Large fractionation of Ca isotopes by zeolite minerals from Iceland

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Hydrothermal calcite in Iceland has much higher $\delta^{44/40}$Ca values compared to basalt[1]. Preferential uptake of ^{40}Ca by coexisting zeolites appears to control the Ca isotope composition of the hydrothermal water from which the calcite precipitates[1]. To test this idea in more detail, we used a high-precision TIMS technique[2] to measure $\delta^{44/40}$Ca values for the operationally-defined exchangeable and silicate fractions of various zeolite minerals collected throughout Iceland. We analyzed co-index pairs from each "zeolite zone," or burial depth range where unique pairs of zeolite minerals form during low-grade basalt metamorphism[3]. Powdered samples (n = 16) for six types of zeolites were reacted with NH_4Cl to isolate the exchangeable fraction, and the remaining residues were digested with HF-HNO_3. The silicate fraction of each co-index pair has contrasting $\delta^{44/40}$Ca values that bracket the value of basalt, which is -1.06‰ on the seawater scale[1]. For example, heulandite and stilbite, which define the lowest burial depth, have silicate $\delta^{44/40}$Ca values averaging -1.70‰ and -0.554‰, respectively. $\delta^{44/40}$Ca values for the exchangeable fraction range from -1.55‰ to -2.68‰. For a single zeolite, the exchangeable fraction has lower $\delta^{44/40}$Ca values than the corresponding silicate fraction. Throughout all burial depths, silicate and exchangeable fractions showing higher affinities for ^{40}Ca also have higher Sr/Ca ratios. To place the apparent fractionations in context, delta value differences between the silicate fractions of the co-index pairs, as well as between the exchangeable and silicate fractions for any given zeolite, are in many instances comparable in magnitude to the fractionation factor ascribed to typical marine carbonate.

[1]Jacobson et al., (2015), [2]Lehn et al., (2013), [3]Walker, George P.L., (1960)