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Tracing Cu and Zn concentrations in Paleoproterozoic seawater decoded by carbonate rocks collected from Francevillian Group, Gabon

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The Paleoproterozoic Francevillian Group (Gabon) preserves one of the oldest archives of macroscopic structures interpreted as eukaryote candidates, making it a key record linking seawater chemistry and biological innovation. However, reconstructing the bio-essential trace-element composition of paleo-seawater remains challenging. Estimates based on BIFs or black shales yield conflicting secular Zn trends and are limited because BIFs are strongly influenced by hydrothermal inputs and black shales represent detrital composites. In contrast, carbonate rocks provide a unique archive of seawater composition because they precipitate directly from seawater and form widely through time, independent of hydrothermal activity. Their trace-element composition, however, can be overprinted by post-depositional alteration and sulfide contamination. Here we evaluate these effects to better constrain primary Cu and Zn in Paleoproterozoic carbonate rocks, enabling estimates of secular trends in seawater Cu and Zn compositions.

We analyzed dolostone samples from the Francevillian B (FB) Formation, Francevillian Group, in the Lastoursville basin. Major and trace elements, including S, Cu, and Zn, were measured with LA-ICP-MS. Based on previous studies, depositional settings were grouped into two environments, below and near the Mn chemocline. In both groups, Cu/Ca and Zn/Ca covary positively with S/Ca.

These relationships are consistent with the presence of fine-grained sulfides within ablated areas, implying mixing between carbonate and sulfide end-members. Using this framework, carbonate end-member concentrations were calculated as 0.82–2.70 and 3.97–5.40 μg/g for Cu and Zn, respectively, in samples deposited below the Mn chemocline, whereas near-chemocline samples yield carbonate end-member values approaching zero. The Zn concentrations in the below-chemocline carbonate end-member exceed those of modern stromatolites and ooids, unlike some BIF-based estimates. We interpret this inconsistency to reflect the fact that modern BIFs record hydrothermal signatures rather than global seawater Zn composition.

Notably, potential early eukaryotic fossils occur in black shales interbedded between the two depositional settings. Our estimates therefore indicate a sharp decrease in Cu and Zn across the fossil-bearing black shale. Because the Lastoursville basin has been interpreted as oxic, allowing efficient dissolution of Cu and Zn in the seawater, the observed depletion may record biological uptake of these elements, linked to emerging eukaryotic ecosystems.