

GEOCHEMISTRY

The Descent of Minerals

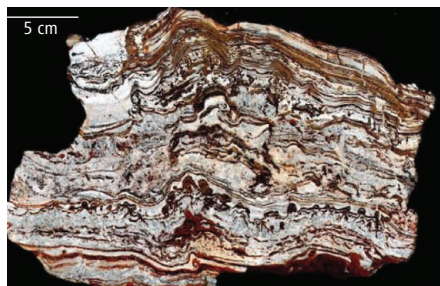
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Evolutionary theory states that some differences between individuals in a population are heritable, so that, when the environment changes, individuals bearing traits that provide the best adaptation to the new environment have the greatest chance for reproductive success. In a recent article in the *American Mineralogist* (1), Hazen *et al.* apply the term “evolution” to minerals in a similar manner, because new mineral patterns will adapt or evolve with changing environmental conditions throughout geologic time. The authors argue that the vast increase in the number of discrete mineral phases—from a sparse ~60 at the time of Earth’s formation to the more than 4300 known mineral species found on the modern Earth’s surface—requires an evolutionary explanation that goes beyond pure physical and chemical considerations.

Hazen *et al.* define three eras comprising 10 stages, which relate mineral evolution to the chronological divisions of Earth’s history. The eras of Earth’s mineral evolution arise from three basic mechanisms: first, the gradual change in the concentration and distribution of elements from the presolar nebula homogeneity to an expanded mineralogical diversity through physical processes during the era of planetary accretion (over 4550 million years ago); second, the introduction of new physicochemical conditions on the Earth’s surface, such as variable pressures and temperatures, as well as the increased activities of H₂O, CO₂, and O₂, led to a marked diversification of minerals in the terrestrial realm during the era of crust and mantle reworking (4550 to 2500 million years ago); and third, the development of widespread non-equilibrium conditions with the rising influence of life on the environment during the era of biologically mediated mineralogy (2500 million years ago to the present).

This process of mineral evolution is irreversible, advancing from sparse diversity to increasingly more variable and complex mineral assemblages. With the establishment of these chronological divisions, the authors present the scientific community with a new way to visualize the origin and evolution of Earth in a logical systematic fashion through its evolving mineralogy.

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Examples of biogeochemical laminae. (Left) A 3500-million-year-old stromatolite sample collected from the Apex Chert Formation in the Pilbara region of Western Australia. The wavy laminae and small digit structures are thought to have been produced by the metabolic activity of primitive microorganisms on early Earth. (Right) Microbial mat cultured under hypersaline conditions in the Geomicrobiology Laboratory, ETH Zürich. In the uppermost green layer, the primary producers, cyanobacteria, photosynthesize the biomass and release free oxygen. The underlying pinkish-brown layers contain other microorganisms, which consume and decompose the primary organic matter. The white layers consist of calcium–magnesium carbonate precipitated in situ as a by-product of the microbes’ metabolism; they will eventually amalgamate to form distinct laminae.

Despite their complexity, the history of the planet and the history of life on Earth are profoundly linked. Science and technology have advanced to the point where this relationship can now be explored. Indeed, Hazen *et al.* relate surface geochemistry and life evolution to mineral diversity. When the Earth’s surface achieved a geochemical state that allowed life to flourish, geomicrobiological processes began to form biominerals, probably via biologically induced precipitation. These processes led to the production of large mineral deposits, such as giant banded iron formations (BIFs), which are a major economic source of iron ore. The deposition of the iron minerals in BIFs is thought to require the presence of microorganisms that can photosynthetically produce O₂ and/or oxidize Fe²⁺ ions (2).

