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Geochemical Society - Patterson Medal Lecture

Exploring biogeochemical environments using in situ electrochemistry

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Overview

In the early 1980's, single analyte microelectrodes were first used to measure O₂ in sedimentary porewaters. Since then, other single analyte sensors have been designed to measure other biologically and geochemically relevant chemical species. These systems are based typically on single point measurements using potentiometry or amperometry. In 1995, our group reported the use of voltammetry (current versus applied voltage curves) to measure the key redox species (O₂, Mn²⁺, Fe²⁺ and H₂S, see Fig. 1) in sedimentary porewaters using a solid-state gold-amalgam (micro)electrode. Since that time we have been able to determine other analytes such as iodide, polysulfides, Fe(III), aqueous FeS molecular clusters and more. In addition, we have now deployed the electrodes to make real time measurements at temperatures up to 120 °C and 260 atm of pressure. Here I report on some of our findings in a range of biogeochemical environments including sediments, microbial mats from Yellowstone National Park, the water column of the Black Sea and hydrothermal vents. Over the last ten years we have been training other scientists including undergraduate students to do similar work in other interesting geochemical environments. A goal is to deploy these electrodes for monitoring needs.

Some Major Findings

In sediments, a major finding is that O_2 and Mn^{2+} profiles do not overlap indicating that O_2 is not the primary oxidant for Mn^{2+} . In addition, Fe²⁺ can be bound to sulfide to form molecular clusters of unknown stoichiometry.

In the microbial mats at Chocolate Pots, Yellowstone Park, profiles show that Fe^{2+} is not measured under light conditions, but is under dark. The data indicate that photosynthetic production of O_2 is a possible pathway to banded iron formations.

The eastern and western basins as well as the central Black Sea show a discrete zonation of redox species from oxic to suboxic to anoxic as expected from organic matter decompostion reactions. However, the southwestern region shows several major O_2 intrusions over a depth of about 5 meters into the suboxic zone as a result of Mediterranean Sea inflow through the Bosphorus. This injection of O_2 results in Mn^{2+} oxidation and consequent oxidation of sulfide (Mn catalytic cycle).

In cooler diffuse flow hydrothermal vent areas, free H_2S is the predominant sulfide species near the tubeworm, *Rifita pachyptila* (Fig. 2), which is the host for a chemosynthetic bacterium. However, in higher temperature waters, where the worm *Alvinella pompejana* resides aqueous FeS molecular clusters are found. Because *Alvinella* does not have a chemosynthetic bacterium requiring free H₂S, sulfide bound to Fe²⁺ appears to be one possible detoxification mechanism.

This work was accomplished with the talent and dedication of many graduate and postdoctoral students working with colleagues, who gave much strong and appreciated encouragement.



Figure 1. Representative cyclic voltammograms for major redox species found in the environment.



Figure 2. A plastic encased electrode at the remora of a *Rifita pachyptila* found at 9° 50' N East Pacific Rise, 2500 m below the surface of the ocean.