Exploring the Affinity and Selectivity of Sedimentary Mackinawite (FeS) Towards Natural Organic Matter

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The biogeochemical cycle of sulfur is intimately linked with those of carbon and iron through the formation of iron-sulfur complexes. Iron sulfide minerals such as mackinawite (FeS) and greigite (Fe₃S₄) form under anoxic conditions in marine and lacustrine sediments. While the ability of iron oxides to sorb and sequester organic carbon (OC) in sediments has been thoroughly explored, the role of FeS in the long-term sequestration of OC remains poorly defined. In this study, we present data from depth concentration profiles for dissolved OC, iron, manganese, and sulfur in the liquid-phase (pore water) along with speciation data from sequential extractions of sulfur in the solid-phase collected from sediment cores from the St. Lawrence Estuary and the Saguenay Fjord, indicating possible evidence of FeSpromoted OC sequestration. Synthetic iron sulfide mineral sorption experiments using natural organic matter (NOM) were also carried out to assess the importance of FeS in sedimentary OC storage. Scanning electron microscopy shows that NOM influences the size and surface area, and therefore the reactivity of FeS aggregates, as also shown by the reduction in the re-oxidation rate of the FeS-NOM aggregates. Synchrotron X-ray characterization of the synthetically prepared FeS, FeS-NOM complexes, and specific anoxic sediments to identify the NOM functional groups that preferentially bind to FeS. The results from this study strongly suggest that FeS plays an active role in sedimentary OC preservation, which may be analogous to that of iron oxides.