

## CALCIUM ISOTOPES: KEYSTONE FOR UNDERSTANDING ISOTOPIC FRACTIONATION AND PLANETARY MATERIAL PROCESSES

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Non-traditional elements like Ca, Mg, Li, Fe, Mo and others have proven to be valuable for assessing the mechanisms and magnitude of non-equilibrium isotopic fractionation processes. These so-called kinetic effects are important not only for low-temperature processes, but also for hydrothermal and magmatic conditions. Theory and experiments are progressing rapidly and are leading to a new level of understanding and a roadmap for further experimental work. This presentation will focus mainly on Ca isotopes, but the principles and effects are applicable to other elements. With respect to mineral growth from aqueous solution, the essential insight is that equilibrium growth can occur only if the molecular exchange fluxes at the mineral-solution interface are large in comparison to the rate of growth. For typical minerals growing at Earth surface temperature, this is unlikely to be the case, the consequence being that the kinetics of the forward reaction strongly influence isotopic fractionation, causing precipitated solids to be enriched in light isotopes. A rough estimate of surface exchange fluxes can be derived from mineral dissolution rates, but more detailed ion-by-ion growth models can be used to develop a more comprehensive description of the forward and backward reaction rates. For calcite, not only solution oversaturation, but also the Ca:CO<sub>3</sub> ion ratio in solution can strongly affect both growth rate and Ca isotopic fractionation. Ionic strength and other aspects of solution composition also modify isotopic fractionation, and analogous models can account for trace element partitioning as well. Preliminary data suggest that Ca isotopic fractionation in calcite and epidote also occurs at hydrothermal temperatures of 150 to 400C, with fractionation factors similar in magnitude to those for calcite at 25C. In magmatic systems, isotopic fractionation can be deduced by both chemical diffusion and thermal gradients in silicate liquids. The magnitude of Ca isotopic fractionation due to chemical diffusion has been shown to be dependent on silicate liquid composition, with high-Si, high-viscosity liquids producing larger fractionations than low-Si liquids. Diffusion in the solar nebula is probably responsible for some Ca isotopic variations observed in carbonaceous chondrites. Both phenocrysts in magmas and nebular condensates are likely to have kinetic fractionation effects if they grow under transport-limited or high oversaturation conditions. Current efforts are directed at experimental testing of model predictions, and modeling the coupling between growth inhibition/catalysis and isotopic fractionation.

## A comparison of shale weathering rates inferred from catchment solute mass balance versus soil profile chemistry at Plynlimon, Wales

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In an effort to quantify the influence of climate on shale weathering rates, a transect of study sites has been established on Silurian shales along a climatic gradient in the northern hemisphere as part of the Susquehanna Shale Hills Critical Zone Observatory, PA (USA). The coldest and most northerly site of this transect is the Hafren watershed in the headwaters of the River Severn, at Plynlimon, Wales, UK. The watershed, which is approximately 24 km from the west Wales coast, has an area of 357 ha and is 70% covered by Sitka spruce plantation forestry. The watershed has been extensively studied with continuous measurements of precipitation and runoff since 1968 and weekly monitoring of rain and stream water chemistry since 1983. These data provide an ideal opportunity to compare weathering rates derived from watershed mass balance to those derived from soil geochemical profiles. Annual solute mass balances over the past 25 years were determined by subtracting stream output fluxes from precipitation input fluxes using Cl as a conservative tracer. Annual mass balance estimates for dissolved elements such as Si are relatively consistent over time (mean value  $23.2 \pm 0.7$  kg Si ha<sup>-1</sup> yr<sup>-1</sup>) while those of Na are more variable (mean value  $2.69 \pm 1.2$  kg Na ha<sup>-1</sup> yr<sup>-1</sup>) and show influence of variations in sea salt input. Area-weighted release rates of Mg (mean value  $5.36 \pm 0.3$  kg ha<sup>-1</sup> yr<sup>-1</sup>) are indicative of weathering rates of the dominant shale minerals illite and chlorite. Weathering rates were also estimated from soil geochemical profiles, where elemental depletions relative to parent shale chemistry were used to calculate a weathering rate over the last 10 ka. Mg release estimates from soil ridgetop samples ( $5.16$  kg Mg ha<sup>-1</sup> yr<sup>-1</sup>) are in close agreement with the watershed mass balance calculations. Conversely, the estimated Si weathering flux derived from soil profiles of  $6.6$  kg ha<sup>-1</sup> yr<sup>-1</sup> is much smaller than the watershed mass balance flux estimate. This may imply that the watershed mass balance estimates for Si are influenced not only by weathering processes in the augerable regolith but also in the fragmented shale bedrock underlying the soil profile. Si cycling through the Sitka spruce trees must also be evaluated. The weathering rates obtained from the two methods at Plynlimon will be placed in context with our observations for the overall shale climosequence, where weathering rate estimates at the other locations are restricted to geochemical profiles alone.