

How mass balance affects isotope ratios in the weathering zone

J.A. SCHUESSLER, J. BOUCHEZ
AND F. VON BLANCKENBURG

GFZ German Research Centre for Geosciences, Helmholtz
Centre Potsdam, Potsdam, Germany
(bouchez@gfz-potsdam.de)

The novel stable isotope signatures in the compartments of the weathering zone are controlled not only by isotope fractionation factors that are characteristic of the chemical processes at play in the weathering zone, but are also controlled by the elemental fluxes between the different compartments, *i.e.* by mass balance effects. To deconvolve these two effects, we designed a steady state, batch reactor, mass balance model representing the weathering zone from the soil scale to the large river scale. We assume the main fractionating processes being formation of secondary precipitates, such as clays, and uptake by plants [1]. The model shows that:

$$\delta_{diss}^X - \delta_{rock}^X = -\Delta^X \cdot \frac{E_{org+sec}^X}{S_{rock+prim}^X} \quad (1)$$

where δ_{diss}^X and δ_{rock}^X are the isotope composition of the metal element X in the dissolved load and in the source rock, respectively, Δ^X the flux-weighted combined isotope fractionation factor, $E_{org+sec}^X$ the export flux of X in isotopically fractionated solids (organics and secondary precipitates), $S_{rock+prim}^X$ the release flux of X to water through primary mineral dissolution.

The main predictions are: (a) For very “soluble” elements (*i.e.* those with a low affinity for secondary precipitates and easily redissolved from plant litter), no fractionated δ_{diss}^X solid is exported, and is likely to be close to the source rock, δ_{rock}^X . Therefore, such elements are not viable tracers of weathering processes. (b) Equation (1) predicts that the largest difference in isotope ratios that can be observed between source rock and dissolved species and is equal to the combined isotope fractionation factor of the processes at play in the weathering zone.

The validity of these predictions are verified using an extensive database of measured water and rock isotope compositions and a compilation of experimentally determined isotope fractionation factors for Li, B, Mg, Si and Ca. It is observed that most $\delta_{diss}^X - \delta_{rock}^X$ data fall indeed between 0 (source rocks) and the best estimate of $-\Delta^X$. Moreover, most of the $\delta_{diss}^{Ca} - \delta_{rock}^{Ca}$ values are small compared to estimates of $-\Delta^{Ca}$, due to its high solubility.

[1] Bouchez *et al.*, *Amer. J. Sci.* **313**, 2013

Early stage Ostwald ripening of submicrometer calcite

L.N. SCHULTZ*, K. DIDERIKSEN, D. MÜTER,
S.S. HAKIM AND S.L.S. STIPP

Nano-Science Center, Department of Chemistry, University of
Copenhagen, Denmark (*correspondence:
lschultz@nano.ku.dk)

Ostwald ripening, also known as grain coarsening, occurs when crystals are at equilibrium with surrounding fluids. Over time, recrystallization favors larger and more thermodynamically stable particles. For calcite (CaCO_3), this affects diagenesis, relevant for aquifers and oil reservoirs and plays a role in industrial products where a thin adsorbed water layer covers crystal surfaces. While saturated conditions are common in nature and industry, rates and consequences of recrystallization at equilibrium are much less known and understood than growth and dissolution far from equilibrium.

We exposed submicrometer scale calcite, with a surface area of $11.8 \text{ m}^2/\text{g}$, to saturated solutions at $23 \text{ }^\circ\text{C}$, $100 \text{ }^\circ\text{C}$ and $200 \text{ }^\circ\text{C}$ and we observed grain coarsening for up to 261 days. Scanning electron microscopy (SEM) showed visible calcite crystal coarsening at $100 \text{ }^\circ\text{C}$ and $200 \text{ }^\circ\text{C}$ (Figure 1) within one day. BET surface area decreased by an order of magnitude and the average diameter grew to $2 \text{ }\mu\text{m}$ or larger. We measured change in particle size distribution and determined that the lognormal shape is indicative of early stage Ostwald ripening, consistent with classical theory.

Coarsening at $23 \text{ }^\circ\text{C}$ was not observable by BET or SEM, but changes in X-ray diffraction peak widths suggest an evolving surface, characterized by crystallite coarsening and fewer defects. These changes affect surface properties during the early stages of Ostwald ripening and have implications in our understanding of Ostwald ripening theories, behaviour in calcitic reservoirs and commercial calcite powder stability.

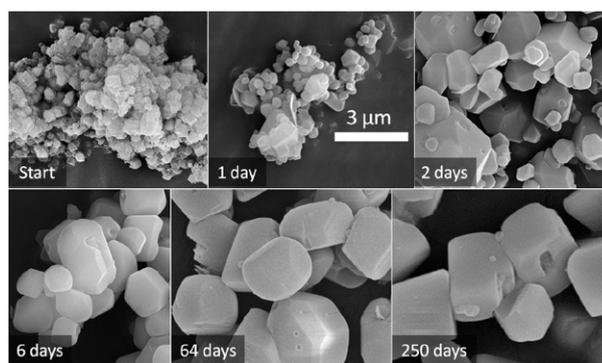


Figure 1. Calcite coarsening at $200 \text{ }^\circ\text{C}$ in saturated solution. The scale bar applies for all images.