eu* departure from the linear trend defined by the west-of-the-arc Tilocálar and Cerro Tujle lavas is indicative of suppression of plagioclase crystallization as these magmas evolved. Data for the compositional range of main arc lavas from the Central Volcanic Zone (CVZ) main arc (gray field) are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010). Back-arc and shoshonite compositions are from Davidson & De Silva (1992) and Hoke & Lamb (2007).
Figure 131 - Interpretive field map of the Puntas Negras-El Laco lava flow showing sampling locations and the approximate divide between the "upper" and "lower" lavas (dotted line). This divide is marked by minor changes in lava textures seen in the field, differences in mineral modality, and more apparent divisions in composition, particularly minor and trace elements (e.g. Ni, Sr). Potentially, there are two vents from which the two separate lavas issued, although more extensive field mapping is needed and the current supposed vent location is indicated from observed flow directions. The Cerro Overo Stratovolcano to the east of the flow(s) is unrelated to the basaltic andesitic Cerro Overo maar included in this study, located some 35 km to the N-NW.
Figure 132 - Chart of Ni vs. MgO, clearly distinguishing the elevated Ni content of olivine-phyric Cerro Overo (red circles) and La Albóndiga Grande (red squares) compared with the modern CVZ arc trend (gray field). High concentrations of Ni can be found in olivine crystallized at asthenospheric temperatures, which may be what distinguishes the elevated Ni content of Overo from that of the other olivine-phyric basaltic andesite of this study, the Puntas Negras-El Laco flow (green diamonds). The upper (dark green) and lower (light green) flows of Puntas Negras-El Laco show a distinction in Ni content, as well, correlated with the high olivine content of the upper flows. The Tilocalars and Cerro Tujle (blue triangles, orange circles) show relatively high Ni content for their degree of evolution, possibly related to absent or minimal crystallization and fractionation of olivine.
Figure 133 – Sr vs. Ni characteristics of volcanic rocks from the Altiplano-Puna region highlighting the high Ni content of the minor volcanism of this study compared with main arc volcanism (gray field). Cerro Overo maar (red circles) and the Puntas Negras – El Laco mafic lava (green diamonds) are enriched in Ni due to the presence of mafic minerals (olivine, clinopyroxene, Cr-spinel) which have not been fractionated out. A clear distinction in Ni content is discernable among the Puntas Negras lava between the olivine-rich Upper Flow (circled) and the somewhat olivine depleted Lower Flow, which also carries a greater amount of plagioclase crystals, apparent in the slightly higher Sr content of the Lower Flow. Olivine-bearing andesitic flank eruptions of the San Pedro – San Pablo complex (gray triangles; data from Mamani et al., 2010) also plot in the high-Ni region alongside the Puntas Negras – El Laco flows. The negative Sr – Ni correlation of the main arc trend (gray field; data from Mamani et al., 2010) represents the concurrent crystallization and removal of plagioclase (rich in Sr) and mafic minerals (enriched in Ni) as the magmas evolve. The greatly enriched Sr content and relatively high Ni content of andesite and dacite of the Tilocalar Group minor volcanic grouping is an indication of the suppression of crystallization these magma batches have experienced.
Figure 134 – Rare Earth Element (REE) element patterns for all monogenetic volcanic centers of this study from the Altiplano-Puna region normalized to chondrite. Compositional range for main arc volcanics from Mamani et al. (2010). Chondrite values from Anders & Grevesse (1989).
Figure 135 - Sr/Y ratios vs. Mg # for volcanic rocks of the Altiplano-Puna region. The extremely high Sr/Y ratios seen in the Tilocálar Group monogenetic volcanism is evidence these magmas may have formed from the melting of mafic rocks, such as subducted oceanic crust (i.e. the slab) or eclogitic lower crust (Defant & Drummond, 1990; Moyen, 2009). Data for the compositional range of Quaternary – Recent lavas from the Central Volcanic Zone (CVZ) main arc (gray field) and Ignimbrites (yellow field) are from GEOROC (accessed 2015) and the compilation of Mamani et al. (2010).
Figure 136 – Nd vs. Mg content. Compositional field for the Central Volcanic Zone (CVZ) main arc from Mamani et al. (2010).
