Earth's Redox History
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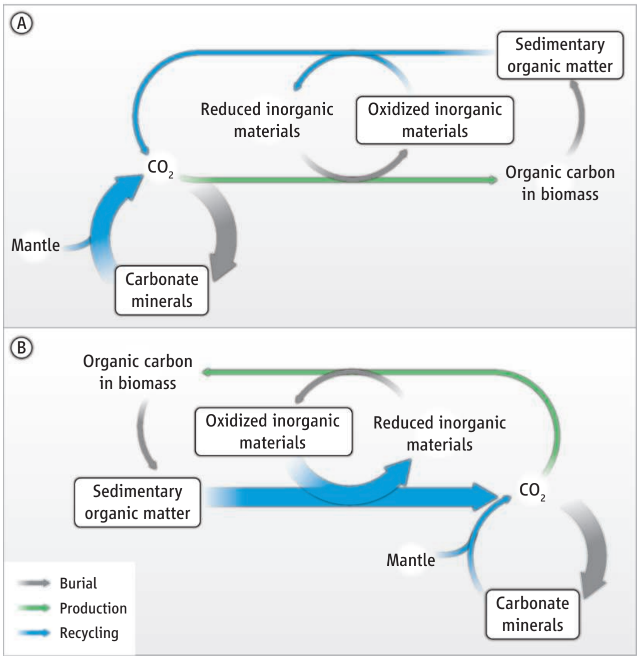
GEOCHEMISTRY

Earth's Redox History

John M. Hayes

About 2 billion years ago, Earth's carbon cycle was severely disrupted by a period of intense oxidation of organic material.

Beginning with photosynthetic bacteria and continuing to green plants, organisms have been transferring electrons from inorganic donors and producing organic carbon for billions of years. The main oxidized products, accumulating in the Earth's crust along with organic material, have been ferric iron (Fe^{3+}) and sulfate (SO_4^{2-}), the former accounting for about 75% of the total (*1*). Molecular oxygen (O_2), confined to the ocean and atmosphere, accounts for only 2 or 3% of the oxidized products. Moreover, O_2 accumulated only if its production overbalanced consumption by reactions with organic carbon, sulfide (S^{2-}), and ferrous iron (Fe^{2+}), all delivered to the ocean by geological processes. On page 1694 of this issue, Kump *et al*. (*2*) provide new information that will strongly affect efforts to decipher Earth's redox history.



The carbon cycle. Carbon is buried as both organic and inorganic carbon through sedimentation. It is then cycled through the Earth's crust through plate tectonics and rereleased into the atmosphere and ocean by volcanic eruptions, tectonic uplift, and erosion. On average (**A**), oxidized carbon is the main input to the atmosphere and ocean. Now, however, Kump *et al*. have provided carbon-isotopic evidence for a period about 2 billion years ago (**B**) during which oxidation of organic material provided the dominant input to the ocean and atmosphere.

Earth's oxidization has been a messy process. The surface of our planet is not a well-stirred titration vessel. At some times and in some places, one reactant or another will have accumulated in excess. Erosion, tectonic movement, or an ecological or evolutionary development will then have changed the conditions. From a human perspective, the ensuing reaction—a redox process involving some combination of carbon, iron, sulfur, and oxygen and possibly occurring over millions of years—can look like an "event," a notable occurrence on the geologic time line. Kump *et al*. now provide the first, definitive evidence of a temporary but massive reversal of the long-term trend, an "event" in which the oxidation of organic material from the crust dominated the carbon cycle.

Geochemists think in terms of exchanges of oxidizing power between the cycles of carbon, iron, sulfur, and oxygen on Earth over time. To monitor the Earth system, they examine not only the accumulation of oxidized products but also the operation of the carbon cycle (see the figure, panel A). The ratios of ^{13}C to ^{12}C in marine limestones and in sedimentary organic materials depend on the division of carbon between its two main geochemical fates, namely burial as carbonate or as organic material. Accordingly, changes in the carbon-isotopic composition of rock samples have been used as a speedometer for the process of oxidation (*3*).

