

Zinc isotopes in calcite – A new pH proxy

MAVROMATIS V.,^{1,2} GONZÁLEZ A.G.,³ DIETZEL M.,²
SCHOTT J.¹

¹ Géosciences Environnement Toulouse (GET), CNRS,
UMR5563, 14 Av. E. Belin, 31400 Toulouse, France

² Institute of Applied Geosciences, Graz University of
Technology, Rechbauerstr. 12, A-8010 Graz, Austria

³ Instituto de Oceanografía y Cambio Global, IOCAG,
Universidad de Las Palmas de Gran Canaria, ULPGC,
35017 Las Palmas de Gran Canaria, Spain

The aqueous speciation of metals is well known to be very sensitive to the solution chemical parameters such as pH and the concentration of inorganic and organic binding ligands. Despite this, to date only a handful of works have dealt with the effect of speciation on isotopic fractionation among aqueous species and/or mineral-fluid pairs. Here as an example we investigate Zn isotopic fractionation during its co-precipitation with calcite in a wide range of pH.

Zinc was co-precipitated with calcite in mixed-flow reactors at 25 °C, $6.1 \leq \text{pH} \leq 8.5$. The results show that the difference between the isotopic composition of the solid and the fluid ($\Delta^{66}\text{Zn}_{\text{calcite-fluid}} = \delta^{66}\text{Zn}_{\text{calcite}} - \delta^{66}\text{Zn}_{\text{fluid}}$) increases by about 0.6‰ as the solution pH decreases from 8.5 to 6.1. In contrast, based on Zn aqueous speciation and the theoretical values of the reduced partition function ratios for zinc species, $\ln\beta$, the isotopic fractionation between calcite and aqueous Zn^{2+} , $\Delta^{66}\text{Zn}_{\text{calcite-Zn}^{2+}}$, remains constant at $0.58 \pm 0.05\text{‰}$ over the entire pH range investigated. The constant value of $\Delta^{66}\text{Zn}_{\text{calcite-Zn}^{2+}}$ suggests that irrespective of the solution pH, the same Zn aqueous species, likely the Zn^{2+} aquo ion interacts with calcite surface sites during the growth of this mineral via ion by ion attachment to advancing steps. The enrichment of calcite in ^{66}Zn is consistent with the formation of mononuclear, inner sphere tetrahedral Zn surface complexes at the calcite surface and the increase of Zn coordination to 6 following its incorporation in the crystal lattice with no further isotopic fractionation. Overall, the results suggest that Zn isotopic composition of natural calcite has the potential to shed light on the prevailing pH at the time of calcite formation in the geological past.