Figure 137 – Total alkali-silica classification of groundmass glass composition for mafic lava from Cerro Overo maar, La Albóndiga Dome, and the Puntas Negras-El Laco lava flow. Glass composition ranges from basaltic andesitic (~55% SiO₂) to rhyolitic (~73% SiO₂) for La Albóndiga and Cerro Overo and spans the same trend as main arc volcanic rocks of the CVZ. Note the clear bifurcation of glass data from Cerro Overo showing a basaltic-andesitic to andesitic grouping and a disparate rhyo-dacitic grouping. Lava from La Albóndiga stretches across this compositional gap, although the 60-65 wt % SiO₂ range is still relatively sparsely populated compared with the end-member groupings. The Puntas Negras-El Laco glass compositions show a similar broad range from basaltic-andesite up through trachyte/trachydacite (high alkali dacite). The composition of these glasses, however, show a notable high-alkali departure from the main-arc trend as the Puntas Negras lava is of intraplate origin, at the eastern margin of the CVZ arc.
Figure 138 - CaO versus SiO$_2$ content of glass from Cerro Overo, La Albóndiga, and Puntas Negras basaltic andesite. Data from microprobe analyses of groundmass glass.
Chapter 3
Olivine Diffusion profiles

Figure 139 – Mg zoning in olivine from Cerro Overo sample CO43, imaged by EPMA WDS x-ray mapping. Overlain profile (white) shows the shape of concentration zoning along the indicated transect (straight white line). WDS map was collected with a 30nA beam at 1.5 x 1.5 \( \mu \text{m} \) intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 140 - Ni zoning in olivine from Cerro Overo sample CO43, imaged by EPMA WDS x-ray mapping. Overlaid profile (white) shows the shape of concentration zoning along the indicated transect (straight white line). WDS map was collected with a 30nA beam at 1.5 x 1.5 μm intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 141 - Compositional zoning in olivine from Cerro Overo sample CO43, imaged by EPMA WDS x-ray mapping. Overlain profiles (white for Mg & Fe, blue for Ni & Mn) show the shapes of concentration zoning along the indicated transect (straight line). WDS maps were collected with a 30nA beam at 1.5 x 1.5 µm intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 142 - Mg zoning in olivine from Cerro Overo sample CO43, imaged by EPMA WDS x-ray mapping. Overlain profile (white) shows the shape of concentration zoning along the indicated transect (straight white line). The color gradient is exaggerated to only encompass 18 – 27 wt % MgO to better highlight Mg content variation within the phenocryst, but also rendering the groundmass invisible. This phenocryst displays skeletal, low-Mg overgrowth only on some crystal faces, possibly indicating growth in a local magmatic compositional and/or thermal gradient. WDS map was collected with a 30nA beam at 1.5 x 1.5 µm intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 143 - Ni zoning in olivine from Cerro Overo sample CO43, imaged by EPMA WDS x-ray mapping. Overlain profile (white) shows the shape of concentration zoning along the indicated transect (straight white line). This phenocryst displays skeletal, low-Ni overgrowth only on some crystal faces, possibly indicating growth in a local magmatic compositional and/or thermal gradient. A thin boundary layer (< 2 µm) enriched in Ni relative to the groundmass at large can be seen (dark blue) immediately outside the phenocryst boundary. WDS map was collected with a 30nA beam at 1.5 x 1.5 µm intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 144 – Fe and Mg zoning in olivine from La Albóniga dome sample CO56, imaged by EPMA WDS x-ray mapping. Overlain profiles (blue on Mg, yellow on Fe) show the shape of concentration zoning along the indicated transects (straight lines). This phenocryst displays microcrystalline overgrowth of phases enriched in Mg relative to the groundmass and Fe relative to both olivine and groundmass. The overgrowth rims intrude into the crystal form, indicating they are formed from breakdown of the olivine. Fe-Ti oxides are visible in the Fe map as a bright yellow-orange region. WDS map was collected with a 30nA beam at 1.5 x 1.5 µm intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 145 - Ni and Mn zoning in olivine from La Albóndiga dome sample CO56, imaged by EPMA WDS x-ray mapping. Overlain profiles (blue on Ni, black on Mn) show the shape of concentration zoning along the indicated transects (straight lines). WDS map was collected with a 30nA beam at 1.5 x 1.5 µm intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 146 - Mg zoning in olivine from Puntas Negras mafic lava sample PN14, imaged by EPMA WDS x-ray mapping. Overlain profile (white) shows the shape of concentration zoning along the indicated transects (straight line). The irregular