favored (*8*). In the case of Mercury, the solar wind impacts the surface directly (*4*) and therefore could sputter sodium from minerals on the surface. Meteoric dust may provide a continuing source of sodium. The flux of meteoric material increases as the sun is approached and is about eight times more intense at the orbit of Mercury than at Earth (*9*). Sodium also appears in the atmosphere of Earth, and its origin has been ascribed to meteoric material (*10*).

The atomic weight of sodium is high enough that the thermal escape of sodium from Mercury should be negligible. However, it has been suggested that the solar wind can sweep away ions produced by photoionization of Mercury's atmosphere (*11, 12*), and this may be a major loss process for atmospheric gases that otherwise would not escape. Mercury's original atmosphere may have been removed by this means. The observed composition of Mercury's atmosphere and the appearance of sodium as a major constituent may then result from a steady-state balance among loss of atoms by ionization and trapping in the solar wind; supply from the surface by outgassing, sputtering, and volatilization; and neutralization of solar wind ions. Mercury's atmosphere may thus resemble a cometary coma rather than an Earth-like planetary atmosphere.

More information is needed before the sources and sinks of sodium in Mercury's atmosphere are understood. By measuring the variation of sodium emission with phase, time, and distance of Mercury from the sun, it may be possible to determine what processes control it.

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Molybdenum Availability, Nitrogen Limitation, and Phytoplankton Growth in Natural Waters

Abstract. *Sulfate inhibits molybdate assimilation by phytoplankton, making molybdate less available in seawater than it is in freshwater. As a result, nitrogen fixation and nitrate assimilation, both processes that require molybdenum, may require a greater expenditure of energy in seawater than in freshwater. This may explain in part why coastal marine ecosystems are usually nitrogen limited whereas lakes usually are not. Experimentally increasing the ratio of sulfate to molybdate (i) inhibits molybdate uptake, (ii) slows nitrogen fixation rates, and (iii) slows the growth of organisms that use nitrate as their nitrogen source.*

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In most lakes, the supply of phosphorus controls primary productivity (*1*), yet phytoplankton productivity in most estuaries and coastal seas is controlled by nitrogen supply (*2*). These facts are commonly used in managing water quality, but no explanation for this major difference between the functioning of lakes and marine ecosystems has been widely accepted. The difference in nutrient limitation between most lakes and oceans is general enough to suggest that there may be a geochemical explanation related to the chemistry of seawater. A related phenomenon is that although nitrogen is limiting in coastal waters, rates of biological nitrogen fixation tend to be quite low (*3*). We propose that rates of nitrogen fixation are low in coastal waters and that phytoplankton growth in these systems is nitrogen limited because molybdenum availability is low. Molybdenum is required for nitrogen fixation (*4*), and although concentrations of dissolved molybdenum in seawater are high for a trace constituent, we found that concentrations of sulfate equal to and below those found in seawater can inhibit molybdenum assimilation by phytoplankton. The resulting molybdenum deficiency leads to low rates of nitrogen fixation, which in turn make coastal seas nitrogen limited.

Coastal waters are nitrogen limited because they are more depleted in nitrogen than in phosphorus. This condition exists in part because available nitrogen is lost from the sediments by denitrification while phosphorus is more efficiently recycled from sediments to the water column (*5*). However, denitrification is also a major process in lakes (*6*) and yet does not appear to lead to nitrogen-limiting conditions there except for brief periods of time. In most lakes, the nitrogen deficit created by denitrification (or by imbalances in loading of nitrogen relative to phosphorus from external sources) is made up through nitrogen fixation (*7*). The ratio of available phosphorus to nitrogen controls the rate of nitrogen fixation in lakes, so that phosphorus and not nitrogen controls phytoplankton productivity in most freshwaters (*7*). In coastal waters, nitrogen fixation rates tend to be much lower than in lakes (*3*), even when phosphorus concentrations are reasonably high (*8*). The nitrogen deficit and nitrogen-limiting character of seawater systems persist. A few lakes also are nitrogen limited, and it has been suggested that nitrogen limitation of one of these, Castle Lake in California, is caused by unusually low molybdenum concentrations (*9*).

