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Editorial: The effects of early diagenesis in various marine environments on the stable isotope records of environmental conditions and biogeochemical processes

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Editorial on the Research Topic

[The effects of early diagenesis in various marine environments on the stable isotope records of environmental conditions and biogeochemical processes](#)

Early diagenesis in marine sediments is predominantly driven by microbial respiration of organic matter, coupled to the reduction of a sequence of electron acceptors with progressively decreasing free energy yield (e.g., [Froelich et al., 1979](#)). These biogeochemical processes govern the chemical composition, oxidation state and pH of sediment pore fluids, as well as the geochemical and isotopic composition of minerals in sediments and sedimentary rocks. A nuanced understanding of early diagenetic processes is vital for the establishment of paleoenvironmental proxies or for the retrieval of paleoenvironmental information from sedimentary archives. Similarly, as diagenesis governs the sinks of many elements from the surface environment (ocean-atmosphere), an understanding of diagenesis is key for construction of global mass balances of elements and isotopes.

Stable isotopes and redox-sensitive trace elements are powerful probes of environmental conditions and biogeochemical processes. Traditional stable isotope systems (e.g., sulfur and carbon isotopes) have greatly improved our understanding of the co-evolution of life and the environment on Earth's surface (e.g., [Bernier, 1984](#); [Strauss, 1997](#)). Insights from these isotope systems are continuously being deepened by targeted studies of modern, application to new sedimentary archives, and modeling techniques of increasing sophistication. New isotopic tools (e.g., multiple sulfur, iron, molybdenum, uranium, carbonate and methane clumped isotopes) have shown exciting prospects for exploring biogeochemical cycles and Earth's surface environment, but our understanding of these new isotopic systems during marine diageneses is still limited (e.g., [Anbar and](#)

Rouxel, 2007; Johnson et al., 2008). This Research Topic includes six original research studies, in which a diversity of geochemical tools (e.g., speciation and isotopes of sulfur, oxygen isotopes, carbon isotopes, methane clumped isotopes, redox-sensitive elements), incubation experiments and numerical modeling were used to assess the biogeochemical process, redox dynamics, and sedimentary cycles of sulfur, carbon and iron during early diagenesis in various marine environments.

Bioturbation, the mixing of sediments and ventilation by benthic animals, enhances the exchange between the sea bed and the overlying seawater and stimulates diagenetic reactions by physically bringing together reactive compounds. Among other effects, bioturbation thus influences the oxidation state of the sediment and the biogeochemical cycling of sulfur within it. Through a combination of microcosm experiments and a numerical model, Riemer et al. showed that bioturbation enhances the drawdown of sulfate from the water column into the sediment. The critical finding in their study is that bioturbation enlarges the sulfur isotope offset between the seawater sulfate and pore water sulfide, the latter of which is preserved in sedimentary sulfide minerals. The sulfate-sulfide sulfur isotope offset is often used to constrain microbial activity within the sediments and aspects of the global sulfur cycle, and an understanding of the processes that control this geochemical signal is crucial for such applications. Riemer et al. empirically demonstrate a long-held assumption about the isotopic impact of bioturbation on the geological record of sulfur isotopes and its environmental effects in modern marine systems.

Sedimentary pyrite is the most common iron sulfide mineral in continental margins and its formation is significantly affected by local depositional conditions. Chang et al. investigated how local depositional conditions impact pyrite formation and its sulfur isotopic composition since marine isotope stage 5 in sediments off the southeast coast of China. They suggested that the content of pyrite sulfur is mainly controlled by the organic matter content and sulfate supplement during glacial-interglacial intervals. The sulfur isotopic composition of pyrite shows a large range. At the lower end of this range, the authors propose a role for early-stage organoclastic sulfate reduction. At the higher end, isotopically “heavy” pyrite appears to be controlled by the combined influence of a sulfate reservoir effect (isotopic distillation of porewater sulfate during microbial sulfate reduction) and depositional factors.

Methane attracts great attention since it is an important energy source and greenhouse gas, which plays a role in global carbon cycling and climate. Thus, identifying its source and migration processes is essential. In recent years, novel methane clumped isotope analyses show promise as a tool for studying the origin of natural methane. Sun et al. optimized the methane purification method by gas chromatography for the determination of methane clumped isotope compositions of natural gas. Their methods yielded methane of exceptionally high purity (~98-99%) and recovery (97-99%), and preliminary measurements of $\Delta^{13}\text{CH}_3\text{D}$ of the purified samples display precision comparable to the internal precision of the measurement.

Methane hydrates are widely distributed in continental margin sediments, where they are stable under the local pressure-temperature conditions. Changes in the sedimentary environment caused by temperature and sea level variations can lead to the destabilization and dissociation of methane hydrates. Wei et al. suggest that abundant authigenic carbonate minerals in the northern South China Sea formed at ~130 ka due to natural gas hydrate dissociation. This inference is based on multiple lines of evidence, including a negative carbon isotope excursion, a positive oxygen isotope excursion, U-Th dating, and an enrichment in redox sensitive elements. Comparing their findings with a global negative excursion of carbon isotope records during the penultimate deglaciation (~130 ka), Wei et al. argue that methane released by massive hydrate dissociation in the South China Sea may play a role in accelerating the global increase of atmospheric methane.

Dynamic methane seeps commonly result in variations in geochemical and isotopic proxy archives through intensively influencing the redox conditions in pore fluids. However, the effects of dynamic methane seeps proxy records are incompletely understood. Liang et al. analyzed stable isotopes and trace elements of seep carbonate minerals in the northern South China Sea. Unique patterns were identified in the chemical composition and mineralogy of the carbonate samples. Specifically, the carbonate concretion rims that are enriched in Fe (oxyhydr)oxides are dominated by high-magnesium calcite, whereas the rims enriched in Mn (oxyhydr)oxides are dominated by aragonite. The authors propose that the chemical-mineralogical patterns reflect the depth of formation of the carbonate phases, pointing to depth-varying redox conditions within the sediments. They forward that such carbonate archives may be used to study the changes of redox conditions and methane fluxes in marine seep systems.

Reduction of iron oxides has been frequently observed in the sulfidic and methanic zones, deeper than is expected based on the biogeochemistry of overlying sediments. However, the potential consequence of this “deep” iron reduction on microbial elemental cycles is still unclear. Yorshansky et al. experimentally quantified the impact of iron oxides on sulfate-driven anaerobic oxidation of methane (AOM) within the sulfate-methane transition zone of marine diffusion-controlled sediments. Their study shows that microbial hematite reduction can co-occur with sulfate-driven AOM in the sulfate-methane transition zone. However, the reduction of hematite seems to slow down sulfate-driven AOM, in contrast to methane seep environments, where iron oxides appear to stimulate sulfate-driven AOM. In the deep methanic zone, the addition of iron oxides appears to inhibit methanogenesis but does not appear to stimulate iron-driven AOM as a competing process (to sulfate-driven AOM) for the methane substrate.

Overall, this Research Topic improves our understanding on the effects of early diagenesis on selected stable isotope proxies with case studies from diverse environmental settings. The contributed

studies further highlight new geochemical tools and modeling applications for studies of early diagenesis.

Author contributions

All authors have made a substantial contribution to the work and approved it for publication.

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