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PERSPECTIVES

cluster. No synthetic cluster has yet been shown to interact with dinitrogen in a way to model the enzyme binding. Therefore, empirical support for such proposals is lacking.

However, the fog is beginning to clear. The structure of the active site revealed by x-ray analysis may change during the eight-electron dinitrogen reduction cycle. The molybdenum is bound into the cluster by three sulfide ions, and is linked to the protein by nitrogen coordination via histidine at position 442. The remaining two coordination sites are occupied by an unusual ion, homocitrate, which is bidentate. The molybdenum is thus six-coordinate and seems not, at least in the crystals, to have an obvious available coordination site for dinitrogen (2–5).

It has recently been shown that the bidentate homocitrate is exactly the correct size and shape to disconnect from one coordination site of the molybdenum and form a hydrogen bond to His⁴⁴². A mutant *nifV* nitrogenase that carries citrate rather than homocitrate can fix nitrogen with less than 10% of the activity of the wild type, but the size and shape of citrate do not allow it to form a hydrogen bond to His⁴⁴² (11, 12). Consequently, it is less able to help open up a coordination site on the molybdenum. Reactivity studies on isolat-

ed cofactors of wild-type and of the mutant nitrogenase support this interpretation.

Now, Yandulov and Schrock show how a molybdenum complex can convert dinitrogen to ammonia in a series of steps that involve no Mo oxidation state lower than III (see the figure, top panel). In their complex, the molybdenum ion is enclosed in a ligand that restricts access to the metal so that only small reactants such as dinitrogen and protons can reach it. With appropriate proton source and reductant, the authors can cycle the system at least four times.

The system does not operate in water and is not as stable during the reaction cycle as nitrogenase. This does not detract from the major advance: the report of a model system for conversion of dinitrogen to ammonia mediated by molybdenum through maximum and minimum oxidation states of VI and III, respectively. These should be comfortably accommodated by a biological system. The chemical species involved are similar to those already established in molybdenum-dinitrogen chemistry (7–10), but the reactions seem much more compatible with what we might expect of dinitrogenase biochemistry and biology. The new cycle can be fitted reasonably well to the widely accepted Lowe-Thorneley model (13) of nitrogenase action.

Coupled with the explanation for the

presence and possible action of homocitrate, these results provide the best model to date for dinitrogen reduction by conventional molybdenum nitrogenases. Vanadium nitrogenases probably undergo similar reactions, but iron-only nitrogenases (14) and the unique molybdenum nitrogenase from *Streptomyces thermoautotrophicus* (15) present further mysteries.

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GEOCHEMISTRY

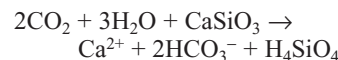
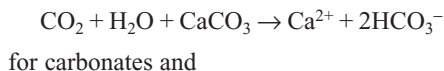
A New Story from the Ol' Man River

Venugopalan Ittekkot

“Plant a trillion trees,” one used to hear more than two decades ago when deforestation was still thought to be a key contributor to the increase in CO₂ concentrations in the atmosphere (1). Today, the CO₂ released by deforestation is probably balanced by enhanced terrestrial CO₂ sequestration (that is, uptake) elsewhere on land, and there might even be a net terrestrial CO₂ sink in forests in the Northern Hemisphere (2–4). Data from the Mississippi River reported by Raymond and Cole on page 88 of this issue (5) indicate that planting trees—in this case converting croplands to forests in river catchments—may even reduce terrestrial CO₂ removal from the enhanced chemical weathering currently occurring in river basins.

Every year, the world's rivers transport about 10¹⁵ g of carbon to the oceans, either in the form of suspended particles or dissolved in the water (6). This amount is relatively small compared to other components of the global carbon cycle. However, in a perturbed global carbon cycle and in the context of finding sinks for anthropogenic CO₂, changes in river transport of carbon—for example, in the form of alkalinity, as reported by Raymond and Cole—become important.

