

Control of chemical weathering rates by secondary mineral precipitation: a reactive transport approach for understanding soil genesis

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The geochemical evolution of a soil chronosequence developed on progressively older marine terraces (65-226 ka) near Santa Cruz, CA is considered using a reactive transport approach. The model includes the aqueous concentrations, quantitative mineral abundances, and mineral-specific cation exchange. Using the reactive transport approach, we are able to quantify the rate of clay precipitation and directly assess the importance of clay precipitation in moderating chemical weathering rates. In the absence of clay precipitation, the model predicts that weathering fronts for plagioclase and K-feldspar would be restricted to the upper 0.5 meters of the profile, while in reality the weathering fronts extend to a depth of 3 meters for a 226 ka soil. This suggests that clay formation is required to generate the observed weathering profiles. Kaolinite precipitation facilitates primary mineral dissolution by removing aqueous Al and Si and therefore controlling the saturation state of the primary minerals, providing the driving force for dissolution. This effect is particularly important in natural systems where fluid residence times range from months to decades and the fluids would be saturated with respect to the primary minerals in the absence of secondary mineral precipitation.

Our analysis suggests that the "bulge" in clay abundance associated with an argillic horizon at about 1 meter depth can be explained by *in situ* clay precipitation and does not require or support significant translocation of clays. The incorporation of mineral-specific cation exchange did not affect the profile evolution. However, the addition of dust to the simulated profile effectively decreased the dissolution rate because of the increase in total mineral abundances. The weathering gradients and location of the reaction fronts were affected by differences in solubility of the primary minerals, the rate of kaolinite precipitation and fluid flow. The best fit to the data suggests kaolinite precipitation rates of $10^{-12.4}$ mol/m²/sec. K-feldspar and plagioclase dissolution rates are $10^{-14.6}$ and $10^{-14.3}$ mol/m²/sec, respectively.

Successes and failures of garnet Lu-Hf and Sm-Nd geochronology: Examples in eclogites from the Western Alps

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The potentially high Lu/Hf and Sm/Nd ratios in garnet make these isotope systems attractive to geochronological applications in garnet-bearing rocks such as eclogites. Rayleigh fractionation modeling predicts that, due to the variation of Lu, Hf, Sm, and Nd distribution coefficients, Lu-Hf ages will tend to date early garnet growth due to high Lu/Hf ratios in the core, whereas Sm-Nd ages should reflect the average garnet growth age (Lapen *et al.*, 2003, **EPSL**), assuming the blocking temperatures of these isotope systems were not exceeded. When Lu-Hf or Sm-Nd data fail to provide statistically meaningful garnet-whole rock-omphacite isochron ages, this is often ascribed to contamination of garnet by inclusions, and partial dissolution, annealing, and leaching strategies have been developed to address this.

The Zermatt-Saas ophiolite in the Western Alps is an example of a relatively cool (500-600 °C), dry eclogite terrane that was metamorphosed to HP and UHP conditions. Core-to-rim zoning of Lu, Hf, Sm and Nd in garnet may be controlled by diffusion-limited uptake, deviating significantly from that predicted by Rayleigh fractionation. If their uptake is limited by diffusion, overall Lu/Hf ratios in garnet will sharply decrease from the garnet core resulting in a low bulk Lu/Hf ratio. Although low Lu/Hf ratios have been commonly ascribed to mineral inclusions such as zircon and rutile, this may not always be the case. For Sm-Nd geochronology, diffusion-limited uptake will produce low Sm/Nd ratios in garnet, reducing isochron precision. Such very low Sm/Nd ratios in garnet have been observed in a number of studies, and our element zoning studies indicate that low-Sm/Nd inclusions are not the sole explanation.

Partial dissolution tests demonstrate that "hot plate" dissolution, often thought to avoid dissolution of low-Lu/Hf phases, cannot always be relied upon to produce meaningful isochrons because the measured ¹⁷⁶Hf/¹⁷⁷Hf ratios may be decoupled from the measured Lu/Hf ratio due to elemental fractionation associated with incomplete sample digestion. Distinction between Rayleigh fractionation and diffusion-limited uptake is critical for successful geochronology, and this requires detailed elemental traverses across central cuts of garnet, guided by 3D x-ray tomography. The likelihood of successful geochronology can be increased through consideration of 3D garnet distribution of specific samples, water contents, and peak metamorphic temperatures.