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Vapor Transport Prior to the October 2004 Eruption of Mount St. Helens, Washington: Insight from Li and 210Pb Systematics.

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Geology

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Notes



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ABSTRACT

Dome lavas from the 2004 eruption of Mount St. Helens show elevated Li contents in plagio-clase phenocrysts at the onset of dome growth in October 2004. These cannot be explained by variations in plagioclase-melt partitioning, but require elevated Li contents in coexisting melt, a fact confirmed by measurements of Li contents as high as 207 μ g/g in coexisting melt inclusions. Similar Li enrichment has been observed in material erupted prior to and during the climactic May 1980 eruption, and is likewise best explained via pre-eruptive transfer of an exsolved alkali-rich vapor phase derived from deeper within the magma transport system. Unlike 1980, however, high Li samples from 2004 show no evidence of excess (210 Pb)/(226 Ra), implying that measurable Li enrichments may occur despite significant differences in the timing and/or extent of magmatic degassing.

Diffusion modeling shows that Li enrichment occurred within ~1 yr before eruption, and that magma remained Li enriched until immediately before eruption and cooling. This short flux time and the very high Li contents in ash produced by phreatomagmatic activity prior to the onset of dome extrusion suggest that vapor transfer and accumulation were associated with initiation of the current eruption. Overall, observation of a high Li signature in both 1980 and 2004 dacites indicates that Li enrichment may be a relatively common phenomenon, and may prove useful for petrologic monitoring of Mount St. Helens and other silicic volcanoes. Lithium diffusion is also sufficiently rapid to constrain vapor transfer on similar time scales to short-lived radionuclides.

Keywords: Mount St. Helens, diffusion, plagioclase, lithium, vapor transport.

INTRODUCTION

Degassing and transfer of volatile components exerts a strong influence over the timing and style of many volcanic eruptions. It has been suggested that accumulation of exsolved vapor at the top of a magma body may assist in triggering eruptions through increases in buoyancy and/or magma reservoir pressure (e.g., Blake, 1984). However, although evidence for vapor saturation and accumulation within magma chambers is relatively widespread-including Cl and metalrich inclusions trapped in volcanic phenocrysts, melt inclusions that show vapor saturation prior to eruption, and emissions of excess sulfur during the initial stages of eruptions (e.g., Lowenstern, 1993; Wallace, 2001; Grancea et al., 2002)these observations do not explicitly constrain the

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temporal relations between vapor transfer, accumulation, and eruptive activity.

In some cases time scales of vapor transfer and accumulation can be constrained by short-lived nuclides. Berlo et al. (2004, 2006) used (210Pb)/(226Ra) activity ratios to track upward movement of exsolved magmatic vapor prior to, and following, the cataclysmic eruption of Mount St. Helens, Washington, on 18 May 1980. Enrichment of Li in plagioclase phenocrysts and high Li, Cl, and B in plagioclase-hosted melt inclusions in the same samples demonstrated vapor phase transport of a range of fluid-mobile elements (Berlo et al., 2004; Blundy et al., 2007). Here we extend these approaches to examine the reactivation of eruptive activity at Mount St. Helens in 2004.

SAMPLES AND ANALYTICAL METHODS

Indications of renewed eruptive activity at Mount St. Helens began in late September 2004, and a series of phreatomagmatic explosions produced ash and steam

1–5 October. Extrusion of a new lava dome started in mid-October 2004 and is ongoing, with an estimated volume of $\sim 81 \times 10^6$ m³ as of April 2006. Samples were collected from the growing dome by helicopter dredging, either directly from the dome flanks or from recent collapse talus (Pallister et al., 2007).

Dome lava is compositionally uniform crystal-rich dacite (64.9 \pm 0.1 wt% SiO₂) with ~40 vol% subhedral and euhedral plagioclase phenocrysts, and lesser hornblende and orthopyroxene in a fine-grained groundmass. Several samples also contain inclusions of hornblende gabbro or gabbronorite similar to those described from 1980-1983 dacites (Heliker, 1995). Anorthite (An) and trace element contents of individual plagioclase phenocrysts were measured by laser ablation inductively coupled plasma-mass spectrometry, and major and trace elements and dissolved H₂O in melt inclusions were measured by electron and ion microprobe. Analytical methods and results are given in the GSA Data Repository¹ and summarized in Table DR1.

