Unleashing the potential of glendonite: A mineral archive for biogeochemical processes and paleoenvironmental conditions

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Ikaite ($CaCO_3 \times 6H_2O$) is a calcium carbonate mineral that forms at low temperatures close to the freezing point of water and is metastable under surface conditions in natural environments. It occurs as an early diagenetic mineral in marine sediments, where it grows close to the sediment-water interface, typically forming centimeter-sized single euhedral crystals to stellate crystal aggregates (Zabel and Schulz, 2001). Its precipitation is favored by elevated carbonate alkalinity, high pH, and high concentrations of dissolved phosphate (Bischoff et al., 1993; Hu et al., 2015; Zhou et al., 2015). Ikaite readily transforms into calcite upon an increase of temperature or a change of pore-water chemistry (Pauly, 1963; Swainson and Hammond, 2001); the external shape of crystals and crystal aggregates is commonly maintained and the product is referred to as glendonite. Glendonite is consequently not a mineral but a pseudomorph of calcite after ikaite. Both ikaite and glendonite have been known for a long time, but the derivation of glendonite from ikaite was only confirmed after crystal aggregates of ikaite resembling glendonite were found in organic-rich sediments of the Bransfield Strait off the Antarctic Peninsula (Suess et al., 1982). The relatively narrow temperature limits under which ikaite can form make this mineral an indicator of glaciomarine and cold deepwater settings (Selleck et al., 2007). The occurrence of glendonite is consequently of paleoclimatic significance and has been used as evidence for cold-water depositional environments in the rock record (James et al., 2005; Wang et al., 2017).

In addition to low temperatures, formation of ikaite in marine sediments requires a local biogeochemical process that increases alkalinity. The two processes that have been proposed that may be capable of inducing ikaite formation are organoclastic sulfate reduction (Suess et al., 1982) and sulfate-driven anaerobic oxidation of methane (Schubert et al. 1997); both are biogeochemical processes in which organic compounds are oxidized at the expense of sulfate. Authigenic minerals resulting from the remineralization of organic compounds are typified by low $\delta^{13}C$ values (Irwin et al., 1977). Because methane is more ^{13}C depleted than organic matter used in organoclastic sulfate reduction (Whiticar, 1999), methane-derived carbonates are characterized by particularly low $\delta^{13}C$ values (Peckmann and Thiel, 2004). Both biogeochemical processes typically increase pore-water alkalinity, adding to the pool of dissolved inorganic carbon in pore water, and resulting in authigenic carbonate minerals that reflect mixing of different carbon sources (Peckmann and Thiel, 2004). Based on average stable carbon isotope compositions of terrestrial organic matter ($\sim -30‰$), marine organic matter ($\sim -20‰$), and methane (-30 to $-110‰$), only ikaite with $\delta^{13}C$ values lower than approximately $-30‰$ can be confidently interpreted to result from anaerobic oxidation of methane (e.g., Teichert and Luppold, 2013). However, many ikaite and glendonite specimens reveal $\delta^{13}C$ values between $-10‰$ and $-25‰$, impeding identification of the biogeochemical process that induced mineral formation. Due to the circumstance that stable carbon isotope signatures are often ambiguous, other proxies are required to decide if mineral formation was induced by organoclastic sulfate reduction or anaerobic oxidation of methane. Unfortunately, such reconstruction is further compromised by the uncertainty regarding the factors that govern the transformation of ikaite to glendonite.

Temperature may not be the only trigger for the disintegration of ikaite. Disintegration has been suggested to be favored by (1) a decrease in alkalinity and concentration of dissolved phosphate (Bischoff et al., 1993), or (2) changing pore-water chemistries reflecting the transition from an environment shaped by organoclastic sulfate reduction to an environment shaped by anaerobic oxidation of methane (Greinert and Derkachev, 2004). Upon destabilization, ikaite transforms into a mush of water and small crystals of calcite and sometimes vaterite, another polymorph of calcium carbonate (Suess et al., 1982; Selleck et al., 2007). The secondary phase formed first is represented by carbonate bundles referred to as 'replacive calcite' (Teichert and Luppold, 2013). The extent to which carbonate ions are exchanged in this process may be variable, likely depending on the actual driving force of the transformation. Interestingly, experiments with ikaite and newly formed calcite resulting from heating treatment revealed no change of stable isotope patterns under laboratory conditions (Greinert and Derkachev, 2004). Knowledge of the extent of potential exchange of carbonate ions in the transformation process is essential for the interpretation of the factors governing ikaite precipitation and the subsequent transformation to other calcium carbonate minerals. The initial transformation of ikaite is accompanied by a decrease of volume of approximately one-third, generating pore space (Selleck et al., 2007). Most of this pore space tends to be filled by a variety of carbonate cements including deeper burial cements, but silica and other minerals may occur (Qu et al., 2017). As glendonite is made up of a complex paragenetic sequence of secondary minerals, it is of limited use as a paleoenvironmental archive. Studies looking into glendonite formation would ideally focus on replacive calcite, but the small size of its crystals and interfingering with later carbonate cements commonly preclude phase-specific sampling for stable isotope analysis.

