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Incongruent dissolution following comminution in karstic carbonates: implications for speleothem trace elements

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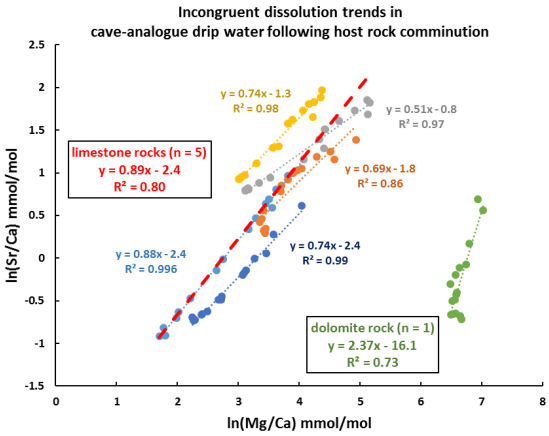

The dissolution of carbonate bedrock is a major source for hydrologically sensitive paleoclimate proxies, such as trace element ratios, in speleothems (e.g. stalagmites). Recently, investigations of prior calcite precipitation, water-rock interaction, and incongruent dissolution (ICD) have hypothesized that a characteristic range (~0.709 – 1.45) in the slope of speleothem ln(Mg/Ca) vs. ln(Sr/Ca) is indicative of specific hydrologically controlled processes[1,2]. However, no observational studies have thoroughly examined the effects of comminution-related ICD (ICD_C) on cave-specific host rocks, leaving out a potentially significant, if short-lived[3], influence on drip water and speleothem chemistry. We have conducted controlled dissolution experiments of comminuted host rocks in a cave-analogue environment ("GeoMIC," University of Waikato) to better characterize ICD_C effects on drip water trace elements.

Preliminary results from leaching experiments in GeoMIC displayed ICD_C effects sensitive to the water/rock ratio and resultant % total dissolution, while the highest observed increase in Mg/Ca (~7.25*$Mg/Ca_{HostRock}$) occurred when total dissolution was less than ~0.48%. Despite their potential brevity in a cave system, systematic ICD_C effects could complicate hydrological interpretations in speleothem climate records, as the average slope in ln(Mg/Ca) vs. ln(Sr/Ca) leached from our various limestone host rocks (~0.89) is identical to that expected from prior calcite precipitation[1,2]. However, we observe a distinctly steeper ICD_C slope (~2.37) in a dolomite sample. We discuss other possibilities for trace elements affected by ICD_C, including a cave-based proxy for past seismic activity or a measure of weathering rates in rapidly evolving or glaciated terrains[3].

[1]Sinclair, D. J. Two mathematical models of Mg and Sr partitioning into solution during incongruent calcite dissolution. Implications for dripwater and speleothem studies. *Chem. Geol.* **283**, 119–133 (2011).

[2]Wassenburg, J. A. *et al*. Calcite Mg and Sr partition coefficients in cave environments: Implications for interpreting prior calcite precipitation in speleothems. *Geochim. Cosmochim. Acta* **269**, 581–596 (2020).

[3]Fairchild, I.J. and Killawee, J.A. 1995. Selective leaching in glacierized terrains and implications for retention of primary chemical signals in carbonate rocks. In: Kharaka, Y.K. & Chudaev, O.V. (editors) Water-Rock Interaction. Proceedings of the 8th International Symposium on Water-Rock Interaction - WRI-8, Vladivostok, Russia, 15-19 August 1995. A.A. Balkema, Rotterdam, 79-82.