

A new look at the thermodynamic control of the isotope composition of Mg and Zn in calcite

V. MAVROMATIS¹, A. G. GONZÁLEZ², T. FUJII³,
A. BALDERMANN¹, M. DIETZEL¹ AND J. SCHOTT²

¹Institute of Applied Geosciences, Graz University of Technology, Rechbauerstrasse 12, A-8010 Graz Austria (mavromatis@tugraz.at)

²Géoscience Environnement Toulouse, Observatoire Midi-Pyrénées, 14, av. Edouard Belin, 31400 Toulouse, France

³Research Reactor Institute, Kyoto University, 2-1010 Asahiro Nishi, Kumatori, Sennan, Osaka 590-0494, Japan

The very contrasting steric and electronic properties of divalent metal cations result in very distinct kinetic and thermodynamic trends of their isotopic composition in aqueous fluids and coexisting carbonate minerals. For example, although all alkaline earths in calcite are depleted in their heavy isotope, only magnesium exhibits a decrease of its isotope fractionation with increasing calcite growth rate [1]. The distinct behaviour of Mg stems from the reduced lability of water molecules in its coordination sphere compared to Ca, Ba and Sr. Transition metals (i.e. Cu, Zn), unlike alkaline earths, exhibit a slight preferential incorporation of their heavy isotopes in calcite which is consistent with their greater affinity for calcite than for the aqueous solution ($D_{Me} \gg 1$).

Herein, based on co-precipitation experiments and ab initio calculations of the isotope fractionation among Mg(II) and Zn(II) aqueous species, we have investigated the impact of solution pH, dissolved CO₂ and aqueous ligands on the isotopic composition of Mg and Zn in calcite. Our results indicate that increasing pH and concentration of aqueous bicarbonate/carbonate result in isotopically lighter Mg²⁺ and Zn²⁺ as well as Mg and Zn in calcite. This is consistent with the reduction of these aquo ions coordination sphere upon their coordination to carbonate/bicarbonate ligands and the enrichment of these metals carbonate/bicarbonate complexes in heavy isotopes. For example, the increase of pH from 7.7 to 8.2 produces a 0.4 ‰ decrease in calcite δ⁶⁶Zn. Thus Zn isotope composition in CaCO₃ is suggested as a promising proxy of pH, e.g. in marine and terrestrial carbonate precipitating surroundings.

These observations provide new insights into the mechanisms controlling the isotope composition of aqueous Me²⁺ in natural waters and set the foundation for the development of new tools to reconstruct paleo-environmental conditions from the isotope composition of Me²⁺ recorded in sedimentary carbonates.

[1] Mavromatis et al., 2013, *Geochim. Cosmochim Acta* **114**, 188-203.