THE MARINE BIOGEOCHEMISTRY OF MOLYBDENUM

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Prevailing wisdom holds that the vertical distribution of molybdenum (Mo) in the open ocean is conservative, despite Mo's important biological role and association with Mn oxides and anoxic sediments. Mo is used in both nitrogenase, the enzyme responsible for N_2 fixation, and nitrate reductase, which catalyzes assimilatory and dissimilatory nitrate reduction. Laboratory culture work on two N_2 fixing marine cyanobacteria, *Trichodesmium* and *Crocosphaera*, and a marine facultative denitrifier, *Marinobacter hydrocarbanoclasticus,* showed that Mo cell quotas in these organisms were positively correlated with Mo-containing enzyme activity. Mo concentrations in *Crocosphaera* dropped almost to blank levels when not fixing N_2 suggesting daily synthesis and destruction of the entire nitrogenase enzyme and release of Mo. *Trichodesmium* cultures, however, retained a pool of cellular Mo even when not fixing N_2. Colonies of *Trichodesmium* collected in the field have Mo:C tenfold higher than seen in culture, these Mo:C ratios were reflected in SPM samples from the same region. Fe:C ratios for Trichodesmium were between 12-160 μmol:mol in field and culured samples. The Fe:C ratio of *Crocosphaera* was established to be 15.8±11.3 under N_2 fixing conditions. Mo cellular concentrations in cultured organisms were too small to significantly influence dissolved Mo distributions, but may slightly affect Suspended Particulate Matter (SPM) distributions. Mean SPM Mo:C ratios were slightly elevated in regions of N_2 fixation and denitrification..

A high precision (±0.5%) isotope dilution ICP-MS method for measuring Mo was developed to re-evaluate the marine distribution of Mo in the dissolved and particulate phase. Mn oxides were not found to significantly influence either the dissolved or SPM Mo distribution. Dissolved Mo profiles from the Sargasso and Arabian Sea were conservative. However, dissolved Mo profiles from the Eastern Tropical Pacific showed both depletion and enrichment of dissolved Mo possibly associated with interaction of Mo with coastal sediments. Dissolved Mo profiles in several California Borderland Basins showed 1-2 nM Mo depletions below sill depth. A more focused study of water column response to sediment fluxes using the high precision Mo analyses is necessary to determine whether these phenomena are related.

Dedication

To my parents

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1.1 Preface

Molybdenum (Mo) is an essential micronutrient, required in a variety of enzymes that catalyze oxygen transfer reactions such as nitrate reduction, as well as nitrogen fixation (Stiefel 1996). Despite its important biological role, Mo has been classified as a conservative element in seawater, similar to the major salts. This classification is based on early studies of the distribution of Mo in the Atlantic and the Pacific, which determined that the Mo concentration in seawater was extremely high (107 nM) and invariant with salinity (Collier 1985; Morris 1975; Prange and Kremling 1985). Collier (1985) saw salinity normalized Mo concentration variations in the upper 300m suggestive of Mo cycling but because these variations were not resolvable at 4-sigma level he concluded that the profiles were conservative. These early studies of Mo in seawater had measurement uncertainties (2.5 to 10 nM) larger than the total concentration range of many biologically critical trace metals (Fe, 0-1 nM ;Zn, 0-10 nM ;Cd, 1-1.2 nM). These high measurement uncertainties may have obscured any biological signature. The high concentration of Mo and its perceived conservative behavior has led to a lack of interest in pursuing the biogeochemical role of Mo in the surface ocean.

The goal of this thesis was to seek evidence of non-conservative behavior of Mo in seawater and to determine what, if any, effect biological utilization has on Mo distribution in seawater. Chapter 2 describes a high precision method for determining Mo concentration in seawater as well as methods for determining trace quantities of Mo, Rb, Mn, Fe, and Al in microbial cells and marine suspended particulate matter. Chapter 3