Prolific organic SiO_2 precipitation in a solute-deficient river: Rio Negro, Brazil

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ABSTRACT

Silicon extracted and precipitated by siliceous algae indicate that the dissolved silicon levels of the Rio Negro, Brazil, are in part controlled by biological activity. Diatoms are the most prolific and adhesive eucaryotic microorganisms found in the study area; wood, leaves, and rocks serve as both solid substrates for the adhesive microbes and as nutrient sources. Scanning electron micrographs of the wood samples revealed a siliceous "gel" precipitated on both the outer surface and within the submerged wood. A biomineralization process was occurring, leading to the silicification of the wood sample. On a regional scale, this process may have important implications for the freshwater silica cycle.

INTRODUCTION

Freshwater environments are generally undersaturated in dissolved silicon, the undissociated monomeric form of silicic acid, $Si(OH)_4$. Dissolved silicon levels have been attributed to an abiological buffering mechanism, whereby sorption reactions involving dissolved silicon and solid phases (i.e., sediments) control the concentration in freshwater environments (Edwards and Liss, 1973). Although the geochemical cycle of Si in freshwater ecosystems is dominated by physicochemical processes, the presence of organisms that concentrate silicon suggests that the dissolved silicon levels are also influenced by biologic activity.

Diatoms are commonly the most abundant freshwater eucaryotic microorganisms, and the development of large populations is invariably accompanied by a marked decline in the amount of dissolved silicon from the waters in rivers (Lack, 1971) and lakes (Schelske and Stoermer, 1971). These unicellular algae remove silicon to fulfill physiological functions such as DNA synthesis and to form their siliceous skeletons (Sullivan and Volcani, 1981).

The freshwater habitat of diatoms includes both planktonic and benthic species. Planktonic diatoms are found freely floating in the open water column, whereas benthic communities in the littoral zone of lakes or rivers must exhibit a strong adhesion to substrates to avoid detachment due to wave energy (Hoagland and Peterson, 1990) or high flow rates. Substrata include various plant, animal, or mineral surfaces.

In this study we have examined the presence of diatom communities on various solid surfaces from the Manaus area in Amazonia, Brazil (Fig. 1). The city of Manaus is built at the confluence of the Rio Solimões and the Rio Negro in cen-

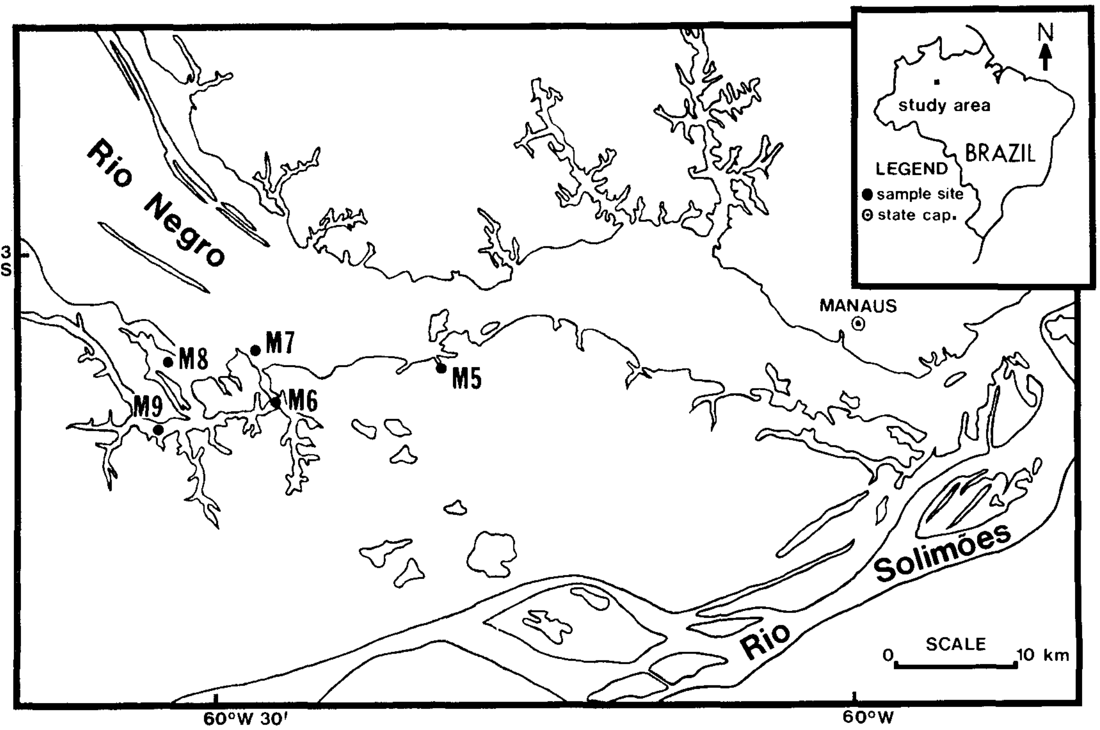

Figure 1. Location of study area and sample sites.

