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Beryllium diffusion in olivine: A new tool to investigate timescales of magmatic processes

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ABSTRACT

The diffusion of beryllium (Be) in pure synthetic forsterite (fo_{100}) and San Carlos olivine (fo_{90}) was studied between 950–1475 °C at atmospheric pressure, as a function of silica activity ($a\mathrm{SiO}_2$), crystallographic orientation, oxygen fugacity ($f\mathrm{O}_2$, for diffusion in San Carlos olivine) and water fugacity ($f\mathrm{H}_2\mathrm{O}$, at 1.15 GPa pressure (P)). The diffusivity of Be in olivine is faster than that of Mg^{2+} or Fe^{2+} but slower than that of H^+, and appears to be insensitive to $a\mathrm{SiO}_2$, $f\mathrm{H}_2\mathrm{O}$ and P, but is highly anisotropic, with diffusivities described by:

$$[001]\text{: } \log D_0 = -5.82\ (\pm 0.15), \quad E_a = 227.6\ (\pm 4.1)\ \mathrm{kJ\,mol^{-1}};$$

$$[010]\text{: } \log D_0 = -4.64\ (\pm 0.38), \quad E_a = 285.8\ (\pm 11.6)\ \mathrm{kJ\,mol^{-1}};$$

$$[100]\text{: } \log D_0 = -4.20\ (\pm 0.27), \quad E_a = 326.1\ (\pm 7.9)\ \mathrm{kJ\,mol^{-1}}.$$

Diffusion of Be^{2+} in natural San Carlos olivine was determined at 1160 to 1350 °C and was found to be similar to that in forsterite. The exception was one experiment in natural olivine in relatively oxidising conditions, where diffusion was slightly faster than its lower $f\mathrm{O}_2$ or pure forsterite counterparts.

The equilibrium solubility of Be in forsterite in equilibrium with BeO (bromellite) and MgO (periclase) is lower than when in equilibrium with BeO and $\mathrm{Mg_2Si_2O_6}$ ((proto)enstatite). This shows that Be^{2+} substitutes into olivine forming a defect with the stoichiometry $\mathrm{Be_2SiO_4}$.

The sensitivity of Be diffusion in olivine to only temperature and crystal orientation means that only these two factors need to be known to extract timescales from natural diffusion profiles (our preliminary experiments show that the dependence of diffusion on $f\mathrm{O}_2$ is minor or negligible in geologically relevant conditions). This represents a considerable advantage over using diffusion profiles of other cations (e.g., Fe^{2+}–Mg^{2+}, Ni^{2+} or Ca^{2+}), where all of the above mentioned variables must be constrained before accurate timescale determinations can be made. Two examples of the potential for using Be diffusion profiles to determine timescales in natural olivine xenocrysts are presented.

1. Introduction

Diffusion profiles in olivine, coupled with experimentally well-constrained diffusion coefficients, can yield timescales of magmatic events regardless of their age (e.g. Costa et al., 2008; Costa and Dungan, 2005; Demouchy et al., 2006; Denis et al., 2013; Jurewicz and Watson, 1988; Peslier et al., 2008; Qian et al., 2010; Ruprecht and Plank, 2013).

The rate of diffusion is dependent on the thermodynamic intensive variables – temperature (T), pressure (P) (see Brady and Cherniak, 2010 for a compilation) and chemical potentials of all relevant components. Chemical potentials encompass not only oxygen fugacity ($f\mathrm{O}_2$), but the potential of any other component that affects either the substitution mechanism of the diffusing species or the point defect populations that provide the diffusion pathways. Major-element chemical potentials (i.e. $a\mathrm{SiO}_2$) and water

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fugacity (fH_2O) likely affect both (Hier-Majumder et al., 2005; Jollands et al., 2014; Zhukova et al., 2014; Wang et al., 2004), and their effects must be evaluated for their significance, and, if found significant, quantified, for observed diffusion profiles to be converted into thermal histories.

Diffusion geospeedometry requires diffusion rates and thermal histories that are neither too slow and/or short to produce a measurable concentration profile, nor so fast and/or long that the concentration gradients have completely relaxed.

Here we confirm an initial observation that beryllium diffuses faster in olivine than other elements except hydrogen (Spandler and O'Neill, 2010, cf. Demouchy and Mackwell, 2003) and lithium, depending on the lithium substitution mechanism (Dohmen et al., 2010; Spandler and O'Neill, 2010), making it potentially useful for recording timescales of short magmatic processes.

In order to calibrate Be diffusion as a geospeedometer, we have measured the diffusivity of Be in forsterite and San Carlos olivine over the temperature range 950–1475 °C, as a function of $a\text{SiO}_2$, fO_2, fH_2O and crystallographic orientation. Our results suggest that Be diffuses by a different mechanism to other species in olivine, which is sensitive only to temperature and crystal orientation (and possibly fO_2, but to a small extent) making its application to deducing timescales particularly convenient. Despite the low concentrations of Be in natural olivine, well constrained diffusion profiles are obtainable on suitable samples by currently available analytical methods, and we demonstrate the potential of Be profiles for geospeedometry on two natural examples.

2. Methods

2.1. Experimental

2.1.1. Diffusion in forsterite

A large crystal of pure forsterite grown by the Czochralski method (Solix corporation, Belarus, trace element composition presented in Zhukova et al., 2014) was cut parallel to either the (100), (010) or (001) faces into 2–3 mm cubes. These oriented cubes were then polished on one principal face using p1200 SiC paper followed by 6 μm, 3 μm and 1 μm diamond paste on cloth laps.

