Ca and Mg isotope fractionation during the stoichiometric dissolution of dolomite and at equilibrium

A. PÉREZ-FERNÁNDEZ[1]*, U.-N. BERNINGER[1],
V. MAVROMATIS[2], P. POGGE VON STRANDMANN[3]
AND E. H. OELKERS[1]

[1]GET, CNRS, UMR 5563, Toulouse, France
(*Corresponding author, andrea.perez@get.obs-mip.fr)
[2]IAG TU Graz, Rechbauerstrasse 12, A-8010 Graz, Austria
[3]IEPS, UCL, Gower Street, London, WC1E 6BT, UK

Dolomite ($CaMg(CO_3)_2$) is the second most abundant carbonate on Earth; the understanding of chemical transfer to and from its surface is therefore critical to the understanding of global chemical cycles and ocean chemical evolution.

Dolomite dissolution experiments were performed in closed-system batch reactors at temperatures of 75 and 125°C and at 5 and 9 bar CO_2 pressure (c.f. [1]). Fluid samples were taken during the dissolution process as well as after the fluid composition attained a stationary state consistent with chemical equilibrium of dolomite. pH was measured immediately after sampling; fluid Ca and Mg concentrations were determined by atomic adsorption spectroscopy; alkalinity was determined by titration; calcium and magnesium isotope ratios were measured using Ar-ICP source mass spectrometer. During dissolution the fluid Ca became enriched in the heavier isotopes, and the isotopic evolution of the fluid continues after the bulk Ca and Mg concentration attained chemical equilibrium with dolomite. A final isotopic steady state in the fluid phase is obtained that has a $\delta^{44/42}Ca_{fluid}$ that is 0.45‰ higher than the dissolving dolomite. Similarly to the observations made in previous carbonates precipitation studies [2, 3] calcium isotope compositions of these dolomite dissolution experiments show little dependence on temperature. Ca isotope fractionation continued after chemical equilibrium was attained.

The behavior of Mg isotopes in these experiments apparently contrasts with that of Ca. Preliminary results suggest that although Mg isotopes seem to fractionate both during dissolution and at equilibrium, the fluid phase becomes isotopically lighter in Mg with time.

[1] Pearce *et al* (2012) *Geochim. Cosmochim. Acta* **92**, 170-183. [2] Marriott *et al* (2004) *Earth Planet Sci. Lett.* **222**, 615-624. [3] Sime *et al* (2005) *Earth Planet Sci. Lett.* **232**, 51-66.