Calcium-isotope fractionation between solution and solids with six, seven, or eight oxygens bound to Ca(II)

C. A. COLLA[1]*, J. WIMPENNY[1], Q-Z. YIN[1], J. R. RUSTAD[1] AND W. H. CASEY[1,2]

[1]Department of Earth and Planetary Sciences, University of California, Davis, USA

[2]Department of Chemistry, University of California, Davis, USA

The aqueous-mineral $\Delta^{44/40}Ca_{solid-solution}$ fractionation factors were measured for equilibrating solutions and a set of inorganic solids that trap solvated calcium in six, seven and eight coordination as an intact solvated ion in the lattice. The measured values were then compared to $\Delta^{44/40}Ca_{solid-solution}$ values predicted from density-functional electronic-structure calculations and vibrational frequencies of molecular models of the solvated ions and their solid hydrates. Experimentally, the $\Delta^{44/40}Ca_{solid-solution}$ values differed by ~2‰ for crystals of six- and seven-hydrated calcium, and by approximately ~2‰ between crystals having seven- and eight-hydrated calcium. In comparison, the calculations predict $\Delta^{44/40}Ca_{solid-solution}$ values between the sixfold- and eightfold-coordinated aquo ions of 5.4‰. Calculations predict 2.6‰ fractionation between the sixfold- and sevenfold-coordinated aquo ions. Stirred and unstirred experiments gave similar results in most, but not all cases. In general, measured isotopic fractionations compare well with the predictions from quantum mecahnics and vibrational analysis. Isotopic fractionation is directly correlated with coordination number.

Colla et al (2013) Geochim Cosmochim Acta **121**, 363-373