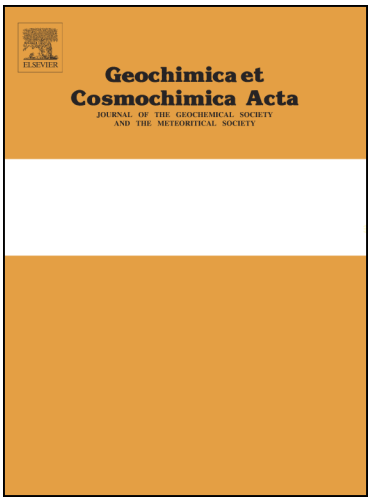

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Christian T. Hansen, Anette Meixner, Simone A. Kasemann, Wolfgang Bach

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New insight on Li and B isotope fractionation during serpentinization derived from batch reaction investigations

Christian T. Hansen[a *], Anette Meixner[a], Simone A. Kasemann[a], Wolfgang Bach[a]

[a] MARUM – Center for Marine Environmental Sciences and Faculty of Geosciences, University of Bremen

Abstract

Multiple batch experiments (100 °C, 200 °C; 40 MPa) were conducted, using Dickson-type reactors, to investigate Li and B partitioning and isotope fractionation between rock and water during serpentinization. We reacted fresh olivine (5g; $Fo_{90;}$ [B] = <0.02 µg/g; $\delta^{11}B_{Olivine}$ -14 ‰; [Li] = 1.7 µg/g; $\delta^{7}Li_{Olivine}$ = +5.3 ‰) with seawater-like fluids (75 ml, 3.2 wt.% NaCl) adjusted with respect to their Li (0.2, 0.5 µg/ml; and $\delta^{7}Li_{Fluid}$ +55 ‰) and B (~10 µg/ml and $\delta^{11}B_{Fluid}$ -0.3 ‰) characteristics. At 200 °C a reaction turnover of about 70% and a serpentinization mineral assemblage matching equilibrium thermodynamic computational results (EQ3/6) developed after 224 days runtime. Characterization of concomitant fluid samples indicated a distinct B incorporation into solid phases ($[B]_{final\_200°C}$ = 55.61 µg/g; $D^{S/F}B_{200°C}$ = 13.42) and a preferential uptake of the lighter ^{10}B isotope ($\Delta^{11}B_{S-F}$ = -3.46 ‰). Despite a low reaction turnover at 100 °C (<12%), considerable amounts of B were again incorporated into solid phases ($[B]_{final\_100°C}$ = 25.33 µg/g; $D^{S/F}B_{100°C}$ = 24.2) with even a larger isotope fractionation factor ($\Delta^{11}B_{S-F}$ = -9.97 ‰). While magnitude of isotope fraction appears anti-correlated with temperature, we argue for an overall attenuation of the isotopic effect through changes in B speciation in saline solutions ($NaB(OH)_4(aq)$ and $B(OH)_3Cl^-$) as well as variable B fixation and fractionation for different serpentinization product minerals (brucite, chrysotile). Breakdown of the Li-rich olivine and limited Li incorporation into product mineral phases resulted in an overall lower Li content of the final solid phase assemblage at 200 °C ($[Li]_{final\_200°C}$ = 0.77 µg/g; $D^{S/F}Li_{200°C}$ = 1.58). First order changes in Li isotopic compositions were defined by mixing of two isotopically distinct sources i.e. the fresh olivine and the fluid rather than by equilibrium isotope fraction. At 200 °C primary olivine is dissolved, releasing its Li budget into the fluid which shifts towards a lower $\delta^{7}Li_F$ of +38.62 ‰. Newly formed serpentine minerals ($\delta^{7}Li_S$ = +30.58 ‰) incorporate fluid derived Li with a minor preference of the ^6Li isotope. At 100 °C Li enrichment of secondary phases exceeded Li release by olivine breakdown ($[Li]_{final\_100°C}$ = 2.10 µg/g; $D^{S/F}Li_{100°C}$ = 11.3) and it was accompanied by preferential