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Calcium Isotope Geochemistry: Research Horizons and Nanoscale Fractionation Processes

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Interest in studies of calcium isotope variations in nature continues to increase. Investigations span human biology, plants and soils, oceanography and paleoclimate,

early solar system processes, aqueous geochemistry, and silicate liquid structure. Variations in the 44Ca/40Ca ratio are generally small, about 5 ‰, but gradual small improvements in analytical capability now yield 0.05 to 0.1 ‰ resolution. The field is still plagued by a lack of universal standards for isotope ratios and data representation, but these are secondary issues. Traditional isotopic systems have been based in equilibrium thermodynamics, which can explain the magnitude and sign of observed mass-dependent fractionation behavior. For Ca isotopes this is not the case. There is still no reliable way to estimate the equilibrium free energy associated with isotopic exchange between most phases of interest. Experiments are difficult to interpret because it is almost impossible to precipitate minerals from aqueous solution at equilibrium at low temperature. Some studies suggest that, for example, there is no equilibrium isotopic fractionation between calcite and dissolved aqueous Ca. There is good evidence that most Ca isotopic fractionation is caused by kinetic effects. The details of the controlling processes are still missing, and without this mechanistic understanding it is difficult to fully understand the implications of natural isotopic variations. Recent work on dissolved Ca, calcite, and sulfates in both laboratory and natural settings is shedding light on where the fractionation may arise. There is emerging evidence for mass dependent fractionation associated with aqueous diffusion, but probably the primary source of the effects is in the details of precipitation of minerals from solution. This makes the fractionation potentially dependent on a number of factors, including solution composition and mineral growth rate. The next challenge is to develop appropriate experimental tests and combine them with micro- and nano-scale characterization, and to capture the critical processes in mathematical models. Some of the largest fractionation effects have been observed for silicate liquids, where both chemical and thermal diffusion generate large isotopic variations. Intake and transport of Ca in plants is also associated with substantial fractionation. Continuing work is beginning to place the fractionation into the context of global Ca cycles.

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