(Figs. 2C and 3B) that is less extensive than the gel shown in Figure 2B.

Samples of *Navicula* sp. obtained from the submerged leaves are different from those seen on the wood (Fig. 2D). The diatoms (quantitatively fewer than on the wood surface) were randomly oriented and overlie a sediment composed of Si, Al, Fe, Mg, K, and Ca (Fig. 3C).

Analysis of the water samples indicated that the dissolved silicon concentrations for the Rio Negro and its tributaries ranged from 1900 μg/L (sites M8 and M9) to 2000 μg/L (site M7) and 2100 μg/L (site M6). These values are considerably lower than the world river average of 7000 μg/L (Bowen, 1979) and the values shown in Table 1. Silicon concentrations and dissolved solutes in the Rio Negro are compared with those of average shield and adjacent soils in Table 2.

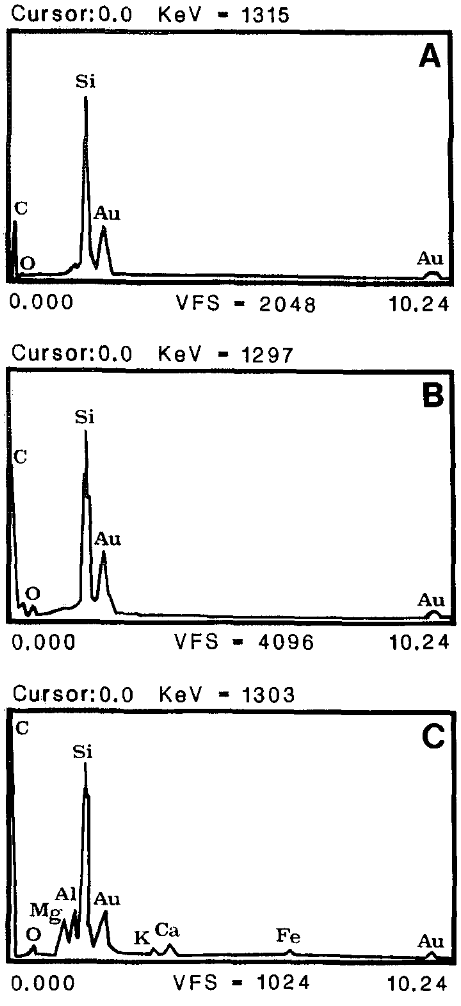

Figure 3. EDX spectra analysis of (A) siliceous gel on outer wood surface, (B) diatoms 3 mm deep in wood, and (C) sediment on leaf. Au peaks are due to scanning electron microscope preparation.

DISCUSSION

The chemistry of the Rio Negro, volumetrically the largest tributary of the Amazon, is characteristic of the highly weathered Precambrian shield through which the river flows. In these stable cratonic regions, the lack of exposed rock and intense chemical weathering over long periods of time results in the development of thick lateritic soils (Kronberg et al., 1979) with low weathering rates (Stallard and Edmond, 1983). As a result, the waters that drain these areas are deficient in solutes and have high silica to cation ratios (Stallard and Edmond, 1983). When compared to other major world rivers (Table 1) it becomes apparent that we are dealing with a unique river.

To date, very little information has been published on the chemistry of the Rio Negro. The few references to the river (e.g., Stallard and Edmond, 1983) tend to attribute its composition almost exclusively to inputs through weathering. Although the major source of solutes to the river is undoubtedly weathering induced, we believe that the widespread occurrence of both benthic and planktonic (K. Konhauser, 1991, unpublished data) diatoms suggests that the dissolved silicon levels of the Rio Negro are partly influenced by biologic activity.

Although the silicon levels in the Rio Negro are inherently low, the waters from this river were capable of supporting prolific diatom growth, wood, rocks, and submerged leaves serving as solid substrates. Although many might suggest that the high silica to cation ratios in the river argue against a significant biological removal of silica, a comparison of these ratios to both the ratios in average shield rocks and adjacent lateritic soils (Table 2) indicates that processes for silica removal are definitely at work.

