

Tracing mass transfer in the subduction cycle: investigation of Li and B equilibrium isotope fractionation between minerals and aqueous fluids at high P and T

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Stable isotopes are widely used in petrology as geochemical tracers. For instance, the measured variations of isotopic signatures in different parts of the subduction zone provide information on the mass transfer processes during the subduction cycle. Among others, the isotopes of light elements such as Li and B strongly fractionate between minerals and aqueous fluids during fluid-rock interaction processes, which is responsible for the variation of isotopic signatures observed across volcanic arcs. In order to use the isotope tracing methods to access information on the processes occurring in the subduction slab, the isotope fractionation mechanisms and fractionation factors between minerals and fluids of interest must be well known and characterized. One of the most important mechanisms leading to the formation of distinct isotopic signatures is the equilibrium isotope fractionation, which can be determined experimentally or modelled on the atomic scale by modern computational methods. The second approach has an advantage of not being limited to certain thermodynamic conditions (such as P or T) and is able to give a unique atomic-scale insight into processes driving the fractionation of isotopes. In order to utilize the modern computational technique in the field of isotope geochemistry we present an efficient ab initio based computational approach for the prediction of equilibrium isotope fractionation factors between complex materials, including fluids and melts at high pressure and temperature. Our predictions for the Li and B equilibrium stable isotope fractionation factors between complex Li/B-bearing crystalline solids (staurolite, spodumene, tourmaline and micas) and aqueous fluids demonstrate the accuracy of the ab initio computations, which is comparable to the accuracy of experimental techniques, also used in the investigation. The ab initio model reproduces correctly the experimental isotope fractionation sequences: staurolite-fluid-mica-spodumene for Li [1,2] and fluid-tourmaline-B[4] micas for B [3], and provides valuable information on the chemical environment (cation coordination, fluid speciation) responsible for production of isotope signatures, which help in better understanding the experimental data and isotopic signatures observed in nature.

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