To test if anaerobic oxidation of methane was responsible for the formation of glendonite enclosed in Paleogene strata of western Washington State (USA), Qu et al. (2017) extracted lipid biomarkers (organic molecules that can be traced back to their source) from large crystal aggregates of glendonite that occur in the periphery of methane-seep deposits. Although the seep deposits formed by anaerobic oxidation of methane and biomarkers of the prokaryotes driving this process are abundant in the seep limestones, the glendonite with $\delta^{13}C$ values as low as $-21‰$ yielded no such biomarkers. Instead, glendonite was found to contain biomarkers of organoclastic sulfate reduction. This finding was surprising based on the ample evidence for anaerobic oxidation of methane in the form of seep deposits occurring in the same strata that bear abundant glendonite. In order to constrain the relative importance of different biogeochemical processes in glendonite formation, it is necessary to identify additional criteria in cases when $\delta^{13}C_{carbonate}$ values do not allow for discrimination between organoclastic sulfate reduction and anaerobic oxidation of methane.

In this issue of *Geology*, Morales et al. (2017) document the link between periods of pronounced methane seepage and glendonite formation, studying an extensive set of glendonites that are widely distributed in Early Jurassic to Early Cretaceous strata of Siberia (Russia). It

is a strength of this study that the factors that govern ikaite precipitation and its transformation to glendonite are not confused. Emphasizing the actual transformation process, the authors coin the phrase 'ikaite fossilization.' They find evidence in support of the hypothesis that anaerobic oxidation of methane is instrumental for the preservation of ikaite. Analyzing the composition of gas inclusions and the stable carbon isotopic composition of gases, Morales et al. document a deep origin of short-chain hydrocarbons. With this sophisticated approach, evidence for (1) a rapid transformation of ikaite to glendonite and (2) a deep reservoir of thermogenic methane is found. The latter observation agrees with seepage of hydrocarbons, and is in accord with low $\delta^{13}C_{carbonate}$ values and the presence of carbonate mineral phases reminiscent of seep carbonates. Although the presence of methane and other low-molecular weight hydrocarbons does not prove that hydrocarbon oxidation contributed to glendonite formation, a sedimentary environment typified by high concentrations of these gases is more conceivable with anaerobic oxidation of methane rather than organoclastic sulfate reduction.

Future attempts to improve the utility of glendonite as a mineral archive will need to integrate different approaches to discriminate between the influence of anaerobic oxidation of methane and organoclastic sulfate reduction. Promising approaches include (1) the recognition of carbonate mineral phases common in seep limestones (Morales et al., 2017), (2) the analysis of the molecular and isotopic composition of gas inclusions (Morales et al., 2017), (3) lipid biomarkers (Qu et al., 2017), and (4) the analysis of the isotopic composition of carbonate-associated sulfate (CAS). The latter two approaches will often be hampered by the large quantities of material required for these analyses, but particularly CAS analysis holds promise to disentangle the considered biogeochemical processes. CAS stable sulfur and oxygen compositions have successfully been used to constrain microbial processes contributing to carbonate authigenesis (Heindel et al., 2012; Loyd et al., 2012). Applying a concept that has been used to identify advective seepage and associated transport of free gas (Antler et al., 2015), Feng et al. (2016) showed that CAS stable isotopes of seep carbonates can be used to identify sulfate-driven anaerobic oxidation of methane as the process responsible for carbonate precipitation. Although the application of this new proxy will be challenging for glendonite —being limited to large enough samples and samples where replacive calcite can be separated from later burial cements—the analysis of CAS stable isotopes will be ideally suited to determine the respective roles of anaerobic oxidation of methane and organoclastic sulfate reduction in glendonite formation. The work of Morales and co-workers sets the stage for a new and promising, but also challenging, use of glendonite as a paleo-proxy. It is very likely to stimulate more research and to provide new insight into the interplay of carbon cycling and climate change.

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