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Elements and Evolution

Changes in elemental abundances in Earth's oceans on geological time scales are intimately linked to evolutionary processes.

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We think of Earth as a biologically thriving world. However, nearly half of the planet's surface is covered by ocean regions in which life is scarce. These thinly populated ecosystems do not lack water or sunshine, nor the bulk biological elements hydrogen, carbon, and oxygen. Instead, they are deficient in one or more of the other elements necessary for life. Hence, the distribution of life on Earth is captive, in part, to the distribution of the 20 or so bioessential nutrient elements—many relatively rare—that are critical components of DNA, RNA, enzymes, and other biomolecules. Having substantially unraveled this relationship in today's oceans, biogeochemists are beginning to examine how it evolved over the ~4-billion-year history of life on Earth.

The distribution of bioessential elements in ancient oceans cannot be studied directly, because we cannot sample seawater from the distant past. Instead, we must draw inferences from the chemical characteristics of rocks formed from ancient seafloor sediments. Some of these characteristics varied over time in ways that are obvious to the naked eye. The best example is the abundance of iron in the geologic record (*1*)—in particular, massive deposits of sedimentary iron minerals older than 1.8 billion years. These "banded iron formations" (BIFs) are the major source of industrial iron ore. Their near-disappearance from the subsequent record is equally obvious. The history of BIFs suggests that iron-rich oceans in the first half of Earth history gave way to later iron scarcity (*2*, *3*). Today, iron is so scarce in the oceans that it is often a limiting nutrient—so much so that some propose "iron fertilization" of the oceans to stimulate marine photosynthesis, thereby drawing down atmospheric CO_2 (*4*).

Changes in the budgets of other bioessential elements are more subtle. They must be deduced using sophisticated analytical methods

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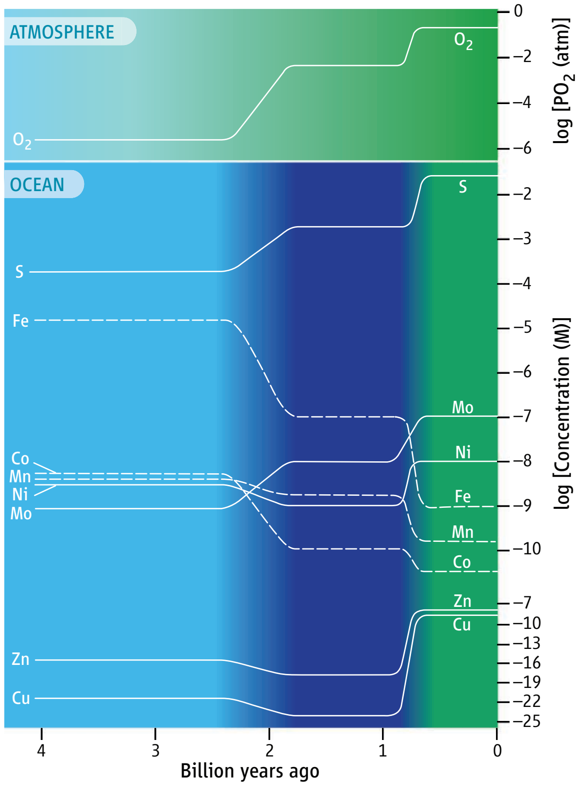
that measure the abundances and isotopic compositions of elements in ancient rocks. For example, mass spectrometric analyses of sulfur isotope ratios in sulfide and sulfate minerals reveal that the sulfur content of the oceans increased by as much as an order of magnitude around 2.4 billion years ago, and then again after 700 million years ago (*2*).



Changes in element abundances through time. These histories are approximate, based on simple geochemical models and inferences from ancient sediments. An expansion in H_2S-rich ocean regions after 2.4 billion years ago is assumed (*2*, *5*). Color gradations indicate a transition from anoxic, S-poor oceans before 2.4 billion years ago (light blue) to H_2S-rich oceans between 1.8 billion and 800 million years ago (dark blue), subsequently giving way to complete ocean oxygenation (green). Different line styles are for clarity only; dashed lines are for elements with falling concentrations. [Adapted from (*26*), based on data from (*2*, *5*, *9*, *10*)].

