

Ca-O bonding controls the Ca isotope geochemistry of hydrothermal zeolites from Iceland

CLAIRE NELSON¹, ANDREW JACOBSON¹, GABRIELLA D. KITCH¹ AND TOBIAS B WEISENBERGER²

¹Northwestern University

²University of Iceland

Presenting Author: annie@earth.northwestern.edu

The hydrothermal alteration of basalt produces zeolites, which are secondary tectosilicate minerals that serve as major sinks of aqueous Ca²⁺ in subsurface environments. However, their Ca isotope geochemistry ($\delta^{44/40}\text{Ca}$) remains overlooked. We used a high-precision TIMS technique to determine $\delta^{44/40}\text{Ca}$ values (‰, ASW) of bulk basalt, primary mineral separates, hydrothermal calcite, and six types of zeolites collected from East Iceland, where the minerals form during progressive burial of the lava pile. Primary mineral separates show a narrow range of $\delta^{44/40}\text{Ca}$ (-0.95‰ to -1.16‰) that bracket values for bulk basalt ($-1.04 \pm 0.04\%$, 1SD, n = 5), whereas calcite shows much higher $\delta^{44/40}\text{Ca}$ ($-0.80 \pm 0.10\%$, 1SD, n = 4). Zeolites exhibit a large $\delta^{44/40}\text{Ca}$ range ($\sim 1.4\%$). Stilbite has the highest average bulk $\delta^{44/40}\text{Ca}$ ($-0.72 \pm 0.12\%$, 1SD, n=3), followed by scolecite (-0.84% , n=1), thomsonite ($-0.94 \pm 0.09\%$, 1SD, n=3), chabazite ($-1.58 \pm 0.11\%$, 1SD, n=4), mesolite (-1.78% , n=1), then heulandite ($-1.81 \pm 0.14\%$, 1SD, n=5). The average $\delta^{44/40}\text{Ca}$ of the zeolites strongly correlates with average mineral Ca-O bond length ($R^2 = 0.99$, $p < 0.001$), with the exception of the one mesolite sample, indicating that equilibrium isotope effects control zeolite $\delta^{44/40}\text{Ca}$. Uptake of ⁴⁰Ca by zeolites satisfactorily explains why natural and artificial (e.g., CarbFix) hydrothermal waters have high $\delta^{44/40}\text{Ca}$. Moreover, the bond length hypothesis reveals that the water-calcite equilibrium isotope fractionation factor is very close to 0‰. Our findings point the way for developing a novel “geothermometer” for studying low-grade basalt metamorphism. They also have clear implications for using Ca isotopes to trace basalt weathering, including its role in long-term climate regulation and exploitation in carbon capture and storage, a leading strategy for mitigating anthropogenic climate change.