

Introduction to coupled biogeochemical cycles

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At the 2009 Annual Meeting of the Ecological Society of America, investigators of ecosystem science and biogeochemistry gathered in a series of sessions sponsored by the National Science Foundation to examine what is known about the coupling of chemical elements in biochemistry and thus in global biogeochemical cycles. As an introduction to the topic, this paper offers some philosophical thoughts about the origins and implications of coupled biogeochemical cycles on Earth. The chemical characteristics of Earth have carried the imprint of biology since the first appearance of life more than 3.5 billion years ago. Movements of about 30 chemical elements essential to life are coupled, so that the behavior of one element can often be used to predict the behavior of other elements – in both the natural and human-perturbed settings of the world. The coupling of biochemical elements stems from basic stoichiometry (the relative quantities of chemical elements in living biomass), the oxidation–reduction or “redox” reactions (in which one substance is oxidized [loses electrons] and another is reduced [gains electrons]) of metabolic activity, and chelation (in which a metal ion binds to an organic compound). Many anthropogenic environmental problems – climate change, eutrophication, acid precipitation, metal pollution – originate from the release of non-stoichiometric and toxic quantities of chemical elements to the environment. Geoengineering proposals as solutions to certain global environmental problems must be consistent with the underlying constraints of coupled biogeochemical cycles. Biogeochemistry has much to offer to policy makers, and biogeochemists must contribute to current deliberations about how to solve environmental problems.

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When Bob Dylan asked, “How many years can a mountain exist, before it is washed to the sea?”, he echoed a question that has intrigued philosophers and geologists for centuries. Since Earth’s beginnings, the atmosphere has interacted with the land surface, and rivers have carried eroded materials, eventually to be buried in ocean sediments. These processes are not unique to Earth; there is also evidence of past fluvial movements of materials on the surface of Mars (Malin and Edgett 2003).

The biosphere extends roughly 10 km above and 10 km below Earth’s surface, defining a thin 20-km peel or zone

where life exists. Each year, geological processes transfer a huge volume of material from one place to another within the biosphere, modifying the surface environment for organisms and supplying the elements required for biochemical processes. In a very real sense, geochemistry (the science dealing with the composition of Earth’s crust, as well as the chemical reactions in and between the crust, the atmosphere, and fresh and ocean waters) has set the stage for the evolutionary show that began more than 3.5 billion years ago (Figure 1).

In a nutshell:

- The presence of life on Earth determines the basic chemical conditions of the atmosphere, the oceans, and Earth’s crust
- The composition of living tissue and its metabolism couple the movements of about 30 chemical elements that constitute life on Earth’s surface
- Coupling of these elements means that the movement of one element in an ecosystem can often be predicted from knowledge of the movement of other elements
- Proposals for geoengineering projects as solutions to global environmental problems must be consistent with the underlying coupling of biochemical elements

■ The stage

Terrestrial vegetation enhances the weathering of rocks but also impedes erosion. Marine phytoplankton enhance not only the transfer of seawater constituents to ocean sediments but also the solubility of phosphorus (P) and some trace metals that promote primary production (ie the conversion of sunlight by plants into chemical energy held in organic matter). Photosynthesis is responsible for the oxygen content of Earth’s atmosphere, setting the redox potential of the planet and allowing the evolution of elaborate (eukaryotic) forms of life. Despite high redox potential, various reduced gases (eg methane, CH₄; ammonia, NH₃) – products of biotic metabolism – are found in Earth’s atmosphere, and most nitrogen (N₂) in the atmosphere can be traced back to bacterial denitrification (reduction of oxidized N [such

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Figure 1. Earth as seen from the Moon, showing the circulation of the atmosphere that links the biogeochemical cycles of land and sea.

as nitrate $\{NO_3^-\}$ coupled to oxidation of organic materials) in wet sediments. As a discipline, *biogeochemistry* recognizes that there is no pure geochemistry at Earth's surface; everywhere, life has left its imprint on the chemistry of the planet.

Based on the current rate of burial of carbon (C; organic and bio-inorganic) in ocean sediments, most of Earth's inventory of C in the crust and upper mantle – estimated at 22×10^{22} g C (Zhang and Zindler 1993) – has spent at least some time in the biosphere. If it were not for the return of C to Earth's surface via tectonic activities, one might find the entire pool of C buried and thus unavailable to life on Earth. Without tectonics, ecology textbooks would be very thin; indeed, life is tied to the movement of the rocks beneath our feet.

