Experimental determination of the geochemical cycle of boron and its isotopes from the slab to the surface

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Enrichment of boron in arc magmas (IAB) relative to fresh MORB and mantle indicates transport of boron from subducted sediments and/or altered oceanic crust into the magma´s source region and finally to the surface by fluids and melts. The different reservoirs (mantle, MORB, altered MORB, sediments) have different boron concentrations and $\delta^{11}B$ values. To use boron and its isotopes as geochemical tracers in subduction zone environments, a quantitative understanding of their geochemical behavior in fluid mediated processes is essential.

We therefore experimentally determined (a) the boron speciation in acidic to basic solutions by in-situ Raman spectroscopy at 22 to 600 °C and 10^{-4} to 3.0 GPa, (b) the boron isotope mica-fluid fractionation at near-neutral and basic conditions at 0.4 and 3.0 GPa and 400 to 700 °C, and (c) the liquid-vapor fraction of boron and its isotopes below 450 °C and 45 MPa.

(a) $B(OH)_3$ is the predominant boron species in the fluid phase at all conditions. Significant amounts of $[B(OH)_4]^-$ are only present in very basic solutions and HBO_2 might occur in acidic to neutral solutions at elevated temperatures. (b) At near-neutral conditions $\Delta^{11}B_{mica-fluid}$ is -11.7 ± 2.6 ‰ at 500 and -6.2 ± 1.3 ‰ at 700 °C. A combination with reported $\Delta^{11}B_{clay,melt-fluid}$ data yields

$$\Delta^{11}B_{mica,clay,melt-neutral\ fluid} = -10.69*(1000/T\ [K]) + 3.88\ ‰.$$

With $\Delta^{11}B_{mica-fluid} = -7.4 \pm 1.0$ ‰ at 400 and -4.8 ± 1.0 ‰ at 500 °C the boron isotope mica-fluid fractionation is notable smaller at basic conditions and reflects increasing amounts of $[B(OH)_4]^-$ in the fluid. (c) The boron liquid-vapor fractionation is generally small. Maximum values at salt saturated conditions are $D_B^{1/v} = 3.7$ (400 °C/17.2 MPa) and 2.6 (450 °C/25 MPa). ^{11}B preferentially fractionates into the vapor. Within analytical and experimental uncertainties, the boron isotope fractionation increases with increasing opening of the solvus according to $\Delta^{11}B_{vapor-liquid} = 0.22 (\pm 0.05) * (P_{crit} - P)$ ‰ (with P in MPa).

A simple Rayleigh fractionation between mica and fluid based on our experimental data reproduces the systematically decreasing $\delta^{11}B$ values in IAB with increasing depth of the subducted plate.

Trace element partitioning between rutile and melt with implications for element transfer in subduction zones

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Rutile/melt trace element partition coefficients were determined experimentally for a large number of trace elements (Zr, Hf, Nb, Ta, V, Co, Cu, Zn, Sr, REE, Cr, Sb, W, U, Th). We find the high field strength elements (Zr, Hf, Nb, Ta) compatible in rutile, whereas most other studied trace elements are incompatible (Co, Zn, Sr, Th, REE). In all experiments we found $D_{Ta}>D_{Nb}$, $D_{Hf}>D_{Zr}$ and $D_U>D_{Th}$.

Experiments were conducted at constant pressure and temperature, but in systems with very different melt compositions. Additionally, a number of experiments were conducted at different oxygen fugacitites. As expected, partition coefficients for polyvalent elements (Sb, W, V) are strongly affected by changes of fO_2. Furthermore, our results imply that melt composition exerts a strong influence on HFSE partition coefficients. With increasing polymerisation of the melt, rutile/melt partition coefficients for the high field strength elements Zr, Hf, Nb and Ta increase for about an order of magnitude. However, D_{Nb}/D_{Ta} and D_{Hf}/D_{Zr} appear not to be affected by melt composition.

Because $D_U>D_{Th}$, partial melting of rutile-bearing eclogite in subducted lithosphere may cause excesses of ^{230}Th over ^{238}U in some island arc lavas, whereas dehydration of subducted lithosphere may cause excesses of ^{238}U over ^{230}Th. From our partitioning results we infer partition coefficients for Pa which we predict to be much lower than previously anticipated. Contrary to previous studies, our data imply that rutile should not significantly influence observed ^{231}Pa-^{235}U disequilibria in certain volcanic rocks.