The beryllium sources for diffusion experiments were three-phase mixtures designed to buffer the three components of the system (i.e., MgO–SiO_2–BeO) according the phase rule. These consisted of bromellite (BeO) plus forsterite (Mg_2SiO_4) and either periclase (MgO) or, depending on temperature, protoenstatite or orthoenstatite ($Mg_2Si_2O_6$). Due to the lack of information on the phase relations in the BeO–MgO–SiO_2 ternary, several potential buffer compositions were sintered in order to determine whether the three-phase assemblages in equilibrium with forsterite contained bromellite (BeO) or phenakite (Be_2SiO_4). At the conditions of sintering (1250–1400 °C), the assemblages were forsterite–(proto)enstatite–bromellite (fo-(pr)En-bro) and forsterite–periclase–bromellite (fo-per-bro). Schuiling et al. (1976) found forsterite plus phenakite at 827 °C, 0.1 GPa. We did not observe phenakite after annealing at 956 °C for 31 days in the diffusion experiment (see below), suggesting that the univariant reaction $Mg_2Si_2O_6 + 2BeO = Mg_2SiO_4 + Be_2SiO_4$ may occur between these temperatures, although this observation is not definitive as it was not reversed.

The two target assemblages (~1:1:1 molar proportions of each phase) were both synthesised from reagent (or higher) grade oxide powders. The oxides were ground under acetone in an agate mortar, dried, pressed into pellets and sintered; the periclase-bearing assemblage at 1400 °C and the (proto)enstatite-bearing assemblage at 1250 °C. Partial melt was observed in the fo-prEn-bro assemblage at 1300 °C. Following sintering, the phases present were identified using X-ray diffraction (XRD).

The pellets were then reground, mixed with polyethylene oxide 'glue' and pasted onto the polished crystal surfaces. The crystal-powder–glue couples were dried at ~110 °C (generally >12 h), then placed onto a bed of the appropriate buffer (pre-sintered fo-prEn or fo-per) on a Pt disc, covered with an upturned Pt crucible, and annealed in a box furnace. The exception was the highest temperature experiment (1475 °C), which was conducted in a vertical gas-mixing furnace. In this experiment, the crystals were placed on a Pt tray and lowered into the pre-heated furnace, eliminating the slow ramp-up time required by the box furnace.

Following annealing, the crystals were mounted in epoxy, ground down by ~500 μm along a direction perpendicular to the diffusion axis (to remove edge effects) and polished for analysis.

2.1.2. Diffusion in San Carlos olivine

Cuboids of San Carlos olivine were prepared from a large single crystal, using a combination of cleavage planes, XRD and optical extinction angles to determine the crystallographic orientation. This method gives up to ~10–15° misorientation from the principal axes.

Buffer assemblages of olivine (~$Mg_{1.8}Fe_{0.2}SiO_4$), bromellite and either orthopyroxene (opx, $Mg_{1.8}Fe_{0.2}Si_2O_6$) or ferropericlase (fpr, $Mg_{0.7}Fe_{0.3}O$) were prepared to be approximately in equilibrium with San Carlos olivine with regards to their Mg/Fe ratios, although it transpired during the course of this study that the rate of Be diffusion is sufficiently faster than Fe–Mg diffusion such that changes in the Mg/Fe of the olivine at the near interface should not affect Be diffusion profiles. Assuming there is negligible Mg or Fe substitution into BeO, opx-bro and fpr-bro assemblages (1:1 molar) were weighed from MgO, Fe_2O_3, SiO_2 and BeO powders, then mixed with powdered San Carlos olivine, pressed into pellets and sintered in a 90% CO_2–10% CO gas mix at 1250 °C in a vertical tube furnace. After phase verification by XRD, the crystal–powder couples were prepared in the same manner as for the forsterite experiments.

The crystals were then placed onto a Pt tray on a bed of crushed San Carlos olivine to stop the crystal welding to the Pt, and annealed in an atmosphere of either 90–10 or 99–1 CO_2–CO mixing ratios (~QFM − 0.5 or ~QFM + 2.1, respectively).

Following annealing, the crystals were treated in the same way as the pure forsterite experiments.

2.1.3. Hydrous experiment

To determine the effect of H_2O on the diffusion of Be, an experiment was conducted at 1050 °C and 1.15 GPa for 71 h 40 min in a piston-cylinder apparatus. An oriented crystal of forsterite, cut into a disc ~3 mm diameter, 1.5 mm thickness with the (polished) flat face parallel to (001), was placed into a 9 mm × 12 mm (outside diameter × length) Cu capsule and packed with fo-bro-prEn powder and ~100 mg distilled H_2O. This was then placed in an MgO sleeve inside a graphite heater inside a talc assembly surrounded by low friction Teflon foil, and annealed in a 3/4″ (19 mm) pressure vessel in an end loaded Boyd-type piston cylinder. Temperatures were continuously monitored using a Type B thermocouple, with the welded bead located inside the capsule lid. The capsule was based on that presented in Hack and Mavrogenes (2006). Following annealing, the capsule was opened using a lathe and the powder and crystal were removed by ultrasonic agitation of the open capsule. The crystal was then mounted in epoxy and doubly polished.