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Molybdenum in the Northeast Pacific Ocean¹

Abstract—The concentration of dissolved molybdenum has been determined in several profiles from the Northeast Pacific Ocean. The salinity-normalized concentration is essentially constant in all open-ocean samples (107 nM, $1\sigma = 2.5$ nM). The dissolved distribution is not significantly affected by biological cycling.

The distributions of dissolved minor elements reflect the major physical, geochemical, and biological processes which determine the nature of the marine environment (Wong et al. 1983). During the past decade, advances in sample collection and analysis have resulted in the characterization of more than 30 minor elements in seawater. Most of the early trace metal determinations were shown to be incorrect owing to sample contamination and limited analytical technologies. One of the most exciting conclusions drawn from the new data is that the distributions of many metals in the oceans are controlled by biological cycling and, to some degree, mimic the distributions of the classical nutrients—nitrogen, phosphorus, and silicon. These new data, coupled with metal-nutritional studies on laboratory algal cultures, suggest the possibility of a broad spectrum of co-limiting nutrients which include some of the metals (Huntsman and Sunda 1980; Morel and Hudson 1985).

Molybdenum is frequently mentioned as a trace nutrient of particular ecological importance (O'Kelley 1974). Most of the analyses of molybdenum in seawater were published before 1975 and have been reviewed by Brewer (1975). Of these, the only systematic analyses of open-ocean samples are from the North Atlantic Ocean (Morris 1975). Berrang and Grill (1974) presented extensive analysis of dissolved and particulate molybdenum in Saanich Inlet, British Columbia, but there are no systematic vertical profile data available from the North Pacific. Due to the large contrast in "age"

between the surface and deep water in the Pacific, this is perhaps the best environment to examine the dissolved distributions of metals as a test of the significance of biological cycling (Collier and Edmond 1984). For these reasons, it seemed appropriate to examine the distribution of molybdenum in the North Pacific using modern trace element sampling and analytical techniques.

The samples to be discussed were collected from several locations in the North Pacific Ocean. These include vertical profiles from 11°N, 140°W (MANOP site S), 0°44'N, 86°10'W (near the Galapagos ridge-crest in the hydrothermal area), 52°N, 145°W (central subarctic Pacific), and from within the anoxic zone of Saanich Inlet, British Columbia. All samples were collected specifically for trace metal determinations using acid-cleaned Niskin samplers deployed on standard hydrographic wire; the same samples have been successfully analyzed for Cu, Ni, Cd (Collier and Edmond 1984), and V (Collier 1984).

Dissolved molybdenum was analyzed by atomic absorption spectrometry with electrothermal atomization. Molybdenum was separated from seawater and preconcentrated by coprecipitation with cobalt-APDC at pH 4 (Boyle et al. 1981; Collier 1984). The limit of detection for a 35-ml seawater sample is 2 nM and the precision (1σ) is 2 nM at 107 nM molybdenum. The method is roughly equivalent in convenience and precision to the chelating resin method of Riley and Taylor (1968) and to the solvent extraction technique of Berrang and Grill (1974). To eliminate small changes in concentration which covary with salinity, we normalized all values to a salinity of 35‰ (normalized Mo = sample Mo \times 35/sample salinity).

The concentration of normalized molybdenum in two open-ocean profiles is shown in Fig. 1. There are almost no significant variations in concentration with depth. The small variations in the upper 500 m at MANOP site S are just barely detectable at

