

Theoretical estimates of solid-fluid Ca isotopes fractionation in soils

M. MÉHEUT¹, M. BENOÎT², R. SCHURHAMMER³, A.D.
SCHMITT⁴

¹GET, OMP, Université de Toulouse, CNRS, UPS, IRD,
CNES, Toulouse, France merlin.meheut@get.omp.eu
²CEMES CNRS, Toulouse, France. Magali.benoit@cemes.fr
³CMC, Strasbourg, France, rschurhammer@unistra.fr
⁴LHYGES, Strasbourg, France, adschmitt@unistra.fr

In plants and soils, Ca occurs in three different reservoirs: in solids (mostly oxalates), « structurally bound » to organic matter, or dissolved. In particular, Schmitt et al 2018 showed that, in beech barks, dissolved Ca was enriched in heavy isotopes w/r to oxalate crystals (by ~0.6‰). To interpret these measures, we undertook theoretical studies of Ca isotopes equilibrium fractionation between various solids and $\text{Ca}^{2+}_{(\text{aq})}$, based on an approach adapted to condensed phases (Dupuis et al 2015). For $\text{Ca}^{2+}_{(\text{aq})}$, we realized a short ab initio Molecular Dynamics (AI-MD) trajectory at 300K. All along this trajectory, Ca was 6-fold coordinated. One snapshot was extracted and computed for its isotope fractionation properties. At 25°C, the predicted fractionations w/r to calcite are ^{44}CaO (+2.2‰) \approx $^{44}\text{Ca}(\text{OH})_2$ portlandite (+2‰) \approx $^{44}\text{Ca}^{2+}_{(\text{aq})}$ (+1.8‰) > $\text{Ba}^{44}\text{Ca}(\text{CO}_3)_2$ baryto-calcite (+0.3‰) \approx $^{44}\text{CaCO}_3$ vaterite (-0.2‰) \approx ($^{44}\text{CaC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$) weddellite (-0.2‰) \approx ($^{44}\text{CaC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$) whewellite (-0.4‰) \approx ($^{44}\text{CaC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$) Caoxite (-0.6‰) \approx $^{44}\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ikaite (-0.8‰) \approx dolomite $^{44}\text{CaMg}(\text{CO}_3)_2$ (-0.9‰) > $^{44}\text{CaCO}_3$ aragonite (-3‰). These calculations emphasize the already reported role of coordination (Colla et al 2012, Moynier & Fujii 2017), materials with small Ca coordination showing enriched in heavy isotopes. The fractionation obtained for $\text{Ca}^{2+}_{(\text{aq})}$ is consistently close to structures where Ca shows similar environment (CaO and $\text{Ca}(\text{OH})_2$ portlandite), and heavier than oxalates by \approx +2‰. This positive fractionation is in contradiction with the conclusions of Moynier & Fujii, but (qualitatively) consistent with the natural observations of Schmitt et al.

This study emphasizes the criticality of a correct account of the liquid structure, which question will be discussed in more details.

References :

Colla *et al.* 2012 GCA V121, 363-373
Moynier & Fujii 2017 Sci Rep Nat V7 44255
Schmitt *et al.* 2018 Biogeochem. V137(1), 197-217,