LITHIUM VARIATIONS IN 2004–2005 DOME SAMPLES

Lithium contents in plagioclase phenocrysts in dome material from October 2004 are enriched by about a factor of two compared to those erupted subsequently. Figure 1A shows the average concentrations of Li measured in plagioclase phenocrysts over time for dome samples erupted between October 2004 and April 2005. Phenocrysts from the first two samples of unequivocally new magma, SH 304–2A and SH 304–2C (erupted ca. 18 October) have

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¹GSA Data Repository item 2007051, measured An, Li, and Ba contents of plagioclase; major, trace, and volatile element data for analyzed melt inclusions from Mount St. Helens dome samples; and details of analytical techniques, is available online at www. geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

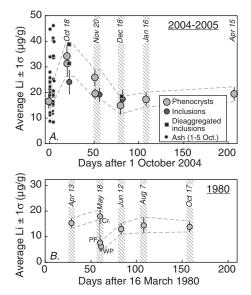


Figure 1. Average Li content (±1σ) of plagioclase phenocrysts vs. time for (A) 2004–2005 and (B) 1980 eruptive sequences at Mount St. Helens. Compositions of plagioclase from inclusions and isolated plagioclase from disaggregated inclusions are shown for 2004–2005 samples. Data for plagioclase fragments in ash collected from explosions on 1, 4, and 5 October 2004 show individual measured Li contents in A (Rowe et al., 2007). Concentration and time scales are same for A and B. Cr.—cryptodome; PF pyroclastic flow; WP—white pumice (Berlo et al., 2004).

average ($\pm 1\sigma$) Li contents of 34.5 \pm 3.4 and 31.5 \pm 3.8 μ g/g. A sample erupted ~32 days later (SH 305–1) has moderately elevated Li (25.9 \pm 2.4 μ g/g), although another sample collected at the same time has lower Li (suggesting that at this time Li enrichment may also have been spatially variable). Plagioclase from samples from December 2004 through April 2005 have lower Li contents (<<30 μ g/g; Fig. 1A), as do those from the first sample collected (SH 300–1A), considered a remnant of the 1980s dome complex (Fig. 1).

Plagioclase phenocrysts from SH 304-2A and SH 304-2C appear to sample a high Li population (distinct at >>99% confidence) compared to plagioclase from both 1980 dome lavas and subsequent 2004-2005 samples, and variations in plagioclase Li contents are decoupled from those of other elements with similar plagioclase-melt partition coefficients (Rb. Pb, K, Ba, Ti, and rare earth elements [REE]; e.g., Fig. 2). Variations in the Li contents of plagioclase phenocrysts are also not reflected in the composition of whole-rock samples, all of which have Li abundances of 20-30 μg/g (Pallister et al., 2007). Lithium concentrations are also strongly elevated in some melt inclusions (Table DR1; see footnote 1).

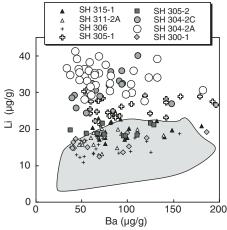


Figure 2. Li vs. Ba for plagioclase phenocrysts from dacite from 2004 to 2005. Data for April–October 1980 are shown for reference as the gray field (Berlo et al., 2004).

Plagioclase-hosted inclusions from SH 304–2A contain 169–207 μ g/g Li and ~3 wt% H₂O, and amphibole-hosted melt inclusions from sample SH 305–1 have Li contents from 103 to 159 μ g/g at low water contents (<1 wt%). Lithium contents preserved in orthopyroxene- and plagioclase-hosted melt inclusions from April 2005 sample SH 315–1 are 15–28 μ g/g.

ORIGIN OF THE HIGH LITHIUM SIGNATURE

A key to understanding the origin of the high Li signature is determining whether high Li in plagioclase reflects variations in plagioclasemelt partitioning, or requires actual changes in magma composition. Two primary controls on plagioclase-melt partitioning are An content and temperature (Bindeman et al., 1998). We can disregard the effects of the former because plagioclase phenocrysts in samples with high and low Li contents have indistinguishable An, and there is no correlation between An and Li for individual samples. Temperature changes are also likely unimportant. Although oxidepair estimates of magmatic temperatures range from an initial eruption temperature of 850 °C for October and November 2004 up to ~950 °C for magma erupted after January 2005 (Pallister et al., 2007), this temperature increase should make Li more compatible in plagioclase (Bindeman et al., 1998), producing ~15% increases, rather than the ~50% decrease that we observe over this period. Changes in magma composition produced by crystal fractionation or mixing are also unlikely to explain the differences in plagioclase Li contents, because all dome samples have restricted whole-rock SiO_{2} (64.9 ± 0.1 wt%), and incompatible trace elements such as Ba, Pb, and REEs vary by <~10% (Pallister et al., 2007).

