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Refining Paleozoic Seawater Calcium Isotopes Across the Devonian–Mississippian Transition

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The Devonian-Mississippian interval represents a pivotal transition in the Earth's history, marking the shift from a warm, greenhouse climate in the Early Palaeozoic to cooler icehouse conditions of the Late Paleozoic. This transition is generally attributed to a long-term decline in atmospheric pCO_2 driven by the diversification of land plants, intensified orogenesis, rifting, and enhanced continental weathering. It is recorded as a prominent positive $\delta^{18}O$ excursion in marine carbonates, yet the underlying cause of this excursion remains contested, with the interpretations invoking either a primary temperature change, shifts in seawater $\delta^{18}O$ linked to oceanic crustal cycling, or artifacts related to restricted seawater circulation. Calcium isotope ratios ($\delta^{44/40}Ca$) in marine carbonates offer an additional proxy for paleoenvironmental reconstruction because they closely track the global calcium cycle, crustal processes, carbon cycling, and the dynamics of $CaCO_3$ precipitation. Through this study, we aim to refine the $\delta^{44/40}Ca$ record across the DMCT, test hypotheses about how crustal cycling influences $\delta^{18}O_{SW,}$ and improve constraints on long-term Paleozoic calcium isotope trends. To achieve this, we present new $\delta^{44/40}Ca$ data from well-preserved brachiopod shells spanning the DMCT, sampled from the U.S. Midcontinent, Canada, and the Russian Platform. Each specimen was thin-sectioned and microsampled from non-luminescent domains by using cathodoluminescence microscopy. We integrate these new measurements with existing $\delta^{44/40}Ca$ data across the DMCT interval to generate a more comprehensive record of seawater calcium isotope variability. Preliminary results reveal a $\delta^{44/40}Ca_{SW}$ baseline of ~-0.7‰ with values reaching up to -0.1‰ higher around 378 Ma, a shift that cannot be explained by changes in calcium fluxes alone, given the long residence time of Ca in seawater. Instead, we interpret this variation as a change in calcium isotope fractionation, potentially driven by restricted basin circulation, and propose that our findings offer new insights into the long-term evolution of the Phanerozoic calcium cycle.