boundary of the high-Mg core is clearly visible in this phenocryst, suggestive of a period of olivine resorption following the initial growth phase(s). The high Mg inner core follows the form of the skeletal overgrowths, indicating Mg zonation is at least partly due to magmatic condition and not entirely controlled by diffusive re-equilibration. A single melt inclusion (with Cr-spinel) is visible near the center of the crystal. The other “spots” of low Mg within the phenocryst are oxide inclusions. This phenocryst displays a thin (< 2 µm) boundary layer enriched in Mg relative to the groundmass. Groundmass crystals of low-Mg olivine (orange) and magnesian clinopyroxene (“cpx”; light blue) are visible in this map. WDS map was collected with a 30nA beam at 1.5 x 1.5 µm intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 147 - Mg zoning in a euhedral olivine with pyroxene overgrowths from Puntas Negras mafic lava sample PN12, imaged by EPMA WDS x-ray mapping. Overlain profile (black) shows the shape of concentration zoning along the indicated transects (straight line). The petrographic relationship between olivine and the pyroxene crystals along the phenocryst rims suggest the clinopyroxene is growing from salvaging of crystal components from the olivine. The high-Mg core displays a regular, symmetric form in this phenocryst. Melt and oxide (Cr-spinel) inclusions are visible within the crystal. This phenocryst displays a thin (< 2 µm) boundary layer enriched in Mg relative to the groundmass. Groundmass crystals of low-Mg olivine (red-orange) and magnesian clinopyroxene (light blue) are visible in this map. WDS map was collected with a 30nA beam at 1.5 x 1.5 µm intervals (pixel size) with 300 ms dwell times. Concentration is calibrated to a natural standard.
Figure 148 - Mg zoning in olivine displaying intermediate euhedral-skeletal features from Punta Negras mafic lava sample PN12, imaged by EPMA WDS x-ray mapping. The shape of concentration zoning along the indicated transects (straight black line, left) suggests high forsterite growth ceased during a period of rapid, diffusion-controlled skeletal growth, followed by incomplete growth of the euhedral crystal habit by lower forsterite olivine. The dark spots near the crystal center, surrounded by lower Mg olivine (also captured by the sudden drop in Mg along the profile line) appear to be comprised of the surrounding groundmass, as indicated by plagioclase growth, and are likely connected to the surrounding melt by a dimension not captured in this thin section slice. Groundmass crystals of low-Mg olivine (red-orange) and magnesian clinopyroxene (light blue) are visible in this map. WDS map was collected with a 30nA beam at 2 x 2 µm intervals (pixel size) with 200 ms dwell times. Concentration is calibrated to a natural standard.
Figure 149 – An example of modelled diffusion profiles for a Puntas Negras olivine from the model of Costa et al. (2008) starting with a 65 µm rim of Fo70 olivine around a 130 µm core of Fo83 olivine, residing at 1200°C. This model considers a case with boundary conditions open to flux. Different diffusivity profiles represent the concentration distribution resulting from different time spans of re-equilibration, listed in the legend in terms of seconds. For reference: 200,000 seconds = 55.6 hours = 2.3 days; 600,000 seconds = 166.7 hours = 6.9 days; 1,000,000 seconds = 277.8 hours = 11.6 days; 2,150,000 seconds = 597.2 hours = 24.9 days; 5,000,000 seconds = 1,388.9 hours = 57.9 days. The phenocryst modeled here displayed a forsterite zoning profile most similar to that formed from approximately 12 days (1,000,000 seconds; green line).
Figure 150 – Magnified view of Mg, Ni, Mn, and P zoning at the end of a tabular olivine phenocryst with swallowtail style skeletal overgrowth from La Albóndiga lava seen in WDS x-ray mapping by EPMA. The scale bar shown in the “Mg” map applies to all maps. In these images, it is clear that Mg, Ni, and Mn compositional zoning is following the rapid growth pattern defined by fine-scale P enrichment. This is an indication that diffusive re-equilibration is not dominant over initial growth in defining the compositional zoning of this crystal (e.g. Shea et al., 2015). The parallel linear pattern in P-zoning indicates this crystal was sectioned orthogonal to the b-axis, along the [010] plane (Figure 167). The outermost low-Mg/low-Ni rim is populated with an increased amount of P-enriched zonations compared with the crystal interior, indicating several episodes of rapid growth occurred in the final stages of crystallization. This crystal also displays inclusions of trapped melt enriched in highly olivine-incompatible P (arrows). WDS map was collected with a 30nA beam at 2 x 2 μm intervals (pixel size) with 50 ms dwell times.
