Defining novel enzymatic and photochemical pathways in the oxidation of manganese

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Oxidation of Mn has sweeping environmental ramifications, impacting the fate and transport of contaminants, the degradation of lignin, and the cycling of nutrients. We have previously discovered a marine α-*Proteobacterium*, *Roseobacter sp.* AzwK-3b, that oxidizes manganese via both an enzymatic and novel photochemical pathway. In-gel assays of crude protein extracts showed one large (>150 kD) protein band active for manganese oxidation, both in the absence and presence of the multicopper oxidase inhibitor, *o*-phenanthroline. Oxidation within filtrates is increased in the presence of light, but is abolished in the light or dark with the addition of superoxide dismutase or various proteases. However, if proteases are added after initial Mn(III/IV) oxide nucleation, they have little effect on oxidation. Proteins concentrated from the filtrate had an in-gel manganese oxidizing protein spot that is similar to the spot found in the crude protein extract. These new results suggest that AzwK-3b initiates oxidation using a novel putative Mn oxidase (haem peroxidase), which is superseded by superoxide-induced oxidation in both the light and dark. Once the manganese oxides are formed the reaction is enhanced by various aqueous and surface-mediated interactions including the Mn(III/IV) oxide, light and potentially another biomolecule. These findings highlight the complexity of microbially mediated metal cycling within the photic zone.

Organism-environment interaction and the productivity of chemosynthetic communities at hydrothermal vents

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Communities dominated by symbiotic invertebrates form large biomasses around deep-sea hydrothermal vents, in sharp contrast with the surrounding benthic habitats. A key to the success of these invertebrates in colonizing hydrothermal environments is the ability to supply their associated chemoautotrophic bacteria with electron donors and acceptors from the surrounding fluids. The mechanisms from which biomass production by chemosynthetic communities may be quantitatively constained are yet poorly understood.

Several studies based on *in situ* characterization, geochemical modeling and analysis of mineral proxies have shed light on the role of organism-environment interactions in controlling micro-habitat conditions and provided some clues to this question. Physico-chemical conditions in vent habitats are now recognized to be much more variable than indicated by their position within the thermal gradient. Recent integrated approaches suggest that primary production is governed, both, by a flexible response of symbiont populations to the geochemical diversity of fluids and by the ability of invertebrate species to buffer environmental variability (Le Bris *et al.* [1], Schmidt *et al.*[2]).

The various strategies employed by different species of invertebrates to optimize available energy budgets beyond their physiological adaptations intimately relate to the type of vent they colonize. Key processes underlying energy transfer from the environment to these populations will be discussed on the basis of the current knowledge of the physico-chemical conditions and thermodynamics properties of the microhabitats they create.

[1] Le Bris *et al.* (2008) In *Biological oceanography research trends*, LP Mertens (ed.) Nova Science Publishers, New York, pp.157-175. [2] Schmidt *et al*. (2008) *Mar Chem* **108**, 18-31.