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Barium in Carbonate as a Proxy of Marine Sulphate: A Case Study on Akasaka and Kamura Limestones at Guadalupian-Lopingian Boundary

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The current reconstruction of seawater sulphate evolution highly relies on sulfur isotope analysis and its derivative methods, while developing new proxies can be meaningful. We test the feasibility of using carbonate barium concentrations to constrain seawater sulphate variations. Though most environments of the modern ocean are in an undersaturated state with respect to barite [1], the seawater barium concentration can be high enough to be controlled by sulfate concentration in some geological periods owing to the low solubility of barite [2]. We selected mid-oceanic atoll limestones from Akasaka and Kamura sections, Japan, crossing the Guadalupian-Lopingian Boundary (G-LB, middle-late Permian), as samples and determined the abundances of major, trace and rare earth elements. Particularly, to eliminate the influence of Ba from non-carbonate phases, we use a stepwise leaching procedure to determine barium concentrations in the samples' calcite fraction accurately [3]. The Ba concentrations of both sections show a rapid decrease in the late Capitanian (end of Guadalupian), which can indicate a drop in seawater Ba concentration. Besides, all samples are relatively depleted in heavy rare earth elements, with a significant negative cerium anomaly coinciding with a positive europium anomaly at the G-LB. This may suggest an increase of hydrothermal or volcanic input and, thus, be in agreement with a lowering of dissolved Ba concentration, caused by an increase of marine sulphate concentration. This demonstrates the potential of carbonate rock barium concentrations as a tracer for constraining geological seawater sulfate variations.

References:

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