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ICE OR FIRE? CONSTRAINING THE ORIGIN OF ISOTOPICALLY ANOMALOUS CAP CARBONATE CEMENTS BY SIMS

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The Marinoan glaciation (a.k.a. the Snowball Earth) represents a profound paleoclimatic anomaly in deep time. However, the detailed mechanism of its termination remains largely unknown. It was hypothesized that massive releases of methane via clathrate destabilization at ~635 Ma may have played a role in terminating the glaciation. A key piece of supporting evidence is the finding of methane-derived authigenic calcite cements (MDACCs, $\delta^{13}C_{carb}$ values down to –48‰) within the Marinoan cap carbonates in South China. However, a more recent study based on clumped isotope (Δ_{47}) measurements suggests that the MDACCs are hydrothermal (T as high as 476 °C) in origin. If correct, the MDACCs cannot be used to infer paleoenvironments right after the glaciation. To test these contrasting hypotheses (ice vs. fire), we conducted a detailed investigation via μXRF, CL, SEM, and SIMS. The SIMS data show a 60‰ range of $\delta^{13}C_{carb}$ values with positive values (as high as +6.3‰) exclusively in dolomites and negative values (as low as –53.8‰) in calcites. Both the positive $\delta^{13}C_{carb}$ values and the lowest $\delta^{13}C_{carb}$ values are revealed in this study for the first time. Our results show that the dolomite crystals are typically euhedral, anomalously large (up to 200 μm) in size, have positive $\delta^{13}C_{carb}$ values, and are Mn-poor with dull or red luminescence under CL, with dolomite cores partly or almost completely replaced by low-$\delta^{13}C_{carb}$ calcite. The calcites have low $\delta^{13}C_{carb}$ values, are Mn-rich with bright orange luminescence under CL, showing multiple stages of vug-filling cements surrounding the preexisting dolomite crystals. These results suggest that the dolomites have been significantly recrystallized during burial or hydrothermal diagenesis and the MDACCs formed even later, postdating the recrystallized dolomites. We conclude that the MDACCs are post-depositional and formed during late diagenesis. Our conclusion is consistent with the prior work based on clumped isotope analysis. The present study casts further doubt on using MDACCs as evidence for methane clathrate in deep time. The role of methane in terminating the Snowball Earth should be re-assessed.

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