

Rare Earth Element Distribution in Marine Carbonates as a Potential Proxy for Seawater pH on Early Earth: A Proof of Concept Study

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Understanding the marine environment of early Earth is crucial for understanding the evolution of climate and early life. However, the master variable of Archean and Proterozoic seawater, the pH, is poorly constrained, and published ideas about the pH range encompass ~7 pH units from mildly acidic to hyperalkaline. To better infer ancient seawater pH, we examine the possibility of a seawater pH proxy using rare earth elements (REEs) in marine carbonates. The principle is based on an increased enrichment of heavy relative to light REEs with decreasing pH due to REE complexation and scavenging into carbonate. We calibrated such an REE pH proxy using pH variability in modern seawater and tested the proxy with REE measurements from 14 carbonate formations over time. We validated our REE-seawater pH proxy by comparing REE-pH estimates to published pH estimates of Cenozoic and Neoproterozoic seawater that use the established pH proxy of boron isotopes ($\delta^{11}\text{B}$). REE-pH estimates roughly agree with the Cenozoic and the Ediacaran $\delta^{11}\text{B}$ -pH proxy. The uncertainty in our REE-pH proxy can be explained by noise from freshwater influence, siliciclastic input, and diagenesis. This proof-of-concept study demonstrates that the REE-pH method provides pH estimates with an accuracy of 1.5 in the range of pH=4.0-9.3, arguably sufficient to resolve the debate about acidic versus alkaline Precambrian seawater and better understand the coevolution of life and early Earth's environment.