Alkalinity derives from the weathering and dissolution of carbonate and silicate minerals. The weathering process involves CO₂ and, in large rivers of today, is mainly correlated with precipitation, stream flow, and temperature (7). In a simplified form it can be represented as

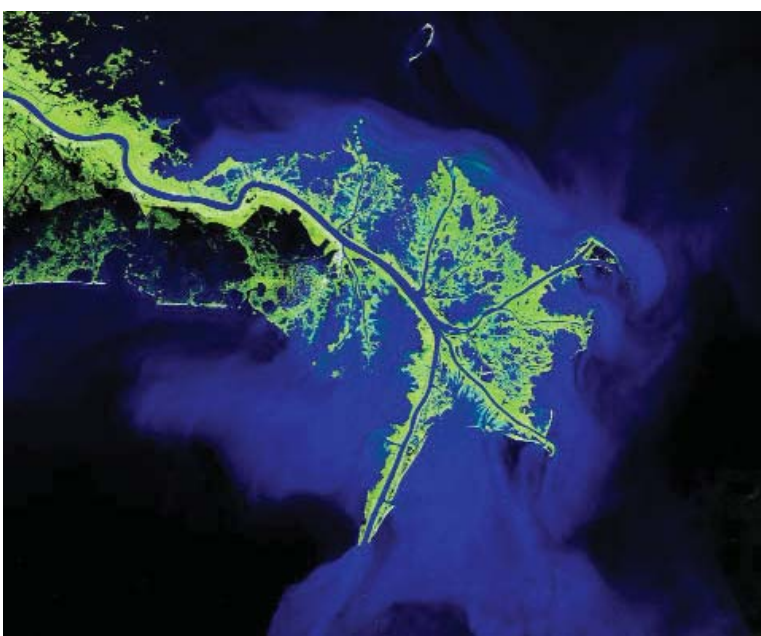


for silicates. CO₂ is supplied either directly from the atmosphere or from soils. The weathering products are transferred to rivers and streams in the form of dissolved cations and alkalinity.

The above reactions are important in the sequestration of atmospheric CO₂ because much of the HCO₃[−] (half in the case of carbonate weathering and all in the case of silicate weathering) is of atmospheric origin. The weathering products are transported to the ocean (see the first figure), where they are used by plankton to build their tissues and skeleton. When the plankton die and fall to the seafloor, they are buried in marine sediments. Subduction to Earth's interior and release of CO₂ to the atmosphere by volcanoes complete the cycle (see the second figure). Such weathering processes appear to control the long-term concentrations of CO₂ and O₂ in Earth's atmosphere and the oceans (8).

Raymond and Cole's analysis of U.S. Geological Survey data on the alkalinity of the Mississippi River shows an acceleration of weathering during the past 50 years, resulting in a steady increase in alkalinity export. An increase in alkalinity has been observed over the past ~20 years in many

The author is at the Centre for Tropical Marine Ecology, Fahrenheitsstrasse 6, 28359 Bremen, Germany. E-mail: ittekkot@zmt.uni-bremen.de



Landsat image of the Mississippi delta, where weathering products from the Mississippi and its tributaries reach the ocean.

freshwater lakes and streams of northern Europe and North America. It has been attributed to a decrease in acidic deposition (9). In the case of the Mississippi, the increase in alkalinity correlates well with precipitation and stream flow. There also appears to be a link to land use in catchments.

A positive correlation between stream flow on the one hand and cation concentrations and alkalinity on the other is a characteristic of watersheds on highly weathered tropical soils, where, in contrast to deep soil mineral weathering in healthy temperate soils, it has been attributed to a biologically mediated near-surface process

up a higher percentage, whereas with increasing forest lands it decreases. When forest land cover is high, there is a decrease in alkalinity with increasing water discharge; no such decrease is seen for mainly agricultural areas.

Rivers can also modify the carbon cycle in other ways. For example, a several-fold increase in the river transport of nutrients such as nitrate and phosphate promotes carbon fixation in rivers, estuaries, and coastal waters. Part of this newly fixed carbon in rivers is thought to be lost to the atmosphere from river basins in the humid tropics and from estuaries (11).

(10). In the Mississippi catchment, forest cutting and the resulting increased availability of CO_2 in soils, combined with high precipitation, might have similarly accelerated certain near-surface biogeochemical processes, leading to the observed trend.