The Li enrichment that we observe in earlyerupted samples from 2004 is markedly similar to that documented in early products of the 1980 eruption of Mount St. Helens, despite the more explosive nature of the 1980 activity (Fig. 1). Similarities include the timing, duration, and extent of the enrichment as well as the decoupling of Li variations from those of other trace elements with similar plagioclase-melt partitioning behavior. Berlo et al. (2004) and Blundy et al. (2007) have argued that Li enrichment in 1980 samples is the result of upward migration of an exsolved alkali-enriched vapor into the uppermost portions of a magma storage chamber prior to eruption. Degassing of an H₂O-saturated magma body stored at moderate depths ($P_{\text{H}_{2O}} = 230\text{--}150$ MPa; Blundy et al., 2007) results in exsolution of an alkali-rich aqueous vapor. Experimental studies of silicarich magmas show that at pressures ≤~400 MPa and 800-900 °C, Li and other alkalies partition preferentially into an aqueous fluid over melt ($D_{\text{fluid/melt}}$ of ~2-13), and the presence of significant chloride further promotes Li partitioning into the fluid phase (Webster et al., 1989). Buoyant upward movement transports Li (and other volatile and soluble elements) to higher levels within the magma chamber. Secondary boiling of the fluid at $P_{\text{H}_2\text{O}} \approx 110 \text{ MPa}$ forms dense alkali-rich brine and low-density vapor (Blundy et al., 2007), and further loss of the buoyant low-density vapor allows subsequent reequilibration between brine and melt. The rapid diffusion rate of Li (Giletti and Shanahan, 1997) plays a decisive role; at magmatic temperatures plagioclase and melt will reequilibrate with brine within a few days. Phase separation is also important because the fluidmelt partition coefficient of Li increases with decreasing pressure (Webster et al., 1989).

This model is also capable of explaining Li enrichment in October 2004 dome samples. The short duration of the Li-rich magma pulse (<~30 days) suggests that the total volume of magma enriched in Li was relatively small (probably <25% of the total volume erupted to date), consistent with restriction of Li enrichment to the top of a larger magma body. The H₂O contents of high Li melt inclusions in SH 304-2A suggest trapping pressures of ~100-120 MPa, close to the pressure (~110 MPa) of vapor-brine unmixing in dilute, low CO, systems, and similar to the trapping pressure of the highest Li melt inclusions in 1980 samples (Berlo et al., 2004; Blundy et al., 2007). Although Li could also potentially derive from other sources, such as hornblende breakdown or via assimilation of brine or hydrothermally altered wall rocks, mass balance and other considerations suggest these are probably of relatively minor importance. In addition, thermal and rheological barriers preclude direct assimilation of brine (Fournier, 1987).

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A model involving addition and subsequent diffusive equilibration of Li also explicitly accounts for the following observations.

- 1. Decoupling of Li from other elements. Lack of correlation between Li and other alkali metals (as well as other elements with similar plagioclase-melt partitioning; Fig. 2) can be readily explained by both preferential transport of alkalies in brine, together with the faster diffusion rates of Li within plagioclase (Giletti and Shanahan, 1997). This allows Li to equilibrate between brine, plagioclase, and melt significantly faster than other trace elements. At 850 °C the Li contents of plagioclase grains 1000-2000 µm in size would re-equilibrate to >90% within a few days (McDougall and Harrison, 1988). In contrast, Rb, which also strongly partitions into an exsolved vapor phase at ≤200 MPa and 800-900 °C (Webster et al., 1989), but has significantly lower diffusivity (Giletti and Shanahan, 1997), will undergo fractional gains of <<1% over this time period.
- 2. High Li in melt inclusions. Plagioclasehosted melt inclusions from October 2004 sample SH 304-2A have measured Li contents from 169 to 207 µg/g (Table DR1; see footnote 1). These are far greater than the Li contents of the current bulk rock (~23 μg/g), but are strikingly similar to the ~140–240 µg/g melt Li concentrations predicted by representative plagioclase-melt partition coefficients (0.17-0.20; Bindeman et al., 1998) and the range of measured plagioclase Li contents for this sample (Table 1). Some amphibole-hosted melt inclusions in November 2004 sample SH 305-1 also have Li contents in excess of 100 µg/g. In contrast, all inclusions analyzed from April 2005 sample SH 315-1, where Li contents in plagioclase are lower (Fig. 1A), have Li contents of 15–28 µg/g, similar to whole-rock values.

