Evolution of Phanerozoic oceans: Isotopic evidence for Early Paleozoic warmth and constant seawater $\delta^{18}O$

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The oxygen isotopic trend for the Phanerozoic has been controversial, with low early-Paleozoic $\delta^{18}O$ interpreted as extreme warmth, low seawater $\delta^{18}O$, or greater diagenetic alteration. We compare a compilation of oxygen isotope data for carbonate and phosphate micro- and macrofossils [1] with a dataset of new and existing clumped isotope data. Importantly, these data are curated with special consideration given to diagenetic screening, and tectonic and burial history. Burial history is critical in the preservation of carbonate clumped isotope temperatures, which can undergo solid-state reordering. We use a reordering kinetics model to screen clumped isotope data for solid-state burial alteration [2]. With minor exception (Late Cretaceous, Early Triassic), average $\delta^{18}O$ values for post-Devonian fossils representing tropical-subtropical surface ocean conditions yield average isotopic temperatures below 30°C (assuming an "ice-free" seawater $\delta^{18}O$ [-1‰ VSMOW]). In contrast, Ordovician to Devonian data show sustained isotopic temperatures of 35-40°C. Published isotopic paleotemperatures from conodont apatite, resistant to oxygen exchange, follow the same general pattern. Clumped isotope data derived from Paleozoic brachiopod shells that experienced minimal burial (<100°C) and reordering (<1%) according to our model yield typical temperatures of 25-30°C for the Carboniferous, and 35-40°C for the Ordovician-Silurian. Inserting clumped temperatures and $\delta^{18}O$ values into the ^{18}O paleotemperature equation yields a mean seawater $\delta^{18}O$ of -0.7 ± 1.4‰ for the Phanerozoic. These findings argue for extreme early Paleozoic warmth and constant seawater $\delta^{18}O$ throughout the last ~450 m.y.

[1] Grossman (2012) *Geol. Time Scale*, Elsevier, 195-220. [2] Henkes *et al.* (2014) *Geochim. Cosmochim. Acta* **139,** 362-382.