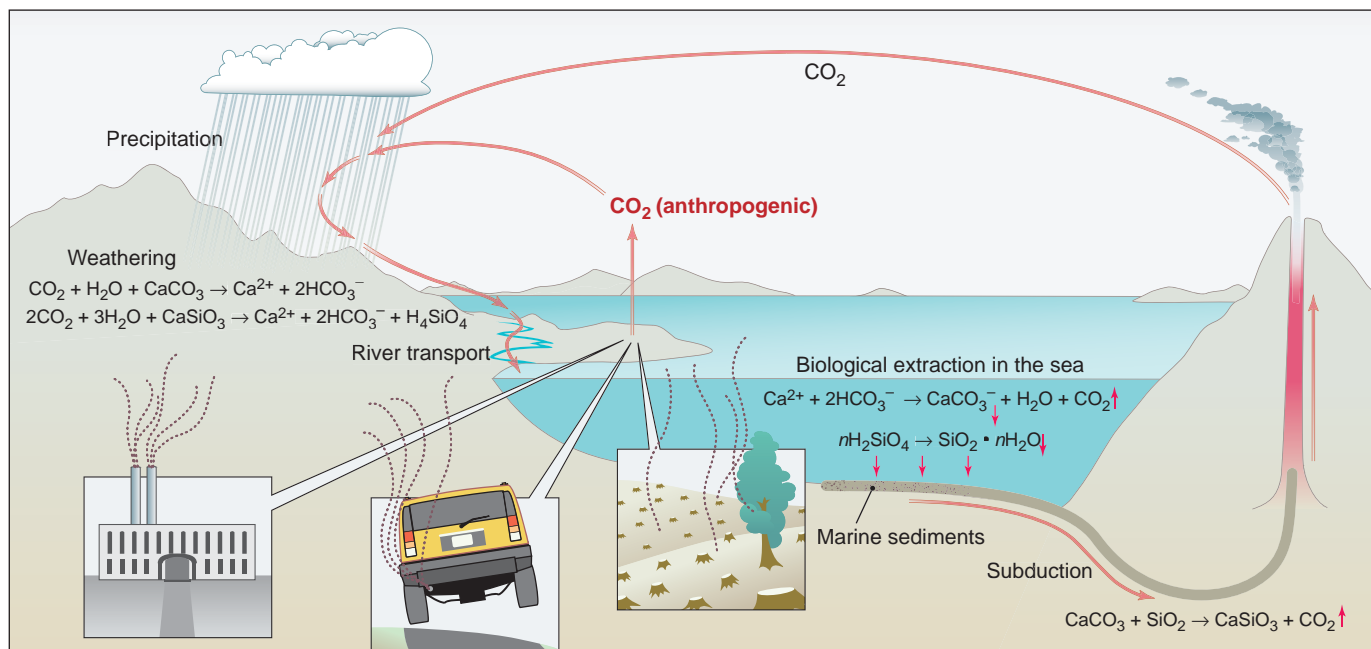
Raymond and Cole's detailed analysis of the alkalinity and discharge data from the catchments of tributaries of the Mississippi shows alkalinity export to increase when croplands make

Deforestation and agricultural activities in drainage basins have caused increased erosion and transport of large quantities of carbon and nitrogen attached to suspended matter in tropical rivers in Asia; these nutrients could become mobilized in the coastal seas (12). The resulting enhanced coastal productivity and subsequent organic matter removal in coastal sediments are carbon sinks that are enhanced by anthropogenic activities.

On the other hand, large-scale hydrological alterations of rivers have changed the ratios of nutrients such as nitrate, phosphate, and silicate reaching coastal waters. These changes affect species composition and diversity, and hence carbon sequestration, in the coastal zone (13).

All these direct and indirect processes must be taken into account when assessing the role of rivers in the carbon cycle and as terrestrial carbon sinks. Some processes may offset each other. Extrapolating from the Mississippi data, Raymond and Cole estimate that the additional global CO_2 sink from alkalinity export is in the range of the reported net carbon sink in Northern Hemispheric forests (4). These forests have also long been perturbed by human activities, with catchment-wide changes in the cycling and fluxes of carbon and other nutrients.