In addition, the lower whole-rock Li contents of host dacite samples (~20–30 $\mu g/g$) suggest that most (~>80%) of the added Li has now been lost from the melt. Although details of this remain uncertain, we believe that it most likely occurred through late syneruptive shallow degassing. Plagioclase phenocrysts show consistent decreases in Li concentration toward crystal margins, consistent with late equilibration between plagioclase and melt with lower Li (Fig. 3A). If this is the case, Li diffusion is sufficiently rapid that, even at these low temperatures, plagioclase phenocrysts require relatively rapid cooling (<~1–2 weeks) after loss of Li from the surrounding matrix to retain high Li signatures.

3. Differences between gabbroic inclusions and plagioclase phenocrysts. Lithium contents in plagioclase in an ~2.5-cm-diameter gabbroic inclusion from sample SH 304–2C are distinctly lower (Fig. 1A) than Li in plagioclase phenocrysts from this sample. This difference is significant at >99% confidence, and is consistent with a model of Li addition and diffusive equili-

TABLE 1. SUMMARY OF MEASURED LI IN PLAGIOCLASE FROM MOUNT ST. HELENS DOME SAMPLES COLLECTED BETWEEN OCTOBER 2004 AND APRIL 2005

	Collection	Estimated eruption	Li (µg/g)				
Sample	date	date*	Mean	1σ	Median	Range	n
SH 300-1A	10/20/04	1985(?)	16.4	2.2	16.6	12.5-19.2	13
SH 304-2A	11/4/04	10/18/04	34.1	3.4	34.5	27.9-41.5	33
SH 304-2C	11/4/04	10/18/04	31.5	3.8	31.6	40-2-24.6	18
Inclusion ³			24.2	3.8	23.1	18.7-32.3	14
SH 305-1	1/3/05	11/20/04	25.9	2.4	25.9	30.2-21.2	28
SH 305-2	1/3/05	11/20/04	19.7	1.5	19.0	18.2-21.8	10
Inclusion ³			19.2	2.2	18.6	16.1-23.1	10
SH 306-1	1/14/05	12/18/04	14.9	2.5	13.8	13.8-18-9	13
Inclusion ³			17.4	2.8	17.9	11.2-21.7	17
SH 311-1	1/19/05	01/16/05	17.4	2.0	17.7	13.3-20.2	17
SH 315-1	4/19/05	04/15/05	19.5	2.1	19.3	15.9-23.0	19

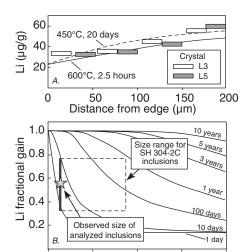
*Estimated from analysis of photographic and other records and typically considered accurate within 7–14 days (Pallister et al., 2007).

bration if the rate of diffusion was insufficient to allow plagioclase within larger and relatively impermeable inclusions to fully reequilibrate with Li-enriched melt prior to eruption. If this inference is correct, it is possible to constrain the timing of vapor transfer.

Figure 3 shows the calculated fractional uptake of Li over time by diffusion into a gabbroic inclusion (we treat this as a sphere with the bulk diffusivity of plagioclase). Preservation of the lower Li in a 2.5-cm-diameter inclusion requires that high magmatic Li contents persisted for <~100 days (at 850 °C). If the original inclusion was actually much larger (many gabbroic inclusions are partially disaggregated; Heliker, 1995), the limiting time would be correspondingly longer. Using the largest inclusion yet found in the 2004-2005 dome material (~19 × 8 cm) as a constraint, and assuming that the diffusion rate that we have used is a maximum (as diffusion along grain boundaries within the inclusion would probably be faster than the self diffusion rate for Li in plagioclase), we estimate a maximum residence time of <1 yr (Fig. 3).

DISCUSSION AND COMPARISON BETWEEN 2004 AND 1980

We believe that the anomalously high Li contents in plagioclase from October to November 2004 most likely reflect buildup and phase separation of a buoyant, alkali-enriched, exsolved magmatic vapor at the top of a shallow magma storage zone. This model is also supported by measurements of other volatile species. High CO, fluxes were observed at the start of the eruption in early October, and considerably more SO, and CO, has been emitted than could plausibly be derived from the volume of erupted magma, consistent with accumulation of vapor within the magma storage chamber prior to ascent (Pallister et al., 2007). The short duration of the Li-rich magma pulse also requires that the volume of magma enriched in Li was relatively small, consistent with accumulation of vapor at the top of a larger magma reservoir.