The first life on Earth may have flourished at or near hydrothermal vents – dark, hot, saline, high pressure, and at that time, anaerobic habitats deep in the oceans. Even today, the special chemical and energetic conditions that characterize hydrothermal vents allow novel ways of securing energy for life processes. Konhauser *et al.* (2009) suggested that a decline in the flux of nickel (Ni) from hydrothermal vents that occurred about 2.5 billion years ago may have led to the coincident increase in oxygen in Earth's atmosphere and subsequently the evolution of eukaryotic organisms. Nickel is essential to methanogens (any of various bacteria and archaea that are capable of producing CH_4 from the decomposition of organic material or the reduction of carbon dioxide $[CO_2]$), and with large amounts of Ni available, high CH_4 production would have consumed the limited amounts of oxygen. Here, we find evidence for coupled biogeochemical cycles, in which the behavior of one element affects the behavior of another, in Earth's early history.

Today, hydrothermal vents remain intriguing habitats for exploration, allowing scientists to delve into our metabolic and genomic origins. But for all the energy from deep inside Earth that is released in those habitats, the biotic

potential of the chemolithotrophic organisms (bacteria capable of deriving energy from the oxidation of reduced inorganic compounds) that inhabit them is limited and would never have led to the elaborate life forms that exist today (Canfield *et al.* 2006). Recognizing the importance of the rocks below and the Sun above, Falkowski *et al.* (2008) stressed that “on longer time scales, perpetuation of life remains contingent on geological processes and the constant flux of solar energy”. Humans should not expect to find elaborate life on Europa, a moon of Jupiter, at hydrothermal vents below its ice-covered oceans (Gaidos *et al.* 1999).

■ The cast

Modern biology textbooks display diagrams of the global cycles of the major elements of life, especially C and N. Most ecologists find it instructive to put their field measurements of net primary production (NPP) and N cycling in the context of these global cycles, to ascertain whether their new data are consistent with expected values for a given natural community. Of course, the C cycle is connected to the N cycle, the N cycle to the boron cycle, and so on, meaning that such diagrams do not reflect the rich complexity of biogeochemistry at any scale. Estimates of NPP must also be compatible with the nitrogen that might be available to support plant growth. Coupled biogeochemistry requires that we view ecology in multiple dimensions – in space, over time, and in the context of all 92 known natural elements.

Scientific examination of the connections between the chemical elements of life has a long history, perhaps beginning with Liebig's (1840) observations of the nutrient limitations of agricultural crops. Redfield's (1958) observation of consistent amounts of C, N, and P in phytoplankton biomass is now honored by a ratio that carries his name. Reiners (1986) extended the concept of predictable stoichiometric ratios in living matter to much of the biosphere, and Sterner and Elser (2002) presented such stoichiometry as a major control on the structure and function of ecosystems.

Biogeochemists who ignore the basic stoichiometry of biomass do so at their peril – witness criticism of the recent postulated incremental sink for C in European forest biomass, subjected to excess N deposition, that would require a biologically extreme ratio of C to N in living biomass, far above that known for any plant material on Earth (Sutton *et al.* 2008). If measuring several elements during their field studies, ecologists should always calculate the ratios between these elements to check for compatibility with, or deviations from, the nominal range of expected values.

Although the stoichiometry of biomass couples the elements in a predictable range of values, the expected ratios of elements in biomass are not absolute (eg the ratio of C to N in a reagent bottle of the amino acid alanine). For instance, a sample of phytoplankton will contain a mix of

species that vary in individual N:P ratios, even though the weighted average is close to that postulated by Redfield (Klausmeier *et al.* 2004). And, of course, a large organism will contain a mix of metabolic compounds (largely protein) and structural components (eg bone) that differ in elemental composition (Reiners 1986). In some sense, organisms are what they eat, but decomposers can adjust their metabolism (Manzoni *et al.* 2008) and production of enzymes (Sinsabaugh *et al.* 2008) to feed on a wide range of materials, even as they maintain a constant stoichiometry in their own biomass.

Mining geologists have long known that some plants and animals are specially adapted to local high concentrations of toxic elements in the environment, even incorporating these elements into biomass (Antonovics *et al.* 1971). Elsewhere, elements that are rare in nature – commonly those with high atomic weights – are toxic to most life, presumably because these elements were not used as the building blocks for life and there has been little chance for natural selection to offer physiological regulation and response to unusual exposures.

■ The plot

Coupling of biogeochemical cycles in metabolism extends beyond the basic biochemical constituents in biomass. Coupled biogeochemistry in metabolism stems from the flow of electrons in redox reactions that power all life processes. Perhaps first articulated by Kluver and Donker (1926), the coupling of elements in metabolism has been advanced by Morowitz (1968), Falkowski *et al.* (2008), and many others. Coupled metabolism is illustrated by a matrix, where each element in a column is reduced while the element in an intersecting row is oxidized (Figure 2). All known metabolisms can be placed in the various cells of this matrix or in a few adjacent cells that would incorporate columns and rows for iron (Fe) and other trace metals; for example, Mikucki *et al.* (2009) showed an unusual coupling of sulfur oxidation to Fe reduction beneath the glacial snows of Antarctica (Figure 3). Some metabolisms are more efficient than others, and not every reaction occurs in every environment. But the matrix shows the range of metabolisms possible on Earth, should the proper conditions exist (Bartlett 1986).