Figure 151 – Concentric zoning of P-enriched regions in olivine from Cerro Overo maar seen in WDS x-ray mapping by EPMA. Additional element zoning patterns for this crystal are shown in Figure 141. Sectioning of this crystal nearly perfectly orthogonal to the c axis (Figure 167) reveals a cyclical concentric pattern of rapid growth has created fine scale zoning in the highly incompatible element P. Additional P-enriched zones are visible in the skeletal overgrowths. The P enrichments (white) seen adjacent to the termini along the long axis of this phenocryst are melts partially trapped by the most recent, syn-eruptive rapid growth phase, representing sampling of the incompatible element enriched compositional boundary layer at the forefront of crystallization (e.g. Welsch et al., 2014; Zellmer et al., 2016). WDS map was collected with a 30nA beam at 1 x 1 µm intervals (pixel size) with 300 ms dwell times.
Figure 152 – Mn (left) and P (right) zoning in an olivine with complex skeletal features from La Albóndiga lava seen in WDS x-ray mapping by EPMA. Mn zoning clearly displays the most recent, low forsterite skeletal growth, seen here in red to pink coloration. Cr-spinel mineral inclusions also concentrate Mn. The P zoning patterns are generally concentric, with some herring bone zoning extending from relict crystal corners, indicating this crystal is sectioned at a slight angle to major crystallographic axes (Figure 167). WDS map was collected with a 30nA beam at 1 x 1 µm intervals (pixel size) with 50 ms dwell times.
Figure 153 – Ni (left) and P (right) zoning in a complex olivine cluster from La Albóndiga lava seen in WDS x-ray mapping by EPMA. Ni zoning shows the higher concentration cores (also high Fo%) are semi-continuous and not separated by low forsterite overgrowth seen at the outer rims and skeletal overgrowths of the crystal. P-zoning is highly complex in this crystal cluster, displaying concentric zoning, dendritic branching zoning, parallel linear zoning, and sector zoning. Melt inclusions enriched in P excluded from the olivine lattice are visible in this compositional map. WDS map was collected with a 30nA beam at 3 x 3 µm intervals (pixel size) with 300 ms dwell times.
Figure 154 – Mg (left) and P (right) zoning in a subhedral olivine phenocryst from the Puntas Negras lower lava flow seen in WDS x-ray mapping by EPMA. A well-defined euhedral core is clearly visible in the traces of concentric high-P zonation. Additional P-enriched micron-scale zones near the outermost rims are faint but present, indicating more recent phases of rapid skeletal growth which have since matured with complete infilling. The high Mg core is relatively symmetric and the lower Mg overgrowth only shows minor skeletal morphology. Clinopyroxene (light green) at the upper left olivine boundary in this image can be seen growing from the dissolution of olivine. WDS map was collected with a 30nA beam at 1.5 x 1.5 µm intervals (pixel size) with 300 ms dwell times.

Figure 155 – Mg (left) and P (right) zoning in a large olivine phenocryst displaying skeletal morphology from the Puntas Negras upper lava flow seen in WDS x-ray mapping by EPMA. Two crystal apexes are clearly visible enriched in P, and fainter micron-scale P-enriched zones near the outer rim of the crystal are parallel to recent low temperature (low Mg) crystallization. WDS map was collected with a 30nA beam at 3 x 3 µm intervals (pixel size) with 300 ms dwell times.
Figure 156 – Histograms of co-crystallization temperature estimates for olivine-spinel pairs calculated from Al exchange between the two phases for rocks from Cerro Overo maar, La Albóndiga dome, and the Puntas Negras-El Laco flow. Olivine values used in these calculations were averages from several points within each phenocryst, eliminating significant outlier results from anomalously high or low Al₂O₃ microprobe measurements in olivine.
Figure 157 – BSE image of an olivine phenocryst from Cerro Overo maar overlain temperatures calculated from olivine-spinel aluminum partitioning (red), measured forsterite content (black, %), and tracing of P-enriched zones indicative of rapid crystallization phases. Olivine appears as a medium-gray and oxides, such as spinel, a bright white.