Reducing uncertainties in the nature and extent of terrestrial sequestration of anthropogenic CO_2 requires long time series of the type analyzed by Raymond and Cole. Data on alkalinity export will be es-



Chemical weathering and the carbon cycle. CO_2 is removed by weathering of silicate and carbonate rocks on land. The weathering products—cations and alkalinity—are transported by rivers to the ocean, where they are removed by sedimentation. When the sedimented minerals are subjected to high temperature and pressures in Earth's interior, CO_2 is again returned to

the atmosphere. This cycle has controlled the CO_2 content of the atmosphere for millions of years. The data of Raymond and Cole imply that the anthropogenic CO_2 increase, together with an increase in precipitation, has accelerated the weathering-river transport segment of this cycle, causing a steady increase in alkalinity export in the Mississippi River. [Adapted from (15)]

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pecially important for the rivers and streams draining the deforested watersheds of Asia, where expansion toward croplands is thought to still be the major contributor to deforestation (14).

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EVOLUTION

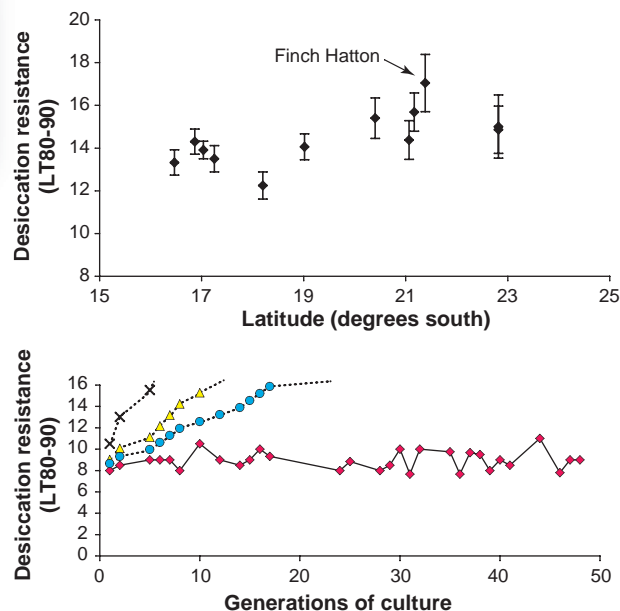
Evolutionary Danger for Rainforest Species

Derek Roff

Evolutionary change requires that the traits subject to selection are heritable. In the absence of genetic variation, natural selection can in any or each generation produce a sorting of the population, but each subsequent generation will have the same characteristics as the preceding unsorted population. The historical fact of plant and animal domestication and the more recent appearance of organisms that are resistant to pesticides, herbicides, and rodenticides provide ample evidence for the abundance of genetic variation. Rapid evolutionary change in natural populations provides further evidence for the abundance of genetic variation (1, 2). Empirically, the overwhelming finding of numerous genetic analyses has been that there is virtually always genetic variance for a trait (3). Indeed, finding genetic variation for a trait has the same import as the headline “Dog bites man.” However, if one were to find an ecologically important trait for which there was no demonstrable additive genetic variation, then this would be equivalent to the headline “Man bites dog.” Such a headline is reported by Hoffmann *et al.* (4) on page 100 of this issue. They have studied a single trait that apparently lacks genetic variation in the fruit fly *Drosophila birchii*, which inhabits patches of Australian coastal rainforest. Of equal import to this observation is the fact that

the trait examined—desiccation resistance—is one that may be critical for survival in the face of global warming.

The evolutionary response of a population can be predicted for a single trait by the breeders’ equation. This equation states that the response to selection is proportional to the heritability of a trait, defined as the proportion of the phenotypic variance that is attributable to additive genetic variance. Heritability varies between 0 and 1:



equal import to this observation is the fact that

Resisting global warming. Clinal variation in desiccation resistance and lack of response to artificial selection in *D. birchii*. (Top right) Hoffmann *et al.* (4) show that there is clinal variation in desiccation resistance in the rainforest fruit fly species *D. birchii*, indicating genetic variation for this trait among populations. (Bottom right) However, artificial selection on a single population of *D. birchii* (red diamonds) in a rainforest patch on the northeastern coast of Australia (Finch Hatton) produced no response, indicating a lack of genetic variation for this trait within this population. The predicted responses, based on estimated heritabilities, are shown for *D. melanogaster* (crosses), *D. simulans* (yellow triangles), and *D. serrata* (blue circles). These three *Drosophila* species inhabit a broader range of Australian habitats than does *D. birchii*. (The definition of desiccation resistance is LT80-90: the hours taken to achieve 80 to 90% mortality at 24 to 26°C.)

The author is in the Department of Biology, University of California, Riverside, CA 92521, USA. E-mail: derek.roff@ucr.edu