

Using electrochemical methods to study redox processes and harvest energy from marine sediments

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Experiments designed to generate electrical power by the principles of a fuel cell are revealing how oxidation and reduction processes in marine sediments depend on mass transport, solution, solid phase, biological and external variables. By positioning graphite electrodes on either side of an oxic-anoxic interface, we are able to study specific half cell reactions and microorganisms responsible for extracellular electron shuttling between available electron donors and electron acceptors.

To date we have conducted field fuel cell experiments in estuarine, shelf, slope and ocean seep environments. Recent laboratory studies have focused on the role of reduced products of anaerobic respiration as electron donors. Our findings include these insights:

1. Dissolved and solid phase sulfides serve as the most immediate and quantitatively important electron donors in typical anoxic marine sediments.

2. Marine sediments enriched artificially with dissolved sulfide yield the highest sustained power output, followed by the same sediments supplied with methane, acetate, and nitrogen, respectively.

3. If a stationary anode is in continuous operation, mass transport of reductants to the electrode surface will severely limit oxidation reactions on times scales of months, in most seafloor environments including seeps.

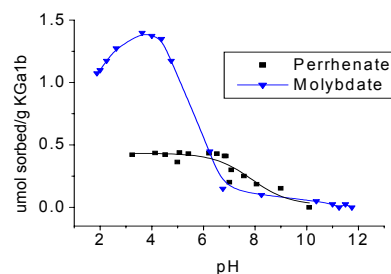
4. Active anode surfaces become coated with biofilms; however the microbial community composition and diversity of these biofilms has been shown to vary along an anode that crosses redox zones. This implies that many groups of microorganisms are capable of extracellular electron shuttling, and that the biofilms represent enrichments influenced by anode reactions, anode potential and the surrounding sediment.

The mechanism of Re fixation in reducing sediments

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Rhenium enrichment in sedimentary rocks is considered a paleoredox indicator, but chemical or biological mechanisms causing enrichment are uncertain. Consequently, what Re enrichment implies about paleoenvironments is unclear. The stable form of Re in oxic water is perrhenate (ReO_4^-), which in many respects behaves like MoO_4^{2-} in the ocean. The following figure relates ReO_4^- adsorption on kaolinite to that of MoO_4^{2-} (the latter determined by Goldberg et al. 1996; both at 0.3 mM in solution). Consistent with both anions' conservative behavior in the ocean, they are only weakly sorbed to



this common clay mineral near pH 8. If ReO_4^- is scavenged abiotically in reducing marine environments, either the sorbing agent has properties very different from kaolinite or preliminary "activation" of ReO_4^- occurs through reduction or ligand substitution. Thermodynamic and geochemical arguments show that Mn^{2+} , Fe^{2+} and NO_2^- are unlikely reductants for ReO_4^- . Experimentally, neither the H-atom donor, BH_4^- , nor H_2S are reactive on the time scale of hours, as judged by negligible promotion of Re scavenging by kaolinite. Even prior formation of thioperrhenates fails to promote scavenging by kaolinite. These results contrast with those for MoO_4^{2-} , which in the presence of H_2S is readily converted to thiomolybdate and scavenged by FeS (from trace Fe(III) in the kaolinite). The results of this study show that the marine geochemistry of MoO_4^{2-} is a poor model for predicting Re behavior. Instead, TcO_4^- , which is known to be microbially scavenged from solution, is a more promising model.

Reference

Goldberg S., Forster H.S. and Godfrey C.L. (1996) Soil Sci. Soc. Am. J. **60**, 425-432.