10

Radius (cm)

15

20

0

Figure 3. A: Profiles of Li concentration at margin of two representative plagioclase phenocrysts in sample SH 304-2A. Width of symbols represents 25 µm laser spot used for analysis, and thickness represents ~±10% uncertainty in measurement. Dashed curves show modeled diffusion profile for Li diffusion from semi-infinite reservoir (concentration at grain margin = 25 µg/g and at grain interior = 55 µg/g) for 450 °C, 20 days, and 600 °C, 2.5 h. B: Calculated diffusive fractional gain of Li in sphere of plagioclase as function of time and radius (McDougall and Harrison, 1988; Giletti and Shanahan 1997). Calculations are for T = 850 °C. The dashed box represents the range of sizes observed for gabbroic inclusions from SH 304-2C. and the star and gray line represent the average fractional gain ± 1 standard deviation in the analyzed inclusion (calculated using the average Li measured for SH 304-2A and SH 306-1 phenocrysts as baseline values.)

Our data also suggest that vapor transfer and accumulation may also have been directly associated with initiation of the 2004 eruption. We base this assertion on the constraints from Li diffusion detailed here that show that accumulation of Li-rich vapor occurred only

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within ~1 yr of eruption and that the high Li contents in the magma were retained to within a few days of eruption, degassing, and cooling. Further evidence is provided by measurements of plagioclase in ash produced by a series of small explosions from 1-5 October, prior to the start of dome extrusion (Fig. 1A). The majority (~80%) of plagioclase fragments from these ashes have low Li (<20 µg/g), and are interpreted to be derived from pulverized 1980-1986 materials. However, a small population with Li >30 µg/g are interpreted as juvenile and have Li contents as high as 47 µg/g, among the highest values measured in the entire 1980-2005 eruption sequence (Fig. 1A; Rowe et al., 2007). If Li content is broadly proportional to total vapor accumulation, then these results suggest that the most volatile-charged magma was located in the highest portions of the magma storage chamber and was involved in the initial explosive activity that cleared the magma conduit prior to the start of dome extrusion.

Although similarities between the observed Li enrichment in 1980 and the 2004 eruption at Mount St. Helens (Fig. 1) are noteworthy, there are also important contrasts in both eruptive and degassing styles between the 2004 and 1980 eruptions. One clear difference lies in (210Pb)-(226Ra) systematics, another potential tracer of vapor transfer. A gas, 222 Rn ($t_{1/2} = 3.8$ days), forms an intermediate in the decay of 226 Ra ($t_{1/2} = 1599 \text{ yr}$) to ²¹⁰Pb ($t_{1/2}$ = 22.6 yr). Exsolution and upward migration of a vapor can transport significant ²²²Rn from magma and, given a sufficient time period and ²²²Rn supply, can produce (²¹⁰Pb)/(²²⁶Ra) activity values >1. Conversely, 222Rn loss from magma degassing at deeper levels can produce (210Pb)/(226Ra) activity ratios <1. Berlo et al. (2004, 2006) reported (210Pb)/(226Ra) 1.11-1.41 in the high-Li cryptodome erupted on 18 May 1980, as well as in pumice samples from 22 July and 7 August explosive eruptions, consistent with vapor transport of both Li and 222Rn.

In contrast, 2004–2005 dome samples show no evidence that $(^{210}\text{Pb})/(^{226}\text{Ra})$ activity differs from secular equilibrium. Both October 2004 sample SH 304–2A, with the highest Li in plagioclase, and SH 306–1, erupted in December 2004 with lower Li concentrations, have $(^{210}\text{Pb})/(^{226}\text{Ra})$ values $(\pm 2\sigma)$ of 0.958 \pm 0.047 and 0.974 \pm 0.031 (Reagan et al., 2007). The lack of $(^{210}\text{Pb})/(^{226}\text{Ra})$ anomalies in 2004 dacite suggest that, unlike 1980, enrichment in Li was not associated with a significant, long-lived ^{222}Rn flux, and overall that development of a $(^{210}\text{Pb})/(^{226}\text{Ra})$ excess may require different conditions than

those under which Li enrichment occurs (Berlo et al., 2006). Unlike (210Pb)/(226Ra) activity ratios, Li enrichment requires no ingrowth time to become apparent and will persist indefinitely after cooling, and thus may prove a more reliable monitor of volatile fluxing.

Observation of a high Li signature in both 1980 and 2004 dacites indicates that Li enrichment is a relatively common phenomenon, and may be useful for petrologic monitoring of Mount St. Helens and other silicic volcanoes. Overall, studies of Li in minerals and melt inclusions, aided by advances in in situ trace element analytical techniques, may provide valuable in constraining vapor transfer and eruption chronologies. We also emphasize that Li diffusion is also sufficiently rapid to provide temporal constraints on time scales comparable to those provided by short-lived radionuclides.

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