



Invited research article

# The effect of melt composition on mineral-melt partition coefficients: The case of beryllium

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## ABSTRACT

The divalent cation  $\text{Be}^{2+}$  is considerably smaller than other divalent cations ( $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ , et cetera), leading to a strong preference for tetrahedral coordination in minerals. Its thermodynamic properties in silicate melts may accordingly differ from these other divalent cations, potentially distinguishing its mineral/melt partition coefficients. In order to investigate this possibility, the partitioning of Be between silicate melt and forsterite was examined for 16 melt compositions in the systems  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  at 1400 °C with additional experiments to investigate the effect of added  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$ , and temperature at 1300 °C. The relative activity coefficient of BeO in the melts decreases with increasing CaO and  $\text{NaO}_{1.5}$ . The results are compared to Mg and Ca partitioning in the same experiments, and to the partitioning of other divalent cations (Ni, Co, Mn) from the literature. While the partition coefficient of the latter correlate positively with the Mg partition coefficient, Be shows only a weak negative correlation. Compared to Ca, Be partitions less strongly into forsterite when the melt has high Na and/or Ca. Partition coefficients for Na, Al and Ti are also reported.

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## 1. Introduction

Beryllium is one of the refractory lithophile elements, which are commonly assumed to have chondritic relative abundances in the Bulk Silicate Earth (e.g., [Palme and O'Neill, 2014](#)), although it should be remembered that this is an assumption ([O'Neill and Palme, 2008](#); [Campbell and O'Neill, 2012](#)). Empirically, Be appears to behave geochemically like Nd, another refractory lithophile element, during the petrogenesis of ocean floor basalts (OFBs), which have Be/Nd of  $0.049 \pm 0.007$  ( $n = 616$ ; [Jenner and O'Neill, 2012](#)), close to the chondritic ratio of 0.046 ([Palme et al., 2014](#)). Given that the geochemical behaviour of Be is determined by its occurrence in magmatic systems as a 2+ cation with a very small ionic radius (0.27 Å and 0.45 Å in IV-fold and VI-fold coordination respectively; [Shannon, 1976](#)), while Nd occurs as a 3+ cation with a large ionic radius (0.98 Å in VI-fold coordination; [Shannon, 1976](#)), the observed constancy in OFBs and the lack of fractionation relative to the chondritic ratio potentially constrains not only the OFB petrogenetic process, but also the processes that have configured the OFB source (a.k.a. the depleted MORB mantle). We note that the average Be/Nd ratio estimated for the upper continental crust is also at present too poorly constrained, at  $0.078 \pm 0.032$  ([Rudnick and Gao, 2014](#)), to tell whether it is different. The significance of these constraints is somewhat obscure, because so little is known about the behaviour of Be in igneous systems at present.

This is understandable given the historical analytical difficulties. The natural abundance of Be is low – in CI chondrites, its abundance of 21.9 ppb is lower than that of all the other refractory lithophile elements except Ta and U ([Palme et al., 2014](#)). Moreover, Be has too low an atomic number ( $Z = 4$ ) to be amenable to analytical methods based on characteristic X-rays such as X-ray fluorescence or electron probe microanalysis (EPMA). However, modern analytical techniques based on mass spectrometry now allow Be to be determined precisely in typical natural concentrations (e.g., [Jenner and O'Neill, 2012](#); [Jollands et al., 2016](#)). Such analytical methods have allowed the substitution mechanism of Be in olivine to be determined ([Jollands et al., 2016](#)), preparing the way for a means of investigating the effect of melt composition on the thermodynamic properties of BeO in silicate melts, which will advance the use of an element with a uniquely distinctive combination of chemical properties in basalt studies.