In some cases, the global cycles of trace elements are coupled to and control the cycles of major elements, such as N, through the action of trace elements as cofactors in enzymatic reac-

		Oxidized → Reduced			
		H ₂ O/O ₂	C	N	S
↑ Oxidized	H ₂ O/O ₂	X	Photosynthesis CO ₂ → C H ₂ O → O ₂		
	C	Respiration C → CO ₂ O ₂ → H ₂ O	X	Denitrification C → CO ₂ NO ₃ → N ₂	Sulfate reduction C → CO ₂ SO ₄ → H ₂ S
↓ Reduced	N	Heterotrophic nitrification NH ₄ → NO ₃ O ₂ → H ₂ O	Chemoautotrophy (nitrification) NH ₄ → NO ₃ CO ₂ → C	Anammox NH ₄ + NO ₂ → N ₂ + 2H ₂ O	?
	S	Sulfur oxidation S → SO ₄ O ₂ → H ₂ O	Chemoautotrophy (sulfur-based photosynthesis) S → SO ₄ CO ₂ → C	Autotrophic denitrification S → SO ₄ NO ₃ → N ₂ /NH ₄	X

Figure 2. Coupled biochemical metabolisms. Each cell in the matrix is defined by one chemical element in the row that is oxidized, coupled to an element from the column that is reduced. From an original concept by Morowitz (1968), updated from Schlesinger (1997).

tions. Howarth and Cole (1985) postulated that the availability of molybdenum (Mo) might control the activity of the N-fixing enzyme nitrogenase and thus the NPP of the oceans. Falkowski *et al.* (1998) suggested a similar role for Fe delivered to the oceans via wind erosion of desert soils and potentially controlling oceanic NPP through glacial and interglacial cycles (conforms with Moore *et al.* 2009).

Connections between the biogeochemical cycles also derive from intrinsic properties of organic compounds, which can often capture certain elements from the environment, changing their solubility in water to higher or lower levels that leave a biotic signature on the planet. In northern latitudes, the profile characteristics of regional soils (spodosols) derive from the chelation of Fe in fulvic



Figure 3. A sulfur-oxidizing, iron-reducing bacterial consortium leaves a characteristic rust-colored stain in outflow waters of an Antarctic glacier.



acids of percolating soil waters and enhanced transport of Fe to the lower soil profile. In contrast, lead derived from atmospheric deposition is bound and held in the surface organic horizons of the soil, inhibiting its disappearance from the soil profile (Kaste *et al.* 2005). Similar mechanisms may control the content of Mo in soils (Wichard *et al.* 2009), and thus the rate of N fixation (Silvester 1989). Downward transport of dissolved seawater constituents that are adsorbed to sinking fecal pellets reduces the mean residence time of many elements in the oceans (Cherry *et al.* 1978). Chelation couples the biogeochemistry of C to many elements that have a greater tendency to bind with organic compounds than to remain dissolved in water.

■ The sequel

Coupled-element biogeochemistry – in biomass, in metabolism, and in chelation – underlies many proposed schemes to “geoengineer” Earth for human benefit. Plans to sequester CO₂ from the atmosphere by stimulating an enhanced C uptake by the oceans – by way of intentionally fertilizing marine phytoplankton with Fe in resource-limited waters – are based on the observation of Fe limitation to marine primary production and predictable Fe:C ratios in phytoplankton biomass. Iron-to-carbon ratios show some variation, from 23×10^{-6} to 6×10^{-4} by weight (Buesseler and Boyd 2003), but either extreme suggests that only a small fraction of the annual production of Fe from the world’s mines would be needed to sequester a couple of billion tons of C in the deep sea. Fortunately, wiser heads have prevailed, and this particular geoengineering idea now has few advocates on account of its high costs and potential impacts on the marine environment (Chisholm *et al.* 2001).

A similar approach can be applied to estimate the efficacy of incremental C storage by fertilizing agricultural soils. Only 0.4×10^{15} g C per year (about 0.8%) of terrestrial NPP (50×10^{15} g C per year) escapes decomposition and is stored in soils (Schlesinger 1990). To store an additional billion tons of C (1×10^{15} g per year) would require an increment of 75×10^{15} g C per year to NPP. At an N:C ratio of 1:50 in terrestrial NPP, about 1.5×10^{15} g of N fertilizer would be required, and the production of that fertilizer would release about 1.28×10^{15} g C as CO₂ from fossil-fuel combustion. Thus, cognizance of coupled biogeochemistry would indicate that this policy is a poor opportunity for investors.

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