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Li isotope systematics during hydrothermal alteration of Brothers submarine volcano and implication to Li global cycle

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Hydrothermal-seafloor interaction contributes to major oceanic Li budgets and controls the long-term evolution of seawater Li isotope compositions. The venting fluids at mid-ocean-ridge (MOR), arc and back-arc hydrothermal sites are enriched in Li relative to seawater but show large variations in both Li concentrations (20 to 6000 mmol/kg) and δ^7Li values (1.3‰ to 15.4‰). The mechanisms controlling Li mobility and isotope fractionation during hydrothermal alteration are not well understood. Additionally, the arc and back-arc hydrothermal systems need to be reassessed for their contribution to the oceanic Li budgets and Li isotope composition because their venting fluids show overall higher Li concentrations and lower δ^7Li values than those from the MORs. Here we report Li isotope behaviors in two distinct types of hydrothermal systems developed at the submarine volcano Brothers (IODP 376). Drill core U1528 is located at the volcano summit whose hydrothermal fluid is influenced by magmatic degassing, and U1530 at the NW caldera wall develops a seawater-dominated hydrothermal system that resembles the one at MORs. Relative to the unaltered precursor, the extreme Li loss of 95% to 99% in U1528 rocks is attributed to intensive primary mineral dissolution under low pH caused by mantle degassing. Samples from U1530 show lower extents of Li depletion between 50% and 95% and are explained by chlorite precipitation and possible seawater Li addition. The decreasing Li concentration in altered rocks is accompanied by elevating δ^7Li values, implying preferential removal of light Li isotope from rock to the hydrothermal fluid. The Raleigh and equilibrium isotope fittings suggest the Li isotope fractionation in hydrothermal alteration is smaller than 3‰. Furthermore, the previously proposed Li influx of 13 x 10^9 mol/yr for high-temperature hydrothermal endmembers would require complete removal of Li in newly formed oceanic crust during alteration at MORs. However, our results indicate that the high-T alteration in seawater-dominated hydrothermal systems is unlikely to leach all the Li in the MORB. Furthermore, magmatic degassing would increase Li input flux to the hydrothermal fluids and further investigation is needed to evaluate such impact on a global scale.