Another example of the early association of minerals and life is exemplified by fossil stromatolites, which are considered to be the oldest evidence for microbial life on Earth. In the rock record, these remarkable structures appear as wavy laminated, lithified sedimentary growth structures, which accrete away from an initiation point or surface (3) (see the figure, left panel). The laminae comprise biominerals, such as carbonates, silica, and phosphates, and represent the former presence of a viable microbial community. This ancient microcosm contained the essential trophic groups needed to maintain life—primary producers, consumers, and decomposers—organized into specific communities that interacted with each other (4). These biological interactions induced mineral precipitation, which may have bene-

fited the microorganisms by providing a mechanism for generating energy.

The biochemical process of lamina formation can be observed in modern microbial mats cultured in the laboratory. The microbial community produces discrete carbonate laminae in an organic matrix, or biofilm, as a by-product of distinct metabolic activity, such as photosynthesis or sulfate reduction (5) (see the figure, right panel). Over time, the organic matrix decomposes, allowing the intercalated laminae to coalesce and eventually become amalgamated into lithified layers, which can potentially be preserved in the rock record.

Thus, the study of modern microbial mats suggests that the oldest evidence for life represents the record of a primitive minimal ecosystem, which is, however, a very complex system evolved from a cooperative and sustainable association of organisms. Indeed, the appearance of stromatolites in the early Archean (~3500 million years ago) implies that life and the associated biominerals most likely coevolved on the primitive planet. This early but complex biogeochemical phenomenon directly links biological evolution with mineral evolution.

With the introduction of mineral evolution, Hazen *et al.* provide a new perspective on the study of Earth history. Combining inorganic and organic processes in a chronological association allows scientists to calibrate geologic events in the context of the 10 stages of mineral evolution, from the simplicity of the presolar dust particles to the biomineral explosion in the past 545 million years. Understanding the formation sequence and the interactions of

minerals associated with life on Earth could be a new proxy or tracer to evaluate the occurrence of life on other planets, that is, associating specific minerals with the physical, chemical, and biological evolution of the planet. Using mineral evolution to interpret planetary evolution has the potential to energize the field of mineralogy, placing mineralogic processes firmly in a geologic time frame.

OCEAN SCIENCE

Old New Nitrogen

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During the last glacial period, both nitrogen fixation and denitrification rates are likely to have been much lower than they are today.

The availability of nitrogen limits primary production in many parts of the ocean, creating a tight link between the fluxes of nitrogen and carbon through marine ecosystems. This coupling between the nitrogen and carbon cycles is often quantified in terms of “new nitrogen,” or nitrogen added to the biologically active pools in the upper ocean by processes such as vertical mixing, river runoff, atmospheric deposition, and nitrogen fixation. On page 244 of this issue, Ren *et al.* (1) introduce a powerful approach for characterizing the history of the oceanic nitrogen cycle and the role of new nitrogen in supporting primary production by measuring the nitrogen isotopic composition of the shells of planktonic foraminifera.

Recent studies have demonstrated the key role currently played by nitrogen fixation in supplying new nitrogen to nutrient-poor regions of the open ocean (2), but the overall magnitude of this key biological flux and the identity and distribution of the organisms responsible remain unclear. It is also uncertain how nitrogen fixation relates to other nitrogen-cycle processes, although stoichiometric considerations suggest that nitrogen fixation and denitrification may act together to control, and perhaps stabilize, the oceanic content of NO_3^- and other forms of combined nitrogen (3). Any global-scale decoupling of denitrification and nitrogen fixation can potentially affect marine primary production; at least one recent effort (4) suggests that the oceanic nitrogen budget is currently far from balanced, with a large excess of losses relative to inputs.

Nitrogen isotope studies have been used to

References and Notes

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6. Stromatolite culture experiments were supported by grants from ETH Zürich and ESF Research Network ArchEnviron.