Figure 158 - BSE image of an olivine phenocryst from La Albóndiga Grande dome overlain temperatures calculated from olivine-spinel aluminum partitioning (red), measured forsterite content (black, %), and tracing of P-enriched zones indicative of rapid crystallization phases. Coloring of the host olivine body indicates regions of higher Ni (dark pink) and lower Ni (light pink). Olivine appears as a medium-gray and oxides, such as spinel, a bright white.
Figure 159 - BSE image of an olivine phenocryst from Cerro Overo maar overlain temperatures calculated from olivine-spinel aluminum partitioning (red), measured forsterite content (black, %), and tracing of P-enriched zones indicative of rapid crystallization phases. Coloring of the host olivine body indicates regions of higher Ni (dark pink) and lower Ni (light pink). Olivine appears as a medium-gray and oxides, such as spinel, a bright white.

Figure 160 - BSE image of an olivine phenocryst from the Puntas Negras-El Laco lava overlain temperatures calculated from olivine-spinel aluminum partitioning (red), measured forsterite content (black, %), and tracing of P-enriched zones (green) indicative of rapid crystallization phases. Coloring of the host olivine body indicates regions of higher Ni (dark pink) and lower Ni (light pink). Olivine appears as a medium-gray and oxides, such as spinel, a bright white.
Figure 161- BSE image of an olivine phenocryst from the Puntas Negras-El Laco lava flow overlain temperatures calculated from olivine-spinel aluminum partitioning (red), measured forsterite content (black, %), and tracing of P-enriched zones indicative of rapid crystallization phases. Coloring of the host olivine body indicates regions of higher Ni (dark pink) and lower Ni (light pink). Olivine appears as a medium-gray and oxides, such as spinel, a bright white.
Figure 162 – Rhodes diagram comparing the Mg-Fe partitioning between olivine phenocrysts of Puntas Negras (triangles) and Cerro Overo (circles) with their host magma whole-rock compositions. Filled symbols represent the compositions of crystal cores and open symbols represent rim compositions.
Figure 163 - NiO versus forsterite content (Fo %) for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóndiga dome (yellow squares), and the Puntas Negras – El Laco lava flow (green diamonds). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis. The Cerro Overo/La Albóndiga olivine crystals form a continuous range of compositions from the core to rim, representing sustained growth from their origin to eruption. The olivine compositions of Puntas Negras – El Laco show a distinct gap (~ 73 – 80 Fo %), possibly representing the superposition of eruption-related low-forsterite olivine on crystal cores grown in a less-differentiated magmatic environment.
Figure 164- MnO versus forsterite content (Fo %) for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóndiga dome (yellow squares), and the Puntas Negras - El Laco lava flow (green diamonds). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Figure 165 - CaO versus forsterite content (Fo %) for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóndiga dome (yellow squares), and the Puntas Negras - El Laco lava flow (green diamonds). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Figure 166 - Co versus forsterite content (Fo %) for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles) and La Albóndiga dome (yellow squares). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Olivine Morphology

Figure 167 – Diagram of how intra-olivine dendritic zoning will appear varied depending on crystal orientation relative to the thin section plane. Yellow represents high-P zones; dark green, low-P zones. The three-dimensional framework of high-P olivine formed first as linear primary branches emanating from the crystal center and rooting lamellar secondary branches. **Section (A)** – plane (100) – hexagonal zoning resulting from a section orthogonal to the a-axis. **Section (B)** – plane (010) – zoning parallel to (010) orientation, visible in a section plane orthogonal to the b-axis. **Section (C1)** – plane (001) – concentric zoning from intersecting multiple P-rich “terraces” perpendicular to the crystallographic c-axis. **Section (C2)** – plane (001) – simple zoning from intersection with a single terrace due to sectioning near the edge of a crystal, perpendicular to the c-axis. **Section (D)** – plane (101) – herring-bone or “feathery” zoning results from sectioning at an oblique angle, exposing the connections between skeletal terraces. From Welsch et al. (2012).
Figure 168 - Backscattered Electron (BSE) image of an olivine phenocryst and surrounding groundmass in Cerro Overo lava. The grayscale of the image is correlated with density: lighter colors represent compositions with higher average atomic number (Z).

Figure 169 - Backscattered Electron (BSE) image of an olivine phenocryst and surrounding groundmass in Cerro Overo lava. The grayscale of the image is correlated with density: lighter colors represent compositions with higher average atomic number (Z).
Figure 170 - Backscattered Electron (BSE) image of an olivine phenocryst and surrounding groundmass in Cerro Overo lava. The grayscale of the image is correlated with density: lighter colors represent compositions with higher average atomic number (Z).