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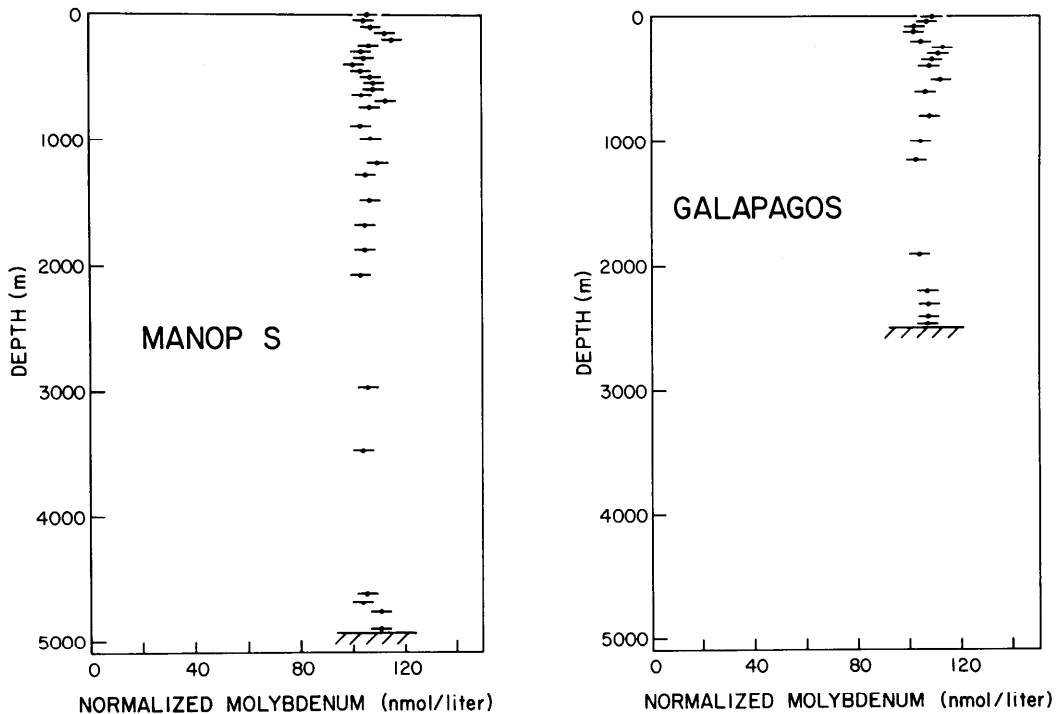


Fig. 1. Concentration of molybdenum (normalized to salinity) vs. depth at two stations in the North Pacific Ocean. Left—MANOP site S (11°N , 140°W); right—Galapagos ($0^{\circ}44'\text{N}$, $86^{\circ}10'\text{W}$). Width of the error bars represents $\sim 2\sigma$ for the analysis. Other hydrographic data for these stations were presented by Collier (1984).

the precision of this analysis. The maximum values in both profiles occur within the oxygen minima but these concentrations are within 4σ of the mean value of all samples. A more precise analysis will be needed to verify and detail these changes. Four samples from the upper water column (at 10, 50, 90, and 500 m) in the subarctic Pacific (station "P"— 50°N , 145°W) were also analyzed. There was no depletion in the surface water and the mean value of normalized molybdenum was within 1σ of the values at other stations.

There is no apparent hydrothermal signal in the deep samples of the Galapagos profile (Fig. 1). Because these water column samples contain very little "hydrothermal" water, the only visible effects (within the precision of this analysis) would be a very large input such as that seen for Mn or ^4He (Edmond et al. 1979).

A set of surface water samples was collected along a horizontal transect off the

coast between 132°W and 126°W along $39^{\circ}38'\text{N}$. This sample strategy has proved useful in identifying processes that affect the concentration of trace materials at the ocean margins, such as proximity to river or shelf sediment inputs, coastal upwelling, and associated increases in biogenic scavenging (Nozaki et al. 1976; Boyle et al. 1981; Bruland and Franks 1983). Consistent with the vertical profiles, there was no systematic change in the normalized concentration of molybdenum along this section. The mean value of these data was within 1σ of the averages of the profile data.

