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 silification 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 Stormer, 1971). These unicellular algae remove silicon to fulfill physiological functions such as DNA synthesis and to form their siliceous skeletons (Sullivan and Volcarni, 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 Solimoes and the Rio Negro in cen-

Figure 1. Location of study area and sample sites.
tral Amazonia, 1600 km from the Atlantic coast. These tributaries of the Amazon have been categorized according to their appearance (Sioli, 1950). White-water rivers such as the Rio Solimões are rich in suspended sediments and dissolved solutes. In contrast, black-water rivers such as the Rio Negro are characterized by low sediment yields and their "tea-colored" (Hedges et al., 1986, p. 719) acidic waters, which are rich in dissolved humic material (Ertel et al., 1986).

The inundated flood-plain forest between the two Amazon tributaries, called Iranduba, is partly influenced by both water types. It consists of the varzea forest that borders the Rio Solimões and the less dense igapo forest, which is annually flooded by the Rio Negro (Hedges et al., 1986).

METHODS

Water samples were collected upstream of Manaus on the Rio Negro and some of its tributaries during an early July 1990 sampling period, following the annual rainy season in the Amazon. A submerged wood sample (0.7 cm thick) coated by a gelatinous algal film was collected from site M8, and several submerged plant leaves, also covered by algae, were taken from site M6 (Fig. 1).

Water samples (~1 L; taken midstream, from four different sites) were collected for analysis of dissolved silicon. The water samples were placed in two 500 mL Nalgene bottles and then acidified on site with 5 mL analytical grade HNO₃. Samples of wood and leaves were gathered from below the water surface by hand (surgical gloves were used to avoid contamination), dried in the sun, and placed in plastic bags.

In the laboratory, sections of wood were cut away from the outer surface to expose the wood 3 mm deep for observation by scanning electron microscopy (SEM). Small sections of the leaves were randomly obtained for similar observation. In preparation for analysis, samples were mounted on a specimen stub with conductive carbon paint and sputtered with gold for 3 min. Samples were examined with an SEM model ISI DS 130, coupled with a Tracer Northern EDX analyzer, model TN 5500.

Prior to multielement analysis, the water samples were filtered through a 0.2 μm Nucleopore membrane (Costar Corporation) to remove suspended sediments. The samples were then analyzed by inductively coupled plasma emission spectroscopy–mass spectrometry: an ICPMS Model PQ1 by Elemental Ltd. was used.

RESULTS

The SEM analysis indicates that both the wood and leaf samples served as substrata for siliceous epiphytic algae (Fig. 2, A–D). The abundance of these benthic communities suggested that where light intensity is sufficient, any available surface would serve as their solid interface for growth. A more detailed study is planned to confirm this.

Samples obtained from the submerged wood revealed morphologically different diatom species on the surface and 3 mm within. The diatoms of the surface community (Navicula sp.) range in size from 50 to 120 μm and are shown oriented in a rosette pattern (Fig. 2A). The density of diatoms on the surface suggests that the wood serves as both a favorable solid substrate and a nutrient source. Remnant frustules are also shown (Fig. 2B) covered by a blanket of siliceous "gel" (Figs. 2B and 3A).

The section of wood obtained from 3 mm depth revealed completely different species of diatoms (Synedra sp. and Eunotia sp.) (Fig. 2C). These diatoms are characteristically smaller (15 to 45 μm), which suggested lower available nutrient levels within the porous wood (C. Trick, 1990, personal commun.). Overlying some of the wood fibers are patches of a siliceous gel...
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 undeniably weathering induced, we believe that the widespread occurrence of both benthic and planktonic (K. Konhauser, 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 latelitic 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-

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**TABLE 1. MAJOR DISSOLVED ION COMPOSITIONS OF PRINCIPLE WORLD RIVERS**

<table>
<thead>
<tr>
<th>River</th>
<th>Ca**</th>
<th>Mg**</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
<th>SiO₂</th>
<th>TDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rio Grande</td>
<td>109</td>
<td>24</td>
<td>117</td>
<td>6.7</td>
<td>171</td>
<td>238</td>
<td>183</td>
<td>30</td>
<td>881</td>
</tr>
<tr>
<td>Danube</td>
<td>49</td>
<td>9</td>
<td>9</td>
<td>1</td>
<td>19.8</td>
<td>24</td>
<td>190</td>
<td>5</td>
<td>307</td>
</tr>
<tr>
<td>Nile</td>
<td>25</td>
<td>7</td>
<td>17</td>
<td>4</td>
<td>7.7</td>
<td>9</td>
<td>134</td>
<td>21</td>
<td>225</td>
</tr>
<tr>
<td>Yangtze</td>
<td>45</td>
<td>6.4</td>
<td>4.1</td>
<td>1.2</td>
<td>4.1</td>
<td>17.9</td>
<td>148</td>
<td>5.8</td>
<td>232</td>
</tr>
<tr>
<td>Upper Amazon</td>
<td>19</td>
<td>2.3</td>
<td>6.4</td>
<td>1.1</td>
<td>6.5</td>
<td>7</td>
<td>68</td>
<td>11.1</td>
<td>122</td>
</tr>
<tr>
<td>Lower Negro</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.7</td>
<td>4.1</td>
<td>6</td>
</tr>
</tbody>
</table>

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**

<table>
<thead>
<tr>
<th>Element</th>
<th>Rio Negro</th>
<th>Average Shield</th>
<th>Average Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>0.213</td>
<td>0.042</td>
<td>0.0006</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.077</td>
<td>0.042</td>
<td>0.0007</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.228</td>
<td>0.009</td>
<td>0.000</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.0047</td>
<td>N.A.</td>
<td>0.0009</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Note: Average Shield values are from Stallard and Edmond (1987).
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 Frye, 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 silification 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 silicic 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.

REFERENCES CITED

ACKNOWLEDGMENTS
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