Figure 171 - Backscattered Electron (BSE) image of an olivine phenocryst and surrounding groundmass in Cerro Overo lava. The grayscale of the image is correlated with density: lighter colors represent compositions with higher average atomic number (Z).
Figure 172 - Backscattered Electron (BSE) image of an olivine phenocryst and surrounding groundmass in Cerro Overo lava. The grayscale of the image is correlated with density: lighter colors represent compositions with higher average atomic number (Z).

Figure 173 - Backscattered Electron (BSE) image of an olivine phenocryst and surrounding groundmass in Cerro Overo lava. The grayscale of the image is correlated with density: lighter colors represent compositions with higher average atomic number (Z).
Figure 174 - Backscattered Electron (BSE) image of a large olivine phenocryst with skeletal morphology and surrounding groundmass in Puntas Negras Upper Flow lava. The grayscale of the image is correlated with density: lighter colors represent compositions with higher average atomic number (Z).
Figure 175 – Ni/Co ratios versus forsterite content (Fo %) for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles) and La Albóniga dome (yellow squares). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Figure 176 - Cr versus forsterite content (Fo %) for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóndiga dome (yellow squares), and the Puntas Negras - El Laco lava flow (green diamonds). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Figure 177 – Mn/Fe ratios versus forsterite content (Fo %) for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóndiga dome (yellow squares), and the Puntas Negras - El Laco lava flow (green diamonds). The notably elevated Mn/Fe ratios per Fo % of the outermost rims of some phenocrysts from La Albóndiga dome are correlated with crystal rims with oxide reaction rims. Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Figure 178 – Ni/(Mg/Fe) ratios versus forsterite content (Fo %) for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóndiga dome (yellow squares), and the Puntas Negras - El Laco lava flow (green diamonds). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Figure 179 – Ni/Mg ratios versus Mn/Fe ratios for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóndiga dome (yellow squares), and the Puntas Negras - El Laco lava flow (green diamonds). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Figure 180 – Ni/(Mg/Fe) ratios versus Mn/Fe ratios for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóniga dome (yellow squares), and the Puntas Negras - El Laco lava flow (green diamonds). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Figure 181 – Ca/Fe ratios versus Mn/Fe for cores and rims of olivine phenocrysts from Cerro Overo maar (red circles), La Albóndiga dome (yellow squares), and the Puntas Negras - El Laco lava flow (green diamonds). Filled symbols represent crystal core compositions and open symbols represent phenocryst rim chemistry. Compositions were measured by high-resolution microprobe analysis.
Pyroxenite-derived component estimates

Figure 182: Estimates of the fraction of the pyroxenite-derived component of the source melt ($X_{px}$) for 189 olivine phenocryst core measurements from Cerro Overo, calculated with the methods of Sobolev et al. (2007) based on the Mn/Fe ratio (Equation 19).
Figure 183 - Estimates of the fraction of the pyroxenite-derived component of the source melt ($X_{px}$) for 109 olivine phenocryst core EPMA measurements from La Albóndiga dome, calculated with the methods of Sobolev et al. (2007) based on the Mn/Fe ratio (Equation 19).
Figure 184 - Estimates of the fraction of the pyroxenite-derived component of the source melt (Xpx) for 52 olivine phenocryst core measurements from Puntas Negras, calculated with the methods of Sobolev et al. (2007) based on the Mn/Fe ratio (Equation 19).
Figure 185 - Backscattered Electron (BSE) image of a small olivine phenocryst and surrounding groundmass in La Albóndiga lava. Plagioclase lathes grown within the empty space around skeletal olivine growth are visible. The grayscale of the image is correlated with density: lighter colors represent compositions with higher average atomic number (Z).
Figure 186 – Generalized W-E cross-sections of the central Andes at approximately 23-24° S. Volcano, magma route, and fault size and location are conceptual, although their distance from the trench is approximately correct. Location, size, and shape of the mafic lower crust (the MASH zone, delaminated block,) and the brittle-ductile transition depth are from the geophysical interpretations and cross-sections of Delph et al. (2017). a) Cross section to-scale for both vertical and horizontal distances. b) Vertical distances are exaggerated approximately 2.5x to emphasize mid- to upper-crustal architecture. Horizontal (E-W) distances are to-scale, identical to the cross section in a).
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