

Preliminary experimental determination of the partitioning of lithium between plagioclase crystals of different anorthite contents

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ABSTRACT

The role of plagioclase anorthite content in controlling the partitioning of Li has been investigated experimentally. Plagioclase crystals of different anorthite contents were equilibrated with a single plagioclase powder at 1000 °C. The results show that the partition coefficient of lithium is a strong function of the anorthite content of the plagioclase, decreasing by a factor of ~3.5 from An_{60} to An_{80} . This has important implications for the interpretation of the distribution of Li in plagioclase in natural samples. An example of the importance of considering the change in partition coefficient with plagioclase anorthite content is given using published plagioclase Li contents in the products of the Soufriere Hills volcano. It is shown that the distribution of Li in these plagioclase phenocrysts can be reproduced using a model in which Li diffuses into, and out of, the plagioclase crystals if the change in partition coefficient with An content is accounted for. Because Li diffusion in plagioclase is very rapid, the distribution of Li in plagioclase crystal rims can record changing conditions during eruption and pyroclastic flow emplacement (second to minute timescales).

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1. Background and previous work

The extremely rapid diffusion of Li in plagioclase (Giletti and Shanahan, 1997) means that the distribution of Li in plagioclase can potentially be used to determine the rates of rapid geological processes including processes that occur on human timescales. Several recent studies have taken advantage of this to investigate rapid geological processes such as determining the rate of cooling of small intrusions in the oceanic crust (Coogan et al., 2005) and investigating explosive volcanic eruption/degassing processes (Berlo et al., 2004; Kent et al., 2007; Genareau et al., 2009; Genareau and Clarke, 2010). However, because plagioclase crystals are commonly zoned in anorthite content, any variation in the partition coefficient of Li as a function of plagioclase anorthite content needs to be taken into account when interpreting the distribution of Li in natural samples.

Experimental studies of plagioclase–melt partition coefficients demonstrate that Li is a moderately incompatible element in plagioclase ($K_d \sim 0.15$ to 0.7 with the majority of measurements between 0.2 and 0.3; Blundy, 1997; Bindeman et al., 1998; Bindeman and Davies, 2000; Aigner-Torres et al., 2007). These experimental data cover a range of temperatures between 1153–1299 °C and anorthite contents (X_{An}) from 39–77. The data show no systematic variation in

plagioclase–melt partition coefficient with either changing temperature at constant X_{An} or changing X_{An} at constant temperature (Fig. 1). Based on this it has been suggested that the melt–crystal partition coefficient is almost independent of X_{An} (Bindeman et al., 1998). It is difficult, however, to isolate the effect of changing crystal composition from changing melt composition in controlling the variation in partition coefficient in these experimental data. In fact, under almost identical conditions (1300 °C and plagioclase An_{71}) plagioclase/melt Li partition coefficients have been reported to be 0.138 and 0.296 in synthetic and natural bulk compositions (Experiments 101-1 and S2-3 of Bindeman et al., 1998 and Bindeman and Davies, 2000 respectively). This discrepancy is most simply explained if the melt composition plays an important role in controlling the partition coefficient of Li between crystals and melt. This makes it difficult to use existing crystal–melt experiments to unambiguously determine the role of plagioclase An content in controlling the partition coefficient. To overcome this, the extremely rapid diffusion of Li in plagioclase is utilized in this study to allow sub-solidus plagioclase–plagioclase Li partition coefficients to be determined.

2. Experimental method

A series of hand picked, apparently inclusion-free, natural plagioclase single crystal fragments ranging from An_{60} to An_{89} were selected as starting materials for the experiment. Additionally, approximately ten fragments of (relatively Li-rich) labradorite crystals

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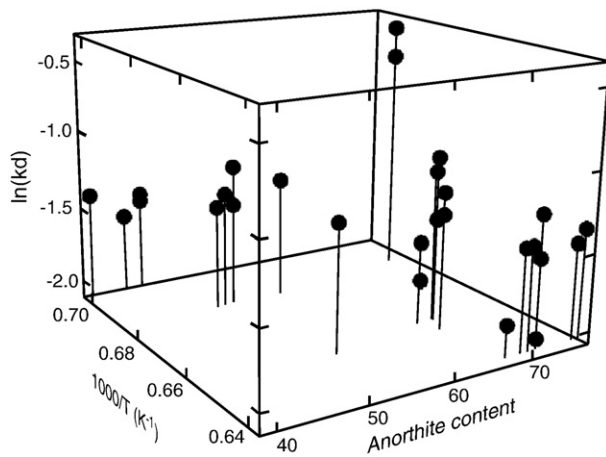


Fig. 1. Published plagioclase–melt Li partition coefficients (kd) as a function of plagioclase An content and experimental run temperature. Note that there is substantial scatter of the partition coefficient even at near constant temperature and plagioclase composition and no significant correlation of the partition coefficient with either temperature or plagioclase An content.

were crushed to produce a fine powder to act as a source of Li for the other crystals during the experiment. Because of the complex structural transitions within low temperature plagioclase, and the possibility that these could impact Li partitioning, a pre-anneal stage was undertaken in an attempt to set the plagioclase to a single, high temperature, structure. This composition range allowed a pre-anneal step at 1200 °C without approaching the melting point of the crystals and meant that for the actual experiment the equilibrium structural state for all of the crystals would be $\bar{I}\bar{1}$ (Carpenter and McConnell, 1984). All starting materials were annealed at 1200 °C for 69.5 h in an attempt to ensure that the crystals were all in the $\bar{I}\bar{1}$ structure (Carpenter and McConnell, 1984). At this temperature the equilibrium structure is $\bar{I}\bar{1}$ for all but the most albitic starting crystal.

