



Trace element mineral/melt partitioning for basaltic and basaltic andesitic melts: An experimental and laser ICP-MS study with application to the oxidation state of mantle source regions



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ABSTRACT

Understanding magmatic processes such as crystallization and melting recorded in natural samples requires calibration of mineral–melt trace element partition coefficients (D) and their dependence on temperature, pressure, oxygen fugacity (fO_2) and chemical composition. However, few experimental studies have focused on measuring trace element partition coefficients for a large number of trace elements, in the various minerals present in basaltic rocks, and under diverse conditions, particularly of variable fO_2 . Twenty-seven 0.1 MPa experiments provide partition coefficients for major elements and Sc, Ti, V, Mn, Co, Ni, Ga, Sr, Y, Nb, Ba, Ce, Nd, Eu, Gd, and Yb for the mineral phases olivine, plagioclase, orthopyroxene and clinopyroxene. The experimental conditions range from 1150 to 1190 °C with oxygen fugacities from QFM to NNO+2. Run products were analyzed by laser-ablation ICP-MS.

The new partition coefficients, combined with previously published data, can be used to model crystallization processes at low pressure. Partitioning of multivalent cations V, Fe and Eu varies as a function of the redox conditions, consistent with previous work, and can be used to constrain oxidation states of magmatic source regions. The V/Yb ratio is shown to be a useful proxy for oxidation state. The V/Yb ratio varies during mantle melting as a function of oxidation state of the mantle source, and it is not modified during fractional crystallization of olivine \pm plag \pm cpx. V/Yb increases from MORB, BABB to arc lavas, suggesting a progressive increase of fO_2 from QFM to NNO+2. Apparent fO_2 of arc lavas, however, is quite variable. These results demonstrate that sub-arc mantle displays a larger range of redox conditions toward a more oxidized mantle than the MORB mantle.

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1. Introduction

Modeling magmatic processes such as crystallization and melting requires calibration of mineral–melt trace element partition coefficients (D) and how they vary with temperature, pressure, oxygen fugacity (fO_2) and chemical composition. Despite the developments in in-situ analytical techniques in the past twenty years that make this task achievable, few studies have focused on measuring partition coefficients for a large number of trace elements under diverse conditions, particularly of variable fO_2 (Aigner-Torres et al., 2007; Bindeman et al., 1998). Oxygen fugacity is of particular current interest because of a debate over how mantle fO_2 may vary in different tectonic environments (Frost and McCammon, 2008).

While convergent margin magmas are generally more oxidized at the surface (e.g. Carmichael, 1991) and sub-arc mantle records more oxidizing conditions (Parkinson and Arculus, 1999), there is dispute over the relative oxidation states of ocean ridge and convergent margin mantle sources (Dauphas et al., 2009; Kelley and Cottrell, 2009; Lee et al., 2005; Lee et al., 2012; Lee et al., 2010; Mallmann and O'Neill, 2009). Lee et al. (2005) and Li and Lee (2004) suggest that arc magma sources are as reduced as MORB sources.

Elements that have variable oxidation states under terrestrial conditions have the potential to constrain the redox state of magmas. V, Fe, and Eu can have multiple oxidation states, influencing their partition coefficients. V occurs as V^{3+} and V^{4+} (Canil, 1999; Gaetani and Grove, 1997). Because V^{3+} is preferentially included in igneous minerals, $D_{V}^{mineral/melt}$ decreases as fO_2 increases since more of the V is in the incompatible $4+$ form. Similarly, Eu and Fe occur both as $2+$ and $3+$ ions in magmas, and

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$D^{mineral/melt}$ decreases as fO_2 increases for minerals that preferentially incorporate the 2+ form (olivine and orthopyroxene for Fe, plagioclase for Eu). Therefore, in the absence of magnetite, V and Fe partitioning between liquid and the phases olivine, orthopyroxene and/or clinopyroxene, and Fe and Eu partitioning between melt and plagioclase or pyroxene can be used to estimate the redox state of magmas.

Previous experimental studies used $D_V^{mineral/melt}$ (Canil, 1999; Canil and Fedortchouk 2000, 2001; Karner et al., 2007; Karner et al., 2008; Mallmann and O'Neill, 2009; Righter et al., 2006a, 2006b; Shearer et al., 2006; Toplis and Corgne, 2002) and $D_{Eu}^{mineral/melt}$ (Aigner-Torres et al., 2007; Karner et al., 2010; McKay et al., 1994; Wadhwa, 2001) to constrain variations of fO_2 . Li and Lee (2004) and Lee et al. (2005) suggest that the ratio V/Sc in magmas is not modified during differentiation, degassing, crustal contamination and metasomatic processes, and on the basis of similar V/Sc in MORB and arc magmas infer that the fO_2 of their source regions was similar. This contrasts with the results of Kelley and Cottrell (2009) that showed higher Fe^{3+}/Fe^{2+} ratios in arc magmas suggesting higher oxidation states in their source regions.

In view of these debates, and in order to appropriately address fractionation in the different magmatic settings we carried out twenty-seven 0.1 MPa crystallization experiments at sub-liquidus temperature and variable fO_2 on two starting compositions, a normal MORB and a basaltic andesite, doped in 13 elements of interest. All phases present in the experimental charges were analyzed by electron microprobe and laser-ablation ICP-MS, with the exception of spinel and clinopyroxene from most experiments due to their very small size. These results supply an internally consistent set of partition coefficients at variable oxidation state that can be used both to model fractionation more reliably, and also to assess oxidation states of terrestrial magmas.