In accordance with low weathering rates, the source of silicon for diatom growth will be largely sustained through the recycling of biogenic silica (Reynolds, 1986). Studies in large, nonflowing lakes (Kingston et al., 1983) and in the marine environment (Hein et al., 1978) have shown that recycled silicon provides >90% of that consumed annually by diatom blooms. Similar processes of silicon recycling should be expected within the almost nonflowing waters of the flooded forests. Calculation of silica recycling in the flowing (2 km/h; N. Falcao, personal commun.) mainstream of the Rio Negro is much more difficult to determine and will be the focus of future work.

The recycling of silicon in diatoms involves the dissolution of opaline skeletons and subsequent biological extraction. Within the small tributaries and flooded forests of the Rio Negro, benthic communities (e.g., *Navicula* sp.) are abundant, and dissolution may begin in situ on the substratum. Upon death of the microorganism, the remnant siliceous frustules become fragmented (Fig. 2B), partially dissolve, and reprecipitate as silica overgrowths within micrometres to millimetres of the surface (Hein et al., 1978; Williams et al., 1985). These amorphous overgrowths are formed when the dissolved silicon levels become locally supersaturated before opal-A dissolution has gone to completion (Hesse, 1990a). Dissolution, there-

TABLE 1. MAJOR DISSOLVED ION COMPOSITIONS
OF PRINCIPLE WORLD RIVERS

	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	SiO_2	TDS
Rio Grande	109	24	117	6.7	171	238	183	30	881
Danube	49	9	9	1	19.5	24	190	5	307
Nile	25	7	17	4	7.7	9	134	21	225
Yangtze	45	6.4	4.1	1.2	4.1	17.9	148	5.8	232
Upper Amazon	19	2.3	6.4	1.1	6.5	7	68	11.1	122
Lower Negro	0.2	0.1	0.4	0.3	0.3	0.2	0.7	4.1	6

Note: Values in mg/L. Data are from Berner and Berner (1987).
TDS = total dissolved solids.

TABLE 2. COMPARISON OF DISSOLVED SOLUTES IN THE RIO NEGRO
WITH AVERAGE SHIELD AND AVERAGE SOILS

Element	Rio Negro	Average Shield	Average Soil
Potassium	0.213	0.062	0.0006
Magnesium	0.077	0.042	0.0007
Calcium	0.228	0.069	0.000
Phosphorus	0.0047	N.A.	0.0009
Silicon	1.000	1.000	1.000

Note: Average Shield values are from Stallard and Edmond (1983).

fore, becomes interrupted by the reprecipitation of a less soluble, nonbiogenic, siliceous ooze referred to as opal-A′ (Hein et al., 1978).

Results from our studies suggest that we are witnessing the first stages of a dissolution-reprecipitation process in which the opal-A skeletons of diatoms are transformed in situ into a textureless, siliceous gel (Figs. 2B and 3A). Under ideal pressure and temperature conditions, this process may continue to follow the diagenetic sequence opal-A → opal-CT → chert (Carr and Fyfe, 1958; Kastner et al., 1977; Williams et al., 1985; Hesse, 1990).

This dissolution-reprecipitation process invariably alters the structure of the wood sample. The ubiquitous nature of the diatoms and the precipitation of the silica gel suggest that the wood sample is undergoing a void-filling process of silicification (Sigleo, 1978). In our samples this process begins with the dissolution of diatoms on the surface and within. The silicic acid produced from the dissolving frustules permeates the wood. Hydrogen bonding between the hydroxyl groups in the silicic acid and the hydroxyl groups in the cellulose then leads to the deposition of opaline silica on the surfaces of individual wood cells (Sigleo, 1978). We are, therefore, not surprised to see a siliceous gel, both on the wood surface (Fig. 2B) and within the wood (Fig. 2C).

The extent of this silicification process may be significant when the vast number of partially submerged trees in the study area is considered. The slow flow of water within the flooded forests and the preferential attachment of diatoms to the outer wood surfaces may allow for silicon levels to build up sufficiently in microenvironments. Therefore, many of the trees within these flooded forests potentially can become vast reserves of highly reactive silica, disrupting the amount of silicon locally recycled through the freshwater system.

The key question for us now is whether the net uptake of silicon by diatoms significantly affects the silica budget of the Rio Negro on a regional scale. To determine the mass balance of silica in the river system, the population of diatoms and their silicon recycling efficiency in the flowing mainstream must be known. These calculations are currently impossible to make; however, continued research in the area will shed more light on this question.

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