

Mechanism of Li diffusion in zircon

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Li isotopes in zircon can potentially be used to infer magmatic sources and/or as a speedometer for magmatic and metamorphic processes. Use of $\delta^7\text{Li}$ in zircon is, however, impeded by uncertainty regarding the degree to which Li diffuses in zircon. We studied natural and synthetic zircons to identify the mechanism(s) of Li diffusion in zircon and the possible role of charge coupling between Li and REE+Y.

High spatial resolution ToF SIMS imaging identified sharp Li concentration gradients and NanoSIMS Li isotope profiled along these gradients in natural zircons show that $\delta^7\text{Li}$ variations ($\geq 20\%$) are prevalent in natural zircons. The range of $\delta^7\text{Li}$ measured within each zircon grain is significantly greater than that observed in all igneous and sedimentary rocks.

We modeled Li in a TTG zircon (C88_29_7_6) that shows a simple Li concentration gradient coupled with a core-rim texture, ideal for studying the Li diffusion mechanism(s). This zircon was previously characterized for its Li isotopic and trace element compositions using conventional SIMS (Bouvier *et al.* [1]). Within the rim of this zircon, the Li isotope profile correlates with Li/Y ratio and anti-correlates with Li concentration, suggesting an important role for Y (and REE) in controlling Li activity and, hence, diffusion. This feature, together with the continuous Li diffusion profiles (dipping $\delta^7\text{Li}$) across the sharp Li concentration boundary, is consistent with the presence of both slow diffusing Li (charge coupled with REE+Y) and fast diffusing Li (charge coupled with other chemical species) in zircon. During Li diffusion, charge coupling between Li and REE+Y takes place as a substitution reaction, in which Li ions substitute for other chemical species that couple with REE and Y in the zircon lattice. We argue that the ratio of slow/fast-diffusing Li is determined by the numbers of REE+Y coupling sites vs. other charge coupling sites for Li and a substitution coefficient.

[1] Bouvier *et al.* (2012) *CMP* **163**, 745-768.