

Molecular model of kinetic isotope fractionation during surface-controlled growth of CaCO₃ from aqueous solution

LAURA C. NIELSEN*, DONALD J. DEPAOLO
AND JAMES J. DE YOREO

Lawrence Berkeley National Laboratory, Berkeley, CA 94720,
USA (*correspondence: lnienl@berkeley.edu)

The attachment and detachment of cations and anions at the mineral-aqueous solution interface control rates of crystal growth and dissolution, and also affect isotope fractionation and trace element partitioning. Recent experimental work has begun to characterize kinetic isotope fractionation during precipitation of CaCO₃ and other di-ionic solids. Proposed models for isotopic and trace element effects deal only with macroscopic properties such as solution saturation state and solid state diffusivity. In this study, we apply molecular models of di-ionic crystal growth to deduce the dependence of kinetic isotope fractionation on growth mechanism, and both solution saturation state and stoichiometry. Recent theoretical advances have underscored the significance of solution stoichiometry—e.g. the ratio of Ca to CO₃ ion activities in solution—for controlling mineral surface kink density and composition and thus growth rate and growth mechanism. Our approach incorporates the effect of solution composition on microscopic mineral surface structure and composition, providing testable hypotheses for growth of sparingly soluble AB crystals such as calcite, namely:

- 1) Oversaturation and solution stoichiometry control growth rate and partitioning of A and B isotopes during precipitation;
- 2) For step growth, distinct rate laws describe dislocation- and 2D nucleation-driven growth, while the expression describing isotope fractionation requires no change;
- 3) Formation of amorphous precursors will generate isotope effects incompatible with ion-by-ion growth theory.

As observed during calcite growth, increasing oversaturation increases growth rate and drives isotope partitioning towards the kinetic limit. Also, increasing concentration of Ca²⁺ relative to CO₃²⁻ should drive new growth towards isotopic equilibrium. These competing effects, as well as the formation of an amorphous precursor, determine the observed magnitude of isotope fractionation. This model provides a clear mechanistic description of processes controlling the cross-over from the near-equilibrium to the kinetic limit of isotope fractionation, allowing us to relate trends in experimental data to environmental conditions of growth.

Large vanadium isotope difference between silicate Earth and meteorites

S.G. NIELSEN^{1,2}, J. PRYTULAK¹, B.J. WOOD¹
AND A.N. HALLIDAY¹

¹University of Oxford, Dept. of Earth Science, South Parks
Rd, OX1 3AN, Oxford, UK

²WHOI, Dept. of Geology and Geophysics, 266 Woods Hole
Rd, 02543 Woods Hole, MA, USA

We have recently developed a technique to measure precise and accurate vanadium (V) isotope ratios [1, 2]. All data are reported in parts per thousand as δ⁵¹V relative to an Alfa Aesar (AA) standard. Processing multiple aliquots of the same sample, including dissolution and column chemistry, yields a long-term external reproducibility of about 0.15‰ (2sd) [2].

Here, we present the first high precision ⁵¹V/⁵⁰V isotope composition data for a range of extraterrestrial materials. The sample set comprises CI, CO, CM, CV and CK carbonaceous chondrites, one ordinary chondrite, one ureilite, three HED parent body achondrites and the martian meteorite Nakhla. The data fall in a relatively narrow range about 1.5 to 2‰ lighter than AA.

If the meteorites are considered as one sample group then they are 0.5–0.8‰ lighter than our current best estimate for bulk silicate Earth [3]. The isotopic offset between Earth and meteorites may be explained by partitioning of isotopically light V into the Earth's core. This conclusion, however, is at odds with the insignificant V isotopic fractionation observed for three metal-silicate equilibration experiments.

Alternatively, the Earth does not have a V isotope composition identical to chondrites. The abundance of ⁵⁰V is sensitive to irradiation [4] and it is therefore conceivable that early solar system processes may have generated a V isotope gradient that could be preserved today in meteorites.

[1] Nielsen, S.G. J. Prytulak, & A.N. Halliday (2011) *Geostand. Geoanal. Res.* in press. [2] Prytulak, J. S.G. Nielsen, & A.N. Halliday (2011, in press) *Geostand. Geoanal. Res.* [3] Prytulak, J. S.G. Nielsen, & A.N. Halliday (2011, in press) *Geochim. Cosmochim. Acta.* [4] Gounelle, M. *et al.* (2001) *Astrophys. J.* **548**(2): 1051–1070.