

Use of voltammetric solid-state (micro)electrodes for studying biogeochemical processes: Laboratory measurements to real time measurements with an in situ electrochemical analyzer (ISEA)

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Solid-state voltammetric (micro)electrodes have been used in a variety of environments to study biogeochemical processes. Here we show the wealth of information that has been obtained in the study of sediments, microbial mats, cultures and the water column including hydrothermal vents. Voltammetric analyzers have been developed to function with operator guidance and in unattended mode for temporal studies with an in situ electrochemical analyzer (ISEA). The electrodes can detect the presence (or absence) of a host of redox species and trace metals simultaneously. The multi-species capacity of the voltammetric electrode can be used to examine complex heterogeneous environments such as the root zone of salt marsh sediments. The data obtained with these systems clearly show that O₂ and Mn²⁺ profiles in marine sedimentary porewaters and in microbial biofilms on metal surfaces rarely overlap indicating that O₂ is not a direct oxidant for Mn²⁺. This lack of overlap was suggested originally by Joris Gieskes' group. In waters emanating from hydrothermal vents, Fe²⁺, H₂S and soluble molecular FeS clusters (FeSaq) are detected indicating that the reactants for the pyrite formation reaction are H₂S and soluble molecular FeS clusters. Using the ISEA with electrodes at fixed positions, data collected continuously over three days near a *Riftia pachyptila* tubeworm field generally show that O₂ and H₂S anti-correlate and that H₂S and temperature generally correlate. Unlike sedimentary environments, the data clearly show that *Riftia* live in areas where both O₂ and H₂S co-exist so that its endosymbiont bacteria can perform chemosynthesis. However, physical mixing of diffuse flow vent waters with oceanic bottom waters above or to the side of the tubeworm field can dampen these correlations or even reverse them. Voltammetry is a powerful technique because it provides chemical speciation data (e.g.; oxidation state and different elemental compounds/ions) as well as quantitative data. Because (micro)organisms occupy environmental niches due to the system's chemistry, it is necessary to know chemical speciation. Voltammetric methods allow us to study how chemistry drives biology and how biology can affect chemistry for its own benefit.

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