SIMS Microanalyses of Li and B Isotopes: Quantification and Applications to the Earth's Crust.

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Calibrating SIMS for δ^7Li and δ^{11}B

Measurements of several bulk-analyzed minerals and glasses by secondary ion mass spectrometry (SIMS, or ion microprobe) has commonly revealed inter- and intra-granular zoning of Li isotopes while B isotopes are more often homogeneous. Surface contamination can also be a significant issue; after removal of adsorbed material, δ^7Li and δ^{11}B of clay minerals may decrease by ~10-15‰ compared to "as received" samples. Homogeneous, clean samples with trace boron show typically minor effects of chemistry on SIMS measurements, but matrix effects appear to be more important for Li isotope ratios. Calibration for δ^7Li in homogeneous olivine crystals, for example, changes by >1‰ per mol% forsterite. In contrast, a suite of basaltic and rhyolite glasses and illitic clay shows nearly identical calibrations for δ^7Li.

Li isotope fractionation

Measurements of Li isotopes in clay minerals equilibrated with H_2O fluid at 300°C suggests that heavy isotopes favor the fluid by ~10‰. Such large fractionation is twice as large as earlier empirical studies. New studies of smectites subjected to the Green-Kelley test, which induces Li substitution in octahedral sheets of smectite also suggests a 10‰ difference between fluid and clay.

Isotope ratios and clay mineral size

Analyses of natural and synthetic clay minerals shows that δ^7Li and δ^{11}B varies with size fraction. These changes can be explained most easily by invoking the "law of proportionate effect", wherein the smallest size fraction represent crystals that stopped growing (and reflect the chemistry of early fluids in the rock) while large size fractions represent crystals that continued to grow throughout diagenesis (and thus represent the chemistry of later fluids). It may be possible to use the different size fractions of clay from a single rock to trace changes in fluid over the entire diagenetic sequence.