One factor determining the behaviour of Be in basalt petrogenesis is the effect of melt composition on the thermodynamic properties, which, because of the small size of the  $\text{Be}^{2+}$  cation, might be expected to differ from other divalent cations (e.g. [Sen and Yu, 2005](#)), and from that of  $\text{Nd}^{3+}$ . The most direct way to determine the effect of melt composition on the thermodynamic properties of a component of a silicate melt would be to use an equilibrium of the component between the melt and a simple, compositionally invariant phase insoluble in the silicate melt, allowing the composition of the melt alone to be varied experimentally with all other components of the equilibrium kept constant. In the case of a handful of elements (e.g. Ni, Co, Mo, W, the platinum group metals) this may be achieved by reduction of the relevant oxide

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component in the silicate melt to a metal phase (e.g. O'Neill and Eggins, 2002; O'Neill et al., 2008; Borisov and Danyushevsky, 2011), but for refractory lithophile elements this metal option is at present experimentally impractical, and for such elements an alternative approach using partitioning into a compositionally invariant crystalline phase appearing on the liquidus of a range of melt compositions is the best choice available. This approach has been used, for example, by Miller (2007) for studying divalent cations (Mg, Sr, Ba) with anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) as the crystalline phase. Compared to the metal-redox method, this approach is restricted, obviously, to those combinations of melt composition and temperature and pressure that have the relevant phase on the liquidus. For forsterite ( $\text{Mg}_2\text{SiO}_4$ ) at low pressures, this restriction still allows a wide range of melt compositions to be investigated. Consequently, the effect of melt composition on several divalent cations (Mn,  $\text{Fe}^{2+}$ , Co, Ni and Zn) have been studied by this method (e.g. Watson, 1977; Hirschmann and Ghiso, 1994; Kohn and Schofield, 1994; Toplis, 2005; Mysen and Dubinsky, 2004; Mysen, 2007; Matzen et al., 2013), as have trace elements with other valences (for example, REE, Y, Sc, Zr, Hf and Al by Evans et al., 2008).

In this study we report forsterite/melt partition coefficients for Be and Ca at 1300 and 1400 °C for a wide range of melt compositions in the system CMAS ( $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ ) and also investigate the effects of adding  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$ , in order to understand the contrasting geochemistry of Be and Nd and hopefully shed light on the significance of the constant Be/Nd ratio of OFBs.

## 2. Methods

Melt compositions were selected by reference to phase diagrams, where available. Compositional sets AB212, AB213 and AB214, and AB215, AB216 and AB217 are defined by addition of varying amounts of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  (respectively) to base composition AB211, which corresponds to composition DFAa of Evans et al. (2008). The bulk composition for each experiment was designed to produce ~20% forsterite crystals. Reagent grade  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , MgO (all dried at 1000 °C) and  $\text{CaCO}_3$ ,  $\text{TiO}_2$  and  $\text{Na}_2\text{CO}_3$  (all dried at 300 °C) were weighed out in the desired proportions; Be was added as a 1000 ppm solution in  $\text{HNO}_3$  using a syringe, or as BeO for composition AB230b. These mixtures were ground under acetone in an agate mortar until dry. For Na-free mixtures, the resulting powders were mixed with polyethylene oxide solution to produce a paste that was affixed to loops of 0.3 mm diameter Pt wire and subsequently air-dried. The Na-bearing mixtures were briefly fired at 900 °C to decarbonate them, then pressed into 3.5 mm Pt capsules that were crimped and welded, leaving a minuscule outlet to prevent pressure build-up at high temperatures while retaining Na. The wire loops and capsules were suspended from a chandelier in the hotspot of a 1 atm vertical furnace, allowing up to 6 melt compositions to be run simultaneously. The furnace was heated to the run temperature and the samples were held there in air for ~7 days before drop-quenching into water (past experience indicates that olivine nucleation is rapid; the long experimental duration allows olivine growth by Ostwald ripening); the temperature was monitored using a Type B thermocouple and is considered accurate to  $\pm 1$  °C. The beads attached to the loops were fragmented to expose a larger area before mounting in epoxy and polishing; the capsules were mounted in epoxy and sectioned with a saw blade (to double the area available for analysis while preserving spatial relationships) before polishing. A brief soak in concentrated Citranox® (Evans et al., 2008; Tuff and O'Neill, 2010) increased the contrast between olivine and glass in reflected light images.

