Solution chemical compositions modulate elemental uptake in calcite: Potential implications for paleo-proxy calibrations.

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Our current understanding of the degrees of and controls on incorporation of trace/minor elements in carbonate minerals (e.g., calcites and aragonites) is largely due to a wealth of experimental studies in which carbonates were precipitated under well-controlled conditions. Most of these studies focused on deriving robust functional relationships between elemental concentrations (measured and often expressed as E/Ca ratios, where E stands for a given trace/minor element) and physicochemical conditions of carbonate precipitation, which can serve as the basis for paleo-proxy development. However, what has been apparently overlooked until recently is the potential subsidiary impacts of certain dissolved/ionic constituents in aqueous solutions on elemental incorporation and thus E/Ca. This can be a critical consideration when experimental data are compared across different studies or extrapolated to natural systems, where precipitation often takes place in solutions with complex and highly variable chemical compositions (seawater, calcifying fluids in organisms, cave drip water, etc.).

In this presentation, we will compile our experimental data on boron incorporation in inorganic calcites over the years and demonstrate that the experimental outcome can be significantly influenced by the choice of solution matrix. For example, our most recent data indicate that the progressive additions of tetrahedral sulfate anions into aqueous solutions of otherwise constant conditions significantly alter not only elemental but also isotopic partitioning of boron in a hitherto unrecognized fashion [1]. This is consistent with a different experimental study in which sulfate anions were likewise shown to influence magnesium incorporation in inorganic calcites [2]. By noting sizable changes in seawater chemical composition over geologic time, we will discuss these data in the context of paleo-proxy calibrations.

[1] Uchikawa et al. (2023) Geochim. Cosmochim. Acta, 343, 353-370.

[2] Goetschl et al. (2019) Geochim. Cosmochim. Acta, 265, 505-519.