

Evidence for crustally-buffered seawater $\delta^{18}\text{O}$ over the last half billion years

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For decades, geoscientists have debated the cause and implications of decreasing $\delta^{18}\text{O}$ in marine sediments with age. Interpretations of Phanerozoic records have centered on three hypotheses: increasing diagenesis with age [1], decreasing seawater $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{sw}}$) with age (e.g. [2]), and high temperatures in the early Paleozoic (e.g., [3]). Identifying the correct hypothesis is fundamental to understanding Earth's climate extremes, habitability, and crustal processes, as well as thermal tolerances of animals.

In 1976, Muehlenbachs & Clayton [4] (and later [5]) presented the case for constancy in the oxygen isotope composition of Earth's hydrosphere due to hydrothermal and weathering processes at mid-ocean ridges, supported by data from ophiolites and chemical sediments and mass balance models. Here, we reexamine the three hypotheses using traditional and new temperature proxies.

First, the robust correlation between the $\delta^{18}\text{O}$ of Phanerozoic carbonate and phosphate fossils confirms that the $\delta^{18}\text{O}$ trend is not an artifact of diagenesis [6]. Combining clumped and oxygen isotope measurements of carbonate marine fossils provides an opportunity to directly calculate $\delta^{18}\text{O}_{\text{sw}}$. Data for Paleozoic (<450 Ma) and Mesozoic macrofossils (e.g., [7]) yield average values (\pm 2SE) of $0.1 \pm 0.6\%$ and $-0.8 \pm 0.3\%$ respectively, and Cenozoic foraminifera yield mean values of $0.2 \pm 0.2\%$ [8]. These data argue for relative constancy in Phanerozoic seawater $\delta^{18}\text{O}$, and by extension, hot early Paleozoic oceans. Other support for crustally-buffered seawater $\delta^{18}\text{O}$ since the early Paleozoic comes from studies of mudrocks [1] and iron oxides [9, 10]. Thus, 48 years after the publication of Muehlenbachs & Clayton [4], their case for crustally-buffered seawater $\delta^{18}\text{O}$ remains solid.

[1] Land & Lynch (1996) *Geochim. Cosmochim. Acta* 60, 3347-3352.

[2] Veizer & Prokoph (2015), *Earth-Sci. Rev.* 146, 92-104).

[3] Knauth & Epstein (1976), *Geochim. Cosmochim. Acta* 40, 1095-1108.

[4] Muehlenbachs & Clayton (1976), *Journal of Geophysical Research* 81, 4365-4369.

[5] Muehlenbachs (1998), *Chemical Geology* 145, 263-273.

[6] Grossman & Joachimski (2022), *Scientific Reports* 12, 1-13.