EPMA of the matrix glasses was performed using a Cameca SX-100 electron probe with an accelerating voltage of 15 kV and a beam current of 20 nA. The standards used were: wollastonite for Si,  $\text{CaAl}_2\text{O}_4$  for Ca and Al, periclase for Mg, rutile for Ti and anorthoclase for Na. To prevent Na mobilisation under the electron beam, the three Na-bearing compositions were analysed using a 20  $\mu\text{m}$  diameter beam. As an additional test of this protocol, an expedited analysis (in which counting times

were reduced from 20 to 10 s for Na and 20 to 15 s for Mg and Al) was performed on one Na-rich glass.

Trace element analysis of the resulting samples was carried out using a Lambda Physik Compex 110 Eximer 193 nm laser with a HeEX ablation chamber coupled to an Agilent 7700 series ICP-MS. The carrier gas was He-Ar, fluence was maintained at ~50 mJ and pulse rate was set to 5 Hz; the spot size was 22 or 28  $\mu\text{m}$ . The isotopes analysed were  $^9\text{Be}$ ,  $^{23}\text{Na}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{43}\text{Ca}$ ,  $^{45}\text{Sc}$  and  $^{47}\text{Ti}$ . NIST610 glass (Jochum et al., 2011) was used as the external standard; Si (by stoichiometry for forsterite; determined by EPMA for the glasses) was used as the internal standard. For the three Na-rich compositions, analysis locations were restricted to near the base of the capsule because of the risk of Na loss from the tops of the capsules. The data were reduced using an in-house Excel spreadsheet that includes a linear drift correction. Occasional spikes in the time-resolved data, mostly attributed to melt inclusions because of correlation between incompatible elements, were removed prior to integration of the signal.

In calculating partition coefficients, where an element was present in the glass at > 1% oxide, the EPMA data for the glass were used in preference to the LA-ICP-MS data.

## 3. Results

The melts quenched to give a homogenous glass and forsterite was the only liquidus phase in these experiments, occurring as equant crystals mostly 40–60  $\mu\text{m}$  (and occasionally up to 100  $\mu\text{m}$ ) in size. Melt compositions are reported in Tables 1 and 2. The two analytical protocols for Na by EPMA gave results within error of each other and so Na mobilisation is believed not to have occurred. Forsterite compositions are reported in Table 3. Apparent Sc concentrations were averaged 2.6 ppm in forsterite, which is close to the magnitude of the  $^{29}\text{Si}^+$  interference; hence the data for this element are not reported. The LA-ICP-MS data for Ca are ~10% lower relative to those obtained by EPMA for the glasses and ~20% lower for the forsterite crystals. The LA-ICP-MS data for Al are in excellent agreement up to 11%  $\text{Al}_2\text{O}_3$  but are commonly lower by 6–9% relative to the EPMA data for glasses with > 13%  $\text{Al}_2\text{O}_3$ . Partition coefficients for Li, Be, Na, Al, Ca and Ti are reported in Table 4.

Be is highly incompatible in olivine, but is slightly more compatible than Na (Borisov et al., 2008; this work) and significantly more compatible than the REE (Beattie, 1994; Evans et al., 2008).  $D_{\text{Be}}$  varies by a factor of 2 across the range of compositions studied.

## 4. Discussion

In silicate glasses, Be occupies a mixture of distorted and undistorted tetrahedral sites (Sen and Yu, 2005). The relative proportion of Be in distorted sites is higher at lower concentrations, which would probably correspond to a majority of the Be at the levels employed in the present experiments. A change in coordination environment as a function of concentration could result in deviations from Henry's Law. At 1300 °C the observed  $D_{\text{Be}}$  for compositions AB230 and AB230b, which differ only in Be content, are within error of each other, and therefore it appears any concentration dependence of Be partitioning is insignificant over the range studied.

Although substitution of Ca into forsterite affects the unit cell volume, this can be excluded as a cause of the observed variations in partitioning of Be. The increase in unit cell volume from pure forsterite to the most calcic olivine studied is equivalent to that for an olivine of composition  $\text{fo}_{88}\text{fa}_{12}$  (Louisnathan and Smith, 1968; Adams and Bishop, 1985), and it has been demonstrated that the maximum solubility of Be in olivine does not change over the range  $\text{fo}_{90}\text{fa}_{10}$  to  $\text{fo}_{100}$  (Jollands et al., 2015). Therefore, melt structure or composition is the only remaining variable that could affect partitioning in the 1400 °C series.

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