These changes in the ocean abundances of iron and sulfur were probably caused by rising amounts of O_2 in the environment (see the figure) (*2*, *3*). In the modern, oxygenated oceans, iron is scarce because it is oxidized to Fe^{3+}, which reacts with OH^- to form insoluble iron oxyhydroxides. In contrast, sulfur accumulates in oxidized oceans as SO_4^{2-}. However, ancient oceans probably contained much less oxygen. Most researchers agree that the redox state of the environment evolved through at least three stages, with major oxygenation events occurring ~2.4 billion to 1.8 billion years ago and 800 million to 500 million years ago. During the first of these stages, the oceans were largely devoid of dissolved O_2, and so iron was abundant in the form of dissolved Fe^{2+} complexes. Much of the sulfur at that time was in the form of insoluble sulfide minerals locked in the continental crust (*2*).

Ocean chemistry during the middle stage remains unclear. A counterintuitive idea gaining support posits a period of nearly a billion years, beginning ~1.8 billion years ago, during which a mildly oxygenated atmosphere overlay large ocean areas rich in H_2S (*5*, *6*). According to this hypothesis, BIFs first disappeared because of the formation of insoluble Fe^{2+} sulfides (*5*).

Regardless, this redox evolution should have affected the budgets of many bioessential elements besides iron and sulfur. In particular, the ocean abundances of transition metals such as manganese, cobalt, nickel, copper, zinc, and molybdenum are sensitive to environmental redox conditions. Analyses of molybdenum concentrations and isotope abundances in ancient rocks reveal the expected three-stage trajectory (*7*–*9*). The histories of other bioessential transition metals have yet to be read from the rock record. However, simple geochemical concepts predict that many element abundances changed markedly at least twice (see the figure) (*10*).

These and other changes in the chemical composition of the oceans surely affected the biosphere. There are many intriguing possibilities. First, transition metal chemistry may link atmospheric O_2 with the macronutrients nitrogen and phosphorus. For example, molybdenum and iron are important for N_2 fixation and NO_3^- assimilation by the nitrogenase and nitrate reductase enzymes. Therefore, low abundances of both elements between ~1.8 billion and 800 million years ago could have hindered the acquisition of nitrogen by the ocean biosphere (*11*). Before 1.8 billion years ago, coprecipitation of PO_4^{3-} with banded iron formations could have rendered phosphorus scarce (*12*). Although both ideas have been challenged (*13*, *14*), they illustrate the potentially complex interplay between micronutrient budgets and wholesale changes in the nutrient status of ancient oceans.

Second, the ocean abundances of trace elements could have influenced the atmospheric budgets of biogenic greenhouse gases. For example, the abundance of N_2O may depend on the ocean availability of copper, which is essential to the enzyme that converts N_2O to N_2 during denitrification. Therefore, copper scarcity in the ocean may have resulted in an N_2O-rich "laughing gas atmosphere" between 1.8 billion and 800 million years ago (*15*). Similarly, atmospheric CH_4 may depend on nickel, necessary for bacterial methanogenesis. CH_4 was probably more abundant in the atmosphere before 1.8 billion years ago. At the same time, the nickel concentration in the oceans may have been surprisingly high (*16*). A subsequent decrease in nickel abundance may have limited the activity of methanogenic bacteria (*16*).

Finally, changes in the availability of bioessential elements must have shaped the evolution of life (*17*). For example, fossil evidence suggests that the ecological diversification of eukaryotes broadly coincided with rising redox potential of the deep oceans after ~800 million years ago (*18*), and hence with increases in zinc, molybdenum, and other elements and decreases in iron, manganese, and cobalt. Bioinformatic analyses of protein-metal binding motifs encoded in genomes reveal that, relative to prokaryotes, eukaryotes require more zinc, and less iron, manganese and cobalt, according to (*19*). Eukaryotes also require molybdenum for nitrate assimilation (*11*) and can use zinc in place of cobalt in the carbonic anhydrase enzyme for carbon assimilation (*10*). Thus, it may be that eukaryotes emerged from ecological niches as bulk ocean chemistry shifted to favor their element requirements (*11*, *18*). Analogous logic may explain the rise of red eukaryotic phytoplankton after 250 million years ago (*20*).

Evaluation of such ideas requires research at the intersection of life sciences, chemistry, and geosciences. It is particularly important to quantify the element makeup of microorganisms [e.g., (*21*)] and their compositional "plasticity." Changes in environmental availability of the elements create selection pressures that should alter the composition of biological macromolecules and the metals used in particular enzymatic pathways (*22*). While a few examples are known (*23*, *24*), such research rarely considers the selection pressures possible in ancient oceans. In addition to shedding light on the history of life on Earth, such research will provoke us to think about alternative biochemistries unknown in living organisms (*25*). Someday, it may even help us to understand the distribution of life on planets other than our own.

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