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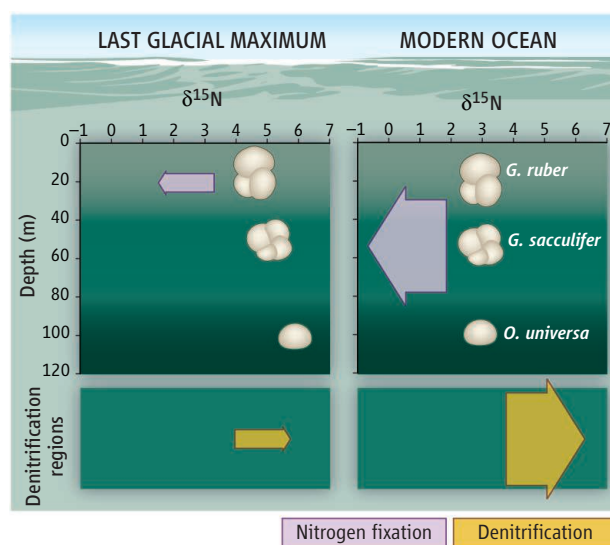
both the quantity and isotopic composition of nitrogen in the ocean (6). In essence, nitrogen fixation adds new nitrogen with a low $\delta^{15}\text{N}$ to the ocean, whereas denitrification removes combined nitrogen from the ocean and increases the $\delta^{15}\text{N}$ of the nitrogen that remains.

The isotopic composition of bulk sedimentary organic matter is relatively easy to measure, but sedimentary nitrogen may undergo alteration after deposition (diagenesis). Ren *et al.* avoid this complication by measuring the isotopic composition of nitrogen in the shells of planktonic foraminifera, which live and grow in the upper water column. This approach is not novel; others have recognized that the nitrogen in the shell matrix is protected from most diagenetic processes (7). However, the small quantities of nitrogen available and the potential for contamination required careful development and testing of methods before the approach could be used profitably on real sediment samples.

Ren *et al.* first confirmed that recently deposited (core-top) foraminifera from various locations in the Atlantic and Pacific basins faithfully reflect the $\delta^{15}\text{N}$ of the inorganic nitrogen in those regions. They then investigated the $\delta^{15}\text{N}$ of nitrogen laid down by foraminifera as they fed and grew over the past 30,000 years at a site in the western Caribbean (ODP Site 999) that provides a record of conditions in the Caribbean and North Atlantic Basins.

The results reveal interesting differences between the glacial and interglacial parts of the record. First, the foraminifera shells record a clear decrease in $\delta^{15}\text{N}$ from the Last Glacial Maximum to

the present (see the figure). This shift mirrors changes previously measured in bulk sedimentary nitrogen from the Cariaco Basin (an anoxic environment in the Eastern Caribbean) (8) and implies a fundamental change in the workings of the oceanic nitrogen cycle. The simplest interpretation is that oceanic nitrogen fixation supported a smaller fraction of total biological production during the glacial period than it does today. Using a simple isotopic mixing model, Ren *et al.* estimate that inputs of new nitrogen by nitrogen fixation in the glacial North Atlantic were roughly 20% of the present-day rate. Nitrogen isotope measurements of



Nitrogen past and present. The nitrogen isotopic composition ($\delta^{15}\text{N}$) of foraminifera shells was different under glacial conditions (left) than in the contemporary ocean (right). Nitrogen fixation adds ^{15}N -depleted (low- $\delta^{15}\text{N}$) nitrogen to the ocean, whereas denitrification removes nitrogen from the ocean and increases the $\delta^{15}\text{N}$ of the remainder. Under glacial conditions, new nitrogen was added to the upper water column at lower rates and at shallower depths than in the contemporary ocean.

resolve some of these uncertainties. The natural abundance ($\delta^{15}\text{N}$) of the stable isotope ^{15}N varies as a result of biologically mediated isotopic discrimination. Therefore, measurements of the $\delta^{15}\text{N}$ of plankton and dissolved inorganic nitrogen can be used to quantify the sources of nitrogen that support production in contemporary pelagic ecosystems (5). The isotopic signature of plankton in the upper water column propagates to the seafloor through sedimentation of organic matter, and the $\delta^{15}\text{N}$ of sedimentary organic matter records the relative importance of nitrogen fixation and denitrification, which have opposing effects on