Data on the relative partitioning of molybdenum between dissolved and particulate phases in natural waters suggest that molybdenum may be less available to phytoplankton in marine ecosystems than in most freshwaters. Molybdenum in rivers and lakes tends to be evenly partitioned between dissolved and particulate phases (*10, 11*), but in seawater there is usually 10,000 times more dissolved molybdenum than particulate molybdenum (*12*). Also, concentrations of dissolved molybdenum in some lakes can change seasonally by a factor of 10 or more (*11*), but dissolved molybdenum is usually a conservative constituent of seawater (*10*). The conservative behavior of molybdenum in seawater and the high ratio of dissolved to particulate molybdenum in seawater are both unusual characteristics in a metal (*13*) and indicate that biological reactivity is low. Moreover, Sugawara *et al.* (*14*) found that concentrations of marine phytoplankton in open seawater have only 2 nmol of molybdenum per gram (dry weight), a value typical of molybdenum-deficient terrestrial plants (*10*). The concentration of molybdenum in lake phytoplankton also is often low (*14*) but can

Table 1. Effect of varying the concentrations of sulfate and molybdate on rates of nitrogen fixation (means and standard errors) in open-water Baltic Sea water of salinity 6 parts per thousand. Concentrations of sulfate and molybdate in seawater of salinity 35.4 parts per thousand, and average freshwater (*10*) are shown for comparison. Four replicates were used for the control; all other treatments had three replicates.

Treatment	Sulfate (mM)	Molybdate (μM)	Sulfate: molybdate	Nitrogen fixation (nmol of C_2H_2 per liter per day)
Control	4.8	0.02	240,000	10.7 (0.35)
Added molybdate	4.8	0.12	40,000	16.3 (1.61)
Added sulfate	9.8	0.02	490,000	8.2 (0.70)
Formalin control	4.8	0.02	240,000	0.05 (0.55)
Average seawater	28.0	0.11	255,000	
Average freshwater	0.3	0.005	60,000	

range up to 230 nmol per gram (dry weight) or higher (*11*). In general, marine plants tend to have lower amounts of molybdenum than do freshwater plants even though the concentration of dissolved molybdenum is some 20 times greater in seawater than in average freshwaters (*10*).

We suggest that the high concentration of sulfate in seawater competes with molybdenum assimilation, making molybdenum uptake more energetically expensive. Sulfate is the second most abundant anion in seawater and is present in concentrations 100 times greater than concentrations in lakes. In oxygenated seawater, molybdate is the only thermodynamically stable species of molybdenum (*10, 15*). The stereochemistry of molybdate is similar to that of sulfate; both ions have nearly identical effective radii and charge distributions (*16*). Molybdate is a well-known inhibitor of sulfate reduction (*17*), and a competitive inhibition of molybdate assimilation by sulfate for *Clostridium pasteurianum* has been reported (*18*).

In a series of experiments examining the uptake of radioactive ^{99}Mo by phytoplankton, we found that environmentally realistic concentrations of sulfate inhibit molybdate assimilation (Fig. 1) (*19*). Molybdate uptake by the phytoplankton in Mirror Lake, New Hampshire, was dependent on light and showed typical enzymatic saturation kinetics. The turnover time of molybdate increased as the sulfate concentration increased, showing sulfate inhibition. Sulfate inhibited molybdate uptake at sulfate concentrations and at sulfate-molybdate ratios much lower than those found in seawater (*19*).

We have also shown that varying the sulfate-molybdate ratio can affect the rate of nitrogen fixation as well as phytoplankton growth with nitrate as a nitrogen source. Our experiments on nitrogen fixation were performed on the R.V. *Argos* in the Baltic Sea during June 1983, in waters with a salinity of 6 parts per thousand, roughly one-sixth that of open seawater. We took surface waters and incubated them in 2-liter polycarbonate bottles in a deck incubator for 4 days. Some of the bottles had additions of 0.1 μM molybdate or 5 mM sulfate. The ambient concentrations of these ions in the unamended seawater were 0.02 μM molybdate and 4.8 mM sulfate (*19*) (Table 1). Thus, the enriched molybdate treatment had a sulfate-molybdate ratio slightly lower than that of average freshwaters, and the enriched sulfate treatment had a sulfate-molybdate ratio approximately twice that of seawater. After the 4-day incubation, we estimated nitrogen fixation rates by acetylene reduction (*20*). The molybdate addition produced a statistically significant increase in the acetylene reduction rate of 5.6 nmol per liter per day (95 percent confidence interval, ±4.5) with rates approximately 50 percent greater than those of the control (Table 1). The sulfate addition produced a significant decrease of 2.6 nmol per liter per day (±1.8), with rates approximately 25 percent less than those of the control (*21*). These results support our proposal that sulfate inhibits molybdate assimilation, thereby affecting nitrogen fixation rates. Data from other estuaries and the Baltic during other seasons are needed, however, to establish the generality of this finding (*22*).

