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Re-investigation of Li and O diffusion behavior in xenocryst-rich zircon from El Chichón volcano (Chiapas, Mexico)

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Zircon has been routinely investigated for oxygen and more recently lithium isotopes in order to unravel the role of crustal recycling in magma genesis. Oxygen is a stoichiometric component in zircon, and self-diffusion of ¹⁸O and ¹⁶O in the zircon lattice is thought to be faster under water-present ("wet") than water-absent ("dry") conditions, although diffusion rates from published experimental data remain ambiguous. On the other hand, Li is a trace component which can enter the zircon lattice in a coupled substitution (e.g., $Li^+ + REE^{3+} = Zr^{4+}$). Hence, Li diffusion is potentially rate-limited by the much slower diffusion of REE. However, diffusion experiments suggest that Li in zircon can diffuse several orders of magnitude faster than major and most trace components. Thus, Li-inzircon has potential as a geospeedometer suitable for short timescales well beyond those accessible by radiometric geochronology. This has been used to infer extremely short timescales (tens of years) of magmatic zircon residence prior to rhyolite eruption (Rubin et al. 2017). Here we re-investigate inferences from Li-in-zircon geospeedometry by studying diffusion of O and Li in xenocrystic-rich zircons from El Chichón volcano. We used combined SIMS high resolution U-Th disequilibrium and U-Pb geochronology, together with δ^{18} O and δ^{7} Li line profiles, as well as Li, Y and Al ion imaging. Results show sharp step-like boundaries in δ^{18} O between xenocrystic and juvenile domains, whereas homogeneous and positive δ^7 Li values over the same areas show re-equilibration between genetically different domains. Lithium ion imaging also reveals that in some cases Li correlates with Al rather than Y, however examples of correlation between Y and Li are also frequent. The preserved sharp Li concentration gradients, however, are inconsistent with the observed isotopic homogenization. Measured O-isotopic profiles disagree with wet O diffusion modeling for durations commensurate to U-Th ages recorded in individual crystals. However, the hydrothermal O diffusion value in Bindeman et al. (2018) agrees with the observed preservation of O isotopic heterogeneity, in support of protracted magmatic residence. Our results indicate that O isotopes remained unchanged despite immersion in hydrous melt through episodes of xenocryst resorption, protracted crystallization of juvenile zircon rims, and heating prior to eruption. On the contrary, Li isotopes in El Chichón re-equilibrated probably within brief timescales, whereas local concentration disparities between crystal domains were maintained during protracted magmatic residence. We conclude that Li isotopes are much better suited for diffusion modeling than Li abundances which may depend on a presently poorly understood crystal-chemical environment in zircon.

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