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Unique C-isotope pattern of calcite versus dolomite precipitates in Ediacaran oceans: Implications for "dolomite problem"

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Massive dolomites precipitated in Paleozoic and Precambrian oceans despite kinetic inhibitions to nucleation and precipitation of dolomite at Earth surface temperatures. This paradoxical observation is known as "dolomite problem." Recent advances in the Precambrian dolomite formation mechanism demonstrated that biologically-derived DOM could have facilitated the formation of Mg-bearing calcites and even proto-dolomites in the Ediacaran oceans. The Ediacaran Period (635~541Ma) witnessed the largest global carbon-cycle perturbation in Earth history with carbonate carbon isotope ($\delta^{13}C_{carb}$) down to -12‰, which has been attributed to the oxidation of a large dissolved organic matter (DOM) reservoir and associated release of isotopically light dissolved inorganic carbon (DIC) in oceans at that time. Many limestone-dolostone transitions exist in the Ediacaran Doushantuo Formation (South China) and equivalent strata in global locations, suggesting transitions of calcite versus dolomite precipitates in the Ediacaran oceans. In this study, we compiled a global dataset (726 samples) with the least diagenetic effects. Our results show that limestones are usually accompanied with either higher or lower $\delta^{13}C_{carb}$ values (mostly >+5‰ or <–8‰) whereas dolostones mostly fall between –8‰ to +5‰. Inspired by the DOM-facilitated mechanism and recent advances in Ediacaran ocean chemistry, the observed carbonate mineral-$\delta^{13}C_{carb}$ relationship can be best explained by variable DOM levels in a redox-stratified Ediacaran ocean. In this model, the limestones with $\delta^{13}C_{carb}$ values of > +5‰ and <–8‰ represent calcite precipitates in oxic surface waters where DOM was low and $\delta^{13}C$ of DIC was high, and in transitional zone between the oxic surface waters and anoxic deep waters where most DOM may have been oxidized to isotopically light DIC, causing extremely low $\delta^{13}C_{carb}$ values and low DOM, respectively. Toward to distal oceans, increasing DOM in more anoxic distal ocean and decreasing DOM oxidation due to decreasing oxidant availability may have facilitated to the increasing formation of Mg-bearing calcite and dolomite while increasing $\delta^{13}C_{carb}$ values. This interpretation is supported by a detailed sedimentary phase analysis of study sections. Our finding highlights the possible linkage between massive formation of dolomites and the development of a larger DOM reservoir in Precambrian anoxic oceans, providing new insights into the "dolomite problem".