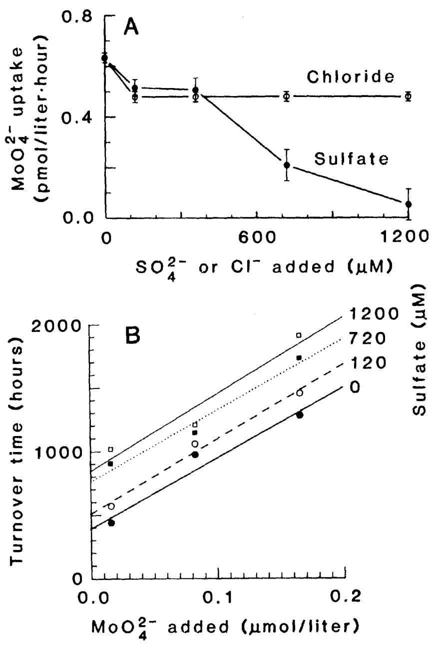

Fig. 1. Effect of sulfate on ^{99}Mo-labeled molybdate uptake by phytoplankton in water from Mirror Lake. Assimilation of label in particulate matter was measured by liquid scintillation after samples were incubated in the light at a variety of sulfate or chloride concentrations. Chloride additions served as a control for osmostic potential effects. Ambient sulfate concentration was 60 μM; ambient molybdenum concentration was less than 0.05 μM. (A) Molybdate uptake as a function of concentration of added sulfate or chloride. Each value is mean (with standard error) of three incubations. (B) Molybdate turnover time as a function of molybdate concentration at four different concentrations of added sulfate (0, 120, 720, and 1200 μM). Each point represents the mean of three separate incubations; the average coefficient of variation is 7.2 percent.

We used a pure-cultured heterotrophic bacterium to examine the effect of varying the sulfate-molybdate ratio (at constant molybdate) on nitrate assimilation (*19*). A freshwater pseudomonad was maintained in nitrogen-limited artificial media with either nitrate or ammonium as the sole nitrogen source. We first established that the growth of this bacterium with nitrate was a hyperbolic function of the molybdate concentration in the medium (*19*). We then held molybdate constant (0.021 μM) but varied the sulfate concentration from 30 to 4030 μM. The ionic strength of the media was kept constant by varying the NaCl concentration. When nitrate was the sole nitrogen source, growth was inhibited by sulfate at sulfate-molybdate ratios representative of seawater (Fig. 2). This effect presumably was due to lowered nitrate reductase activity caused by sulfate inhibition of molybdate uptake. That the effect was not merely a result of added salt is shown by growth when ammonium was the sole nitrogen source; no effect of molybdate availability on growth is expected when ammonium is the nitrogen source (*4*), and no effect of higher sulfate was observed (Fig. 2) (*23*).

Under reducing conditions, molybdate is not thermodynamically stable, and reduced molybdenum compounds would be expected to dominate (*10, 15*). The assimilation of these compounds should not be inhibited by sulfate. Thus, our proposal that nitrogen fixation in seawater is limited by sulfate inhibition of molybdate uptake pertains only to oxic environments. The highest rates of nitro-

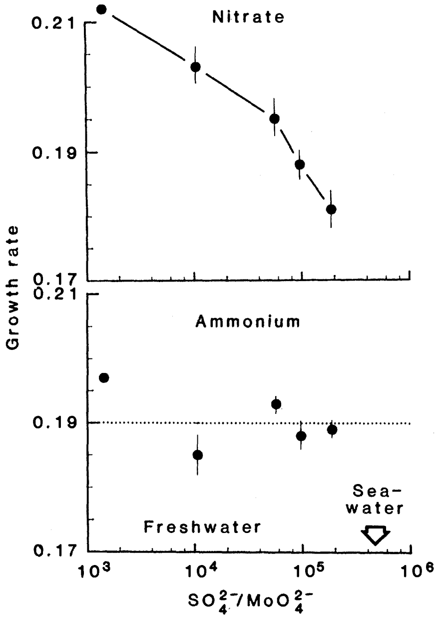

Fig. 2. Growth of a freshwater bacterium in artificial media as a function of sulfate-molybdate ratio. Cultures were grown with either nitrate or ammonium as the sole nitrogen source. Growth was measured during exponential growth as the increase in cell numbers, counted by epifluorescence microscopy (*19*). Mean and standard errors are shown for three separate incubations for each treatment (note the log scale). Sulfate-molybdate ratios for seawater and freshwaters are indicated for reference.

gen fixation in the oceans are generally found in or near reducing environments such as salt marshes, eelgrass beds, and coral reef ecosystems (*3*, *24*), perhaps because the presence of reduced molybdenum there allows molybdenum uptake without inhibition by sulfate.