Rocks containing samples of organic and carbonate carbon are preserved for billions of years. By collecting and analyzing them, a record of carbon-isotopic abundances can be constructed. This record provides information about variations in the inputs and outputs of the carbon cycle. Conventional interpretations assume a steady state in which the ratio of ^{13}C to ^{12}C entering the system is equal to the average ratio in Earth's crust. On long time scales, this must be true, but the new evidence provided by Kump *et al*. is the first proof that short-term deviations from the average can be very large.

Analyzing material made newly available by continental drilling, the authors show that about 2 billion years ago, a surging flow of oxidizing power from inorganic materials to the carbon cycle reoxidized so much organic carbon, and the burial of new organic material was so impeded, that $^{13}C/^{12}C$ in limestones dropped well below the crustal average (see the figure, panel B). A similar event might have occurred 600 million years ago (*4*) but, as noted by the present authors, the evidence is less strong.

The present evidence deserves attention for two reasons. First, the isotopic signal—a sharp decline in $^{13}C/^{12}C$—appears in both the carbonate and organic records, as expected if the CO_2 was the reactant from which the organic material formed. Second, it is observed at the same time in two widely separated sedimentary basins, indicating a global event. However, the organic $^{13}C/^{12}C$ signals in the different basins have identical shapes but different values. That isotopic offset is not unprecedented and does not immediately suggest an alternative explanation, but it clouds the picture.

More broadly, the new results should inform our thinking about Earth's redox history. For the carbon cycle, the assumption of crustal-average inputs is safe on billion-year time scales but is now shown to be wrong on time scales long enough to influence the sedimentary record. If there was at least one such big deviation, then there must have been thousands of smaller ones, intervals in which either carbonate or organic inputs were favored, but not strongly enough to push $^{13}C/^{12}C$ to otherwise unexplainable values. When an "event" appears in the carbon-isotopic record, geochemists must now ask how much of the signal is driven by redox variations and how much by variations in inputs to the carbon cycle.

Despite the uncertainty about shorter-term details highlighted by Kump *et al*.'s findings, the development of a breathable atmosphere was mainly a long slog, a slow but almost continuous oxidation over billions of years (*1*). The O_2 is merely the frosting on a ferric sulfate cake.

What finally laid that frosting on thickly enough for respiring, complex animals?

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Within the marine photic zone (the part of the ocean where enough light is available for photosynthesis), it has to have been some change in the local balance between the sources and sinks that affect O_2. A signal monitoring inputs to and outputs from the carbon cycle could miss that entirely. An earlier suggestion (*5*), that the evolution of animals that produced fecal pellets altered the balance in the photic zone by increasing the sinking rate of organic material and leaving more O_2 in surface waters, foundered. However, a brilliant recent analysis (*6*), well supported by organic-geochemical and microfossil evidence, shows how the convergent evolution of animals and larger algae would also have increased the sinking rate of organic material. Very possibly, this presents a robust solution to the O_2-driver problem.

References

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PALEONTOLOGY

Terminal Developments in Ediacaran Embryology

Fossils previously interpreted as the earliest evidence for animals represent a simpler level of eukaryotic organization.

N. J. Butterfield

Ever since Darwin there has been a disturbing void, both paleontological and psychological, at the base of the Phanerozoic eon. If his theory of gradualistic evolution be true, then surely the pre-Phanerozoic oceans must have swarmed with living animals—despite their conspicuous absence from the early fossil record. Thus, the 1998 report of fossilized animal embryos in the early Ediacaran Doushantuo Formation of South China (*1*) was met with almost palpable relief. It was indeed the fossil record that had let us down, not the textbooks, and certainly not the exciting new insights from molecular clocks. All was not as it seemed, however, and new data from Huldtgren *et al*. on page 1696 of this issue (*2*) look set to revoke the status of these most celebrated Ediacaran fossils.

