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“Seeing through” diagenesis in late Ordovician-early Silurian brachiopods from Anticosti Island, Canada using triple oxygen isotope values

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The marine fossil $\delta^{18}O$ record has an overall secular increase through the Phanerozoic, suggesting Paleozoic oceans were exceedingly warm (+40°C) or were ~6‰ lower than the modern ocean oxygen isotope composition ($\delta^{18}O_w$). Alternatively, this secular trend can be interpreted as a diagenetic overprint where older fossils are more likely to be altered relative to younger samples. Triple oxygen isotope values (paired $\delta^{17}O$-$\delta^{18}O$ measurements, or $\Delta'^{17}O$) provide additional constraints on paleotemperature reconstructions than traditional $\delta^{18}O$ measurements. Thus, we can leverage triple oxygen isotope values of fossil carbonate to better understand changing $\delta^{18}O_w$ values and/or changing average ocean temperatures over the early Paleozoic.

Here, we present $\Delta'^{17}O$ measurements from 24 well-preserved brachiopod shells and two spar infill samples from Anticosti Island, Canada (15-20°S paleolatitude) across the late Ordovician-early Silurian boundary (~455-434 Ma). This interval is marked with expansive continental ice sheet coverage across the southern pole and global seafloor anoxia. Prior temperature estimates suggest a ~8°C drop in ocean temperature with $\delta^{18}O_w$ values of +3.5‰ during the Hirnantian glacial maximum. Based on the $\Delta'^{17}O$ and $\delta^{18}O$ values, all brachiopod fossils in our dataset were diagenetically altered, likely by meteoric fluid. We applied a fluid-rock mixing model to “see through” diagenesis and estimate initial formation temperatures. Similar to previous work, we find a 10°C cooling between the pre-glacial Katian and glacial Hirnantian. A modest 5°C increase is seen between the Hirnantian and the post-glacial Rhuddanian. However, our paleotemperature estimates are ~10-20°C lower than previously reported. We conclude that our measured triple oxygen isotope values of these fossils paired with our fluid-rock mixing model has revealed a potentially more accurate paleoenvironmental context of the icehouse conditions over the Ordovician-Silurian boundary in this region. More broadly, our data support the idea that the Paleozoic fossil record should be more intensely scrutinized for potential warm temperature biases due to diagenesis impacting their oxygen isotope values.