A single experiment was conducted. A layer of the labradorite powder was loaded into an aluminum crucible and packed down. Approximately 500 μm wide fragments of all of the plagioclase crystals were then placed onto this bed of labradorite powder and covered with further labradorite powder. By having all of the crystals in a single experimental charge the aim was that they would be forced towards equilibrium with the same matrix powder and hence with one another at exactly the same run temperature. The crucible was then placed in a 1 atmosphere furnace (in air) for 6 days at 1000 °C with the temperature calibrated against the melting point of Au (1064 °C). After the experiment both the single crystals and some of the powdered labradorite were mounted in epoxy and polished for analysis.

3. Analytical method

The experimental charges were analyzed by electron microprobe at the University of Leicester using a JEOL 8600 Superprobe using a 30 nA beam, 15 kV accelerating voltage and a 10 μm spot size. Lithium concentrations were determined by laser ablation ICP-MS (LA-ICP-MS) at the University of Victoria using a New Wave 213 nm laser and a Thermo X7 ICP-MS. LA-ICP-MS analyses were calibrated against NIST 613 and 615 using Ca as the internal standard (using the Ca concentrations from the electron microprobe analyses). Ablation pits were ~30–40 μm wide and were analyzed as short line scans using a 10 Hz laser pulse rate. The relative standard deviation for Li in ten analyses of NIST 613 and NIST 615 throughout the course of the analytical session were 2% and 7% respectively. A gas blank was removed from each analysis but this was negligible at all concentrations measured (~5 counts per second).

4. Experimental results and interpretation

Fig. 2 and Table 1 shows that the Li content of the plagioclase crystals after the experiments correlates strongly with their An content. The single plagioclase crystals increased their Li content during the experiments (Table 1) presumably due to diffusion of Li out of the plagioclase powder and into the single crystals. For the single crystals zoning profiles were measured in all crystals and no systematic core to rim variation was found in any crystal. The change in Li content of the plagioclase from the composition of the starting materials, and a lack of any systematic zoning in any of the charges, are consistent with the crystals closely approaching Li-exchange equilibrium with the matrix powder and hence with one another.

The results indicate that the An content of plagioclase plays an important role in controlling the partitioning of Li between plagioclase and melt. The origin of the discrepancy between these new results and those of previous experiments (Fig. 1) is unclear. The new results are consistent with the replacement of Na^{1+} by Li^{1+} being energetically favorable over the replacement of Ca^{2+} by Li^{1+} as might be expected if charge balance plays an important role in controlling the partition coefficient. It is possible that during growth from a melt Li partitioning into plagioclase can be charge balanced by mechanisms other than simple replacement of Na but that during diffusive exchange of Li the only charge balance may come from this exchange. This is speculative but could explain the discrepancy between these datasets; if correct then the impact of An content on the partitioning of Li into plagioclase will only be seen when the activity of Li in the surroundings changes after crystal growth.

5. Application to the timescales of explosive volcanic events—a test case

To determine whether the experimental results presented above are consistent with observations from natural samples a series of detailed depth profiles through plagioclase phenocrysts erupted in 1997 from the Soufriere Hills, Montserrat (Genareau et al., 2007, 2009)

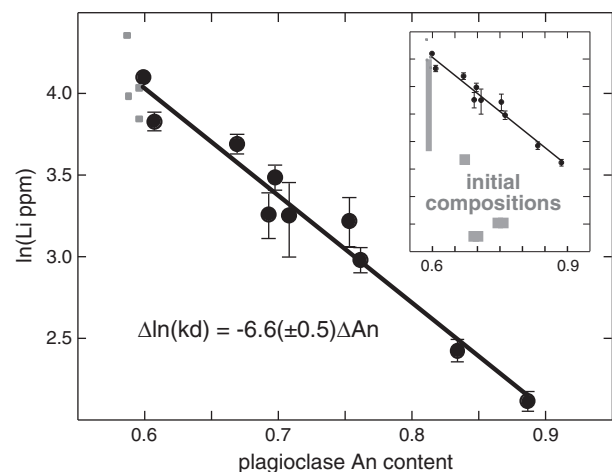


Fig. 2. Variation in Li content of plagioclase crystals of different An contents equilibrated with the same plagioclase powder. The strong correlation between plagioclase An content and $\ln(\text{Li})$ indicates that the partitioning of Li into plagioclase is strongly dependent on the An content of the plagioclase over this composition range at 1000 °C. Filled symbols with error bars are measurements of single large plagioclase crystals and the standard deviation of multiple analyses performed as rim to core profiles within these. Small gray squares are individual analyses of the powder in which these plagioclase were embedded during the experiment, measured after the experiment was run. The equation is from the slope of a linear regression through the data and relates the change in the partition coefficient as a function of the change in An content. The inset is a vertically expanded view showing the starting compositions as gray boxes.

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