We have concentrated on nitrogen limitation in coastal waters rather than in the open ocean since in open-ocean waters nitrogen and phosphorus usually are recycled in proportion to the needs of the phytoplankton; we would therefore not expect nitrogen to be more limiting than phosphorus in open-ocean waters. Nonetheless, if our proposal is true, then molybdate assimilation should also be difficult for such open-ocean nitrogen fixers as *Trichodesmium*. We have no ready explanation for the occurrence of *Trichodesmium* blooms in open waters but note that a bloom near Mozambique was correlated with an unusually high molybdenum concentration of 23 nM (*25*). Also, *Trichodesmium* is a slow-growing organism and blooms only where there is an abundant supply of light energy; perhaps it can afford the energetic cost of discriminating between sulfate and molybdate. Perhaps also *Trichodesmium* encourages the formation of anoxic microzones; these zones may allow the extracellular reduction of molybdate, and perhaps, therefore, the cells are assimilating reduced molybdenum rather than molybdate. Paerl (*26*) noted the role of anoxic microzones in favoring nitrogen fixation on detritus in coastal waters. *Trichodesmium* blooms usually occur in calm waters, which may be conducive to the formation of anoxic microzones.

Smith (*27*) argued that phosphorus should be considered the prime variable controlling productivity in estuaries and coastal seas, as is true in lakes. In his view, nitrogen limitation in estuaries occurs merely because hydrographic fluxes are so rapid that nitrogen-fixing organisms have insufficient time to alleviate nitrogen limitation. We agree that for the oceans as a whole on a geological time scale, phosphorus is probably the controlling variable (*28*). However, given lakes and coastal seas with similar hydrographic residence times, it appears to us that nitrogen-fixing organisms in the coastal seas respond much more slowly and are less effective in alleviating nitrogen limitation than are nitrogen-fixing organisms in most lakes. For example, the New York Bight is nitrogen limited despite the long residence time of water there (*2*). We conclude that the low availability of molybdate in seawater is in part responsible (*29*).

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20. Our method was modified from that described by R. J. Flett, R. D. Hamilton, and N. E. R. Campbell [*Can. J. Microbiol.* **22**, 43 (1976)]. Samples of 100 ml each were placed in 115-ml serum bottles, 50 ml of acetelyene was added, and the head space was degassed and replaced with air three times. This degassing removed contaminant ethylene, thereby lowering the ethylene blank sufficiently to allow measurement of very low rates, but left sufficient acetylene to saturate nitrogenase. Bottles were incubated in an on-deck incubator for periods of 6 hours to 2 days; rates were linear over time.
21. An analysis of variance of all data in Table 1 showed a statistically significant treatment effect ($P = 0.005$). Subsequent tests for planned multiple comparisons among class means indicated that both the molybdate addition ($P < 0.05$; 2 df) and the sulfate addition ($P < 0.025$; 3 df) produced significant changes. The test used allows for classes of unequal size and dissimilar variances. Degrees of freedom were estimated by an extension of Satterwaite's rule [G. W. Snedecor and W. G. Cochran, *Statistical Methods* (Iowa State Univ. Press, Ames, ed. 7, 1980), pp. 228–229].
22. Our nitrogen fixation rates were low, probably both because of the low water temperature (5°C) and because of a high ratio of dissolved nitrogen to phosphorus (50:1). Unlike many blooms in coastal waters, blooms of nitrogen-fixing cyanobacteria are common in the Baltic [A. Nemi, *Acta Bot. Fennica* **110**, 57 (1979)]. However, these blooms usually occur later in the summer after the N:P ratio falls below the Redfield ratio of 16:1. Our sampling was performed before blooms developed.
23. We have also performed several growth experiments and nitrogen fixation experiments with freshwaters and with pure cultures of various organisms where we found no effect of varying the molybdate concentration (*19*). In each case there was also no effect of added sulfate. These experiments suggest that there are further complexities to the biogeochemistry of molybdenum. Some organisms are capable of luxury uptake of molybdenum [P. T. Pienkos and W. J. Brill, *J. Bacteriol.* **145**, 743 (1981)], which may allow them to live through several generations with no further molybdenum assimilation.
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30. We thank R. Marino, S. Nolan, and S. Merkel for assistance; F. Manheim, A. Hagstrom, and D. Schindler for advice, encouragement, and facilities; and G. Likens, F. Manheim, R. Marino, B. Peterson, D. Schindler, and J. Waterbury for commenting on the manuscript. R.W.H. was on the staff of the Marine Biological Laboratory, Woods Hole, during most of the work reported here; he was a visiting scientist at the Institute of Ecosystem Studies, The New York Botanical Garden, during the preparation of this manuscript. J.J.C. was a postdoctoral fellow at the Marine Biological Laboratory at the beginning of this work. Supported by NSF grants BSR-83-05176 and INT-83-04275.

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