2. Experimental and analytical methods

2.1. Starting materials

The two starting compositions were a MORB (AII96–3–18–1) from the Kane Fracture Zone (mid-Atlantic ridge; Bryan et al., 1981) and the basaltic andesite 85–44 from Mt. Shasta in the Cascade Volcanic Arc, N California (Baker et al., 1994; Grove et al., 2002). Both compositions have been previously used in experimental studies (Baker et al., 1994; Grove et al., 2003; Müntener et al., 2001; Tormey et al., 1987).

The starting materials were doped in 13 elements (Sc, V, Cr, Co, Ni, Sr, Zr, Nb, Ba, Nd, Eu, Gd and Yb) by addition of standard elemental solutions. The added concentrations vary from 100 ppm for Eu to 2000 ppm for Nb for 1 gram of the powdered starting material. Major and trace element compositions of the starting materials are reported in Table S1 (Supplementary material). The absence of significant effects of the enrichment technique on phase stability will be demonstrated by comparing enriched experiments with experiments on non-enriched starting materials. After the enrichment procedure, the samples were ground under ethanol in an agate mortar to a homogeneous powder mixture.

2.2. Experimental methods

Experiments under anhydrous conditions at 0.1 MPa were performed at MIT in a vertical-tube DelTech quenching furnace, with a CO_2-H_2 gas atmosphere. The oxygen fugacity was monitored using a ZrO_2-CaO oxygen cell calibrated against the Fe–FeO, Ni–NiO and Cu–Cu₂O buffers. In order to cover a range of redox conditions, experiments were performed at three fO_2 conditions in order of increasing fO_2 : the quartz–fayalite–magnetite buffer (QFM), the nickel–nickel oxide buffer (NNO) and NNO+2. The sample material

for these experiments consisted of ~50 mg of the mixture that had been mixed with polyvinyl alcohol and pressed into a pellet. This pellet was then sintered on to an iron–platinum alloy loop, which had been previously annealed with 4–6 or 7–9 wt.% Fe depending on the starting composition and fO_2 conditions. The annealing process helps prevent Fe loss to the alloy during the experiment. When possible, loops that had previously been run with the same initial composition were used to further minimize the possibility of Fe loss. The run temperature was continuously monitored using a Pt–Pt₉₀Rh₁₀ thermocouple calibrated against the melting points of NaCl, Au, and Pd on the IPTS 1968 temperature scale (Biggar, 1972). The thermocouple was placed in the hotspot of the furnace, where the thermal gradient is <1 °C. The sample was suspended alongside the thermocouple, so they were at the same level within the furnace, minimizing the difference between the temperature of the sample and the reading of the thermocouple. The reproducibility and measurement of this arrangement is better than 5 °C.

Before each experiment, each pellet was conditioned by fusing at 1230 °C (AII96–3–18–1) and 1300 °C (85–44) for 2 h in the hotspot of the furnace with the fO_2 controlled near the buffer fO_2 . This dissolved crystals that were present in the starting material. After this glassing step, the experiment was removed, the temperature was adjusted to the run temperature and the sample was reinserted into the furnace. The range in temperature was 1150–1175 °C for the experiments performed on the MORB composition and 1155–1190 °C for the basaltic andesite. These experiments were run isothermally in order to ensure achievement of equilibrium. Experiments were typically run for 72 h.

For comparative purposes, two “rapid-cooling” experiments were performed for the MORB and two constant cooling rate experiments were carried out with the basaltic andesite. For the cooling rate experiments with 85–44, samples were loaded into the furnace when it had equilibrated at 1170 °C (MTEP18) or 1175 °C (MTEP20), and were then cooled at 4–5 °C/h until they reached the run temperature. Charges were quenched by dropping into water.

Details of the experimental conditions and resulting phase assemblages for each run, as well as full analytical details and evaluation of equilibrium can be found in the Supplementary material.

3. Experimental results

3.1. Mineral appearances

The phase proportions for both starting compositions are reported in Table S2.

3.1.1. MORB AII96–3–18–1

In the isothermal experiments, olivine, plagioclase and spinel coexist from the highest temperature in our series, 1175 °C, to 1165 °C. Clinopyroxene appears at 1165 °C. The non-doped experiment (MTEP10) shows similar results to the doped experiments, indicating no influence of doping on phase stability. In rapid-cooling experiments (MTEP5&9), the phase proportions differ from those in the isothermal runs: cpx is absent at 1165 °C and the ratio of the proportion of melt to that of the mineral phases is higher. Along with chemical evidence discussed below these observations suggest that equilibrium was not reached in the rapid-cooling experiments.

3.1.2. Basaltic andesite 85–44

In the isothermal experiments, plag, oliv and spinel coexist at 1190 °C, then opx appears at 1180 °C, and cpx at 1160 °C. The non-doped experiment (MTEP28) shows similar results to the doped experiments. The cooling rate experiments (MTEP18&20) differ from the rapid-cooling rate experiments performed on the MORB

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