The mean value of molybdenum for all of the open-ocean data (92 samples) is 107 nM ($1\sigma = 2.5$ nM). This is essentially identical to the concentration in the Atlantic Ocean reported by Morris (1975) and to the value suggested by Brewer (1975) in his review of earlier molybdenum analyses in seawater. The oceanic residence time of molybdenum with respect to its dissolved input

from rivers (avg concn—5 nM; Martin and Meybeck 1979) is about 7×10^5 years—one of the longest known of any transition element.

The distribution of molybdenum was also determined in the anoxic water column at Saanich Inlet, British Columbia (sampled June 1981). The concentration of normalized molybdenum at 120 m is similar to the open-ocean value (100 nM) but drops steadily to below 80 nM at the bottom. This occurs in parallel with the disappearance of dissolved oxygen and nitrate and with an increase in dissolved Mn. Free hydrogen sulfide was not detected in the water column. These results are similar to those of Berrang and Grill (1974), who presented a 9-month time series for dissolved and particulate molybdenum at Saanich Inlet and suggested on the basis of correlations of particulate Mo with particulate Mn that the depletion occurs through the adsorption of Mo on freshly precipitated manganese oxides. These particles are transported into the anoxic deep water or sediments where the Mo is coprecipitated with iron sulfides (perhaps as MoS_3). Related cycles have been noted for other metals in Saanich Inlet (Emerson et al. 1979) and in other anoxic basins (Spencer and Brewer 1971). However, as shown by Berrang and Grill (1974), the cycling of molybdenum by manganese scavenging does not affect the open-ocean distribution of molybdenum and does not directly account for a major fraction of the removal of the riverine input of molybdenum.

Molybdenum-containing proteins are essential units in two of the three enzyme systems responsible for the reduction of nitrogen to ammonium in marine organisms. These include algal nitrate reductase ($\text{NO}_3^- \rightarrow \text{NO}_2^-$) and nitrogenase found in N_2 -fixing procaryotes; the biochemistry of these systems was reviewed by Falkowski (1983). Even though these important enzymes contain molybdenum, there is no evidence that the ambient concentration of molybdenum in seawater limits any of their activities. Although it is not a necessary property of a "limiting" substance, there is no systematic depletion of molybdenum in

surface water characteristic of other algal nutrients. However, in oligotrophic surface waters, such as the North Pacific Central Gyre, the concentration of molybdate is actually higher than that of nitrate or phosphate. The lack of depletion simply demonstrates that the uptake and removal of molybdenum from the surface ocean with settling particulate organic matter constitutes a vertical flux that is small compared with the input of "new" molybdenum by exchange with the deep ocean (Collier and Edmond 1984).

Low concentrations of phosphorus and iron and the low molybdate:sulfate ratio in seawater have each been cited as factors contributing to the relative scarcity of nitrogen fixation in the world oceans (Doremus 1982; Rueter 1982; Cole et al. 1984). As noted above, molybdenum is necessary for the reduction of both nitrate and dinitrogen. The utilization of nitrate accounts for at least 20% of the total nitrogen assimilated during primary production in the world ocean (Eppley and Peterson 1979; King and Devol 1979). Therefore, there is enough molybdenum available for phytoplankton to maintain at least a minimum cell quota to reduce nitrate. It is not clear why nitrogen fixers would be molybdenum-limited in this same chemical environment unless they have a substantially higher demand (minimum cell quota) or an inefficient uptake system. Further discussions of "limitation" are not yet warranted because there is essentially no quantitative information available on molybdenum composition or nutrition of marine organisms.

In conclusion, molybdenum is homogeneously distributed throughout the water column in all open-ocean North Pacific samples examined, and its salinity-normalized concentration is 107 nM ($1\sigma = 2.5$ nM), identical to that given by Morris (1975) for the North Atlantic Ocean. Further, there is no evidence found in the distribution of the form of dissolved molybdate to suggest that it undergoes significant biological cycling analogous to nitrogen or phosphorus. This observation is consistent with a conclusion that the concentration of molybdenum in seawater does not limit primary production.

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