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Iron diagenesis within and below the zone of anaerobic oxidation of methane

N. RIEDINGER[1], K. PFEIFER[1], S. KASTEN[1], J.F.L. GARMING[1], C. VOGT[1], AND C. HENSEN[2]

[1] Department of Geosciences, University of Bremen, Klagenfurter Str., 28359 Bremen, Germany (nar@uni-bremen.de)
[2] GEOMAR, Wischofstr. 1-3, 24148 Kiel, Germany

Geochemical investigations of sediments from the western Argentine Basin were carried out to study diagenetic processes related to anaerobic oxidation of methane (AOM) with focus on iron minerals. The continental margin off Argentina and Uruguay represents a suitable sedimentary environment to study non-steady state processes because it is characterized by highly dynamic sedimentary conditions such as gravity driven mass flow deposits. The sediment of the studied sites is characterized by a high content of iron (hydr)oxide minerals and geophysical data reveal specific magnetic records with distinct minima in the magnetic susceptibility. Iron (hydr)oxides are a common component of marine sediments and important carriers of magnetostratigraphic and paleomagnetic information.

After deposition, primary iron mineral assemblages pass through a sequence of early diagenetic alteration. One important process is the alteration of iron (hydr)oxides by hydrogen sulfide. In the study area the reduction of sulfate by AOM is the dominant process in the production of H_2S. The released hydrogen sulfide reacts with the abundant iron (hydr)oxides resulting in the precipitation of iron sulfides. This diagenetic process leads to a transformation of primary magnetic records resulting in distinct minima of magnetic susceptibility in the sulfidic zone. Pore water and solid phase data of the investigated sediment reveal that the magnetic signals in this area are highly influenced by drastic changes in sedimentation rates. Rapid sedimentation during the last glacial would be necessary for the preservation of magnetite, whereas a consecutively strong decrease in sedimentation rate during the Holocene would fix the sulfate/methane transition (SMT) at a specific depth. Such stagnation would cause an enhanced diagenetic overprint of iron (hydr)oxides at a distinct interval. This assumption can be proven by numerical modeling (CoTReM), confirming that the strong decrease in sedimentation rate coincides with the glacial/interglacial transition. Furthermore we assign the occurrence of ferrous iron in the pore water below the SMT as the result of ferric iron reduction due to methanogens as described by Bond and Lovley [1] on the base of laboratory results.

References

[1] Bond D.R. and Lovley D.R. (2002) *Environ. Microbio.* **4,** 115-124.

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Sedimentary sulfur cycling and productivity near methane seeps

W.P. GILHOOLY AND S.A. MACKO

Department of Environmental Sciences, University of Virginia, Charlottesville, VA 22901, USA (wpg6n@virginia.edu; sam8f@virginia.edu)

The abundant biomass of thiotrophic organisms, found in cold seeps at the Brine Pool on the Louisiana Slope of the Gulf of Mexico and at the Blake Ridge off the coast of South Carolina, is dependent upon *in situ* sulfide production. Stable isotopic tracing of the origins and fates of the sulfur can help determine whether the sulfide produced from the reduction of seawater sulfate is in sufficient supply to sustain the local chemosynthetic productivity. Intensive sulfur cycling in these anoxic sediments, underlying oxic bottom waters, is fueled by interstitial bacterial consumption of marine organic matter and/or light aliphatic hydrocarbons. Bacterial sulfate reduction becomes thermodynamically favorable in such organic rich sediments when free oxygen, metal oxides, and nitrate concentrations become depleted. Bacterial sulfate reduction is thus the likely precursor to sulfide in both of these locations with a high supply of organic matter. The majority of the source organic carbon at both locations is methane of either thermogenic or biogenic origin with CH_4 primarily in the Blake Ridge and a complex suite of hydrocarbons generally ranging from C1 to C5 in the northern Gulf of Mexico.

The sedimentary sulfur cycle was characterized for the Blake Ridge and Louisiana Slope from sulfate and sulfide precipitated from extracted porewaters. Seawater sulfate, originating at +20‰, tends to become isotopically enriched as a result of kinetic isotope effects associated with bacterial sulfate reduction. Progressive downcore isotopic enrichments in Blake Ridge porewater sulfates, ranging from +20‰ in the upper most sediment to +26‰ at depth, reflects this microbially mediated process. Likewise, in the Gulf of Mexico, concomitant downcore isotopic enrichments in $\delta^{34}S^{2-}$ and $\delta^{34}SO_4^{2-}$ result from the distinct fractionation associated with dissimilatory sulfate reduction (DSR). Thus, it appears that organic matter produced at these seep sites is significantly influenced by DSR. Significant portions of the total sulfate reduced are not observed in the porewater sulfide. Furthermore, anomalous isotope values together with heightened salinities in some samples indicates an additional source of the sulfur.