



Unraveling carbon isotope signals from glendonites using NanoSIMS

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Glendonites - fossilized pseudomorphs after ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) - show complex diagenetic histories expressed in early and late stage carbonate mineral phases, as well as highly variable oxygen and carbon isotope values within single specimen. Recent experimental results have shown that ikaite precipitates up to temperatures of 15 °C, although in nature specimens are restricted to low temperature environments. Other factors, like kinetic surface inhibitors (orthophosphate and Mg) and high levels of saturation, might also have favored the formation of ikaite over anhydrous carbonate minerals. Combined with the complex internal textures, this precludes earlier assertions that glendonite occurrences mark cold intervals or even ice. Another key process driving ikaite/glendonite formation likely includes methane oxidation coupled to sulfate reduction leading to elevated alkalinity in generally carbonate-poor high-latitude sediments. Despite a link between modern occurrences of ikaite and methane, a role for anaerobic methane oxidation has generally been neglected in studies on glendonites. This is likely because bulk carbonate carbon isotope values of glendonites show a 30.0 ‰ (VPDB) spread, with most values centered around -20.0 ‰ suggesting organic matter remineralization as the principal source of dissolved inorganic carbon (DIC). Here, we show, using nano-scale secondary ion mass spectrometry (NanoSIMS) that different carbonate mineral phases within glendonites have distinctly different carbon isotope signatures. The range in glendonite carbonate-carbon isotope values far exceeds those of a reference carbonate, which has been independently validated by means of conventional gasbench isotope ratio mass spectrometry. The same standard also serves to correct for the instrumental mass fractionation associated with NanoSIMS, which ranges up to several per mil. The rosette phase, considered to be the primordial phase after ikaite, shows the lowest carbon isotope values at -32.0 ‰ (se = 2.4), whereas succeeding carbonate phases of the paragenetic sequence record carbon isotope values that range up to +13.8 ‰ (se = 2.4). Rosette phase carbon isotope values are compatible with carbon derived from methane oxidation mixed with native sources of DIC. These findings suggest that massive occurrences of glendonites might trace past intervals of an intensified methane efflux from the sediment.