Originally described as colonial green algae (*3*), the Doushantuo fossils were reinterpreted as animals based largely on the recognition of a developmental pattern involving serial cell division without accompanying size increase, a process known as palintomy (see the first figure). The comparison with early animal development was compelling enough to induce a flurry of follow-up studies, which yielded sightings of later-stage embryos and even adult metazoans (*4*). Such claims proved controversial, however, with particular concerns raised over the interpretation and biological origin of key diagnostic features (*5*).

In 2006 Hagadorn *et al*. (*6*) presented synchrotron-based tomographic evidence for nuclei within individual cells, although the

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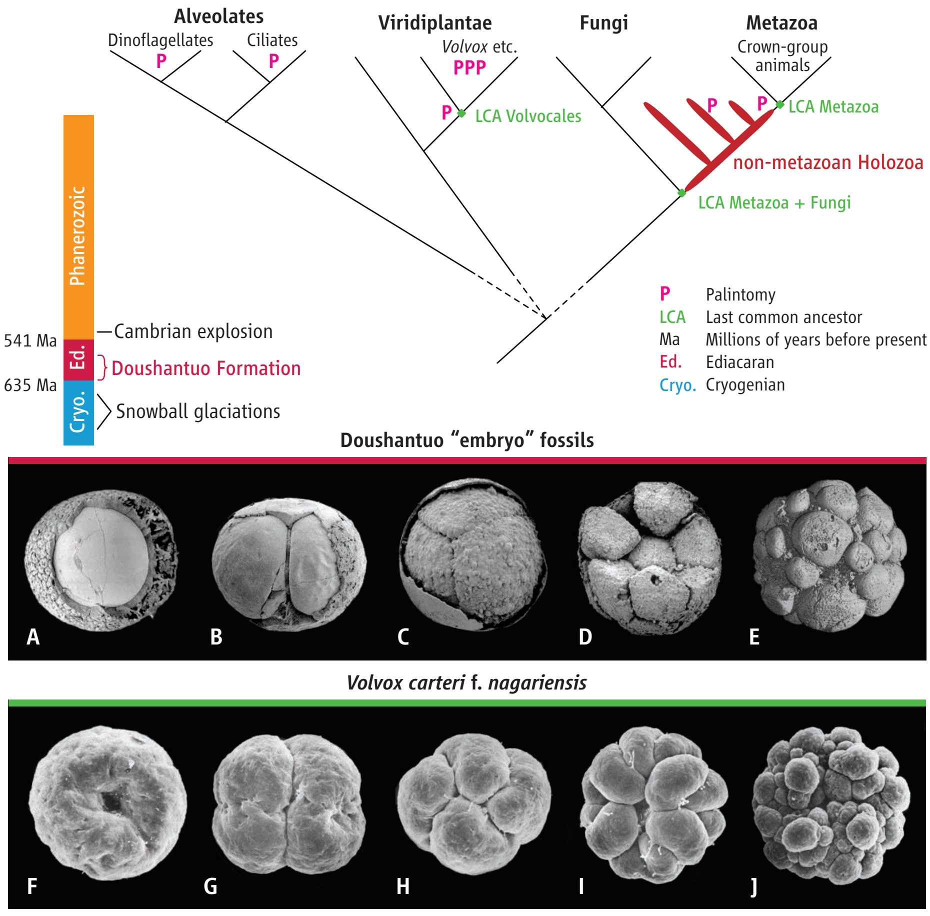

Palintomic cell division. "Embryo" fossils from the Doushantuo Formation of South China have been interpreted as the oldest known animal remains, but the key diagnostic feature—palintomic cell division—occurs widely within eukaryotes, including various "nonmetazoan holozoans" (*2*) and the volvocacean green algae. (**A** to **E**) "Embryo fossils" exhibiting serial palintomy (division without accompanying growth), beginning with a single large cell [the "embryo fossil" in (E) shows marked differences in cell sizes]. These specimens are all roughly 400 to 700 μm in diameter. (**F** to **J**) Palintomic cell division in asexual *Volvox carteri* f. *nagariensis*; note the appearance of reproductive gonidia beginning at the 64-cell stage (I). These specimens are all roughly 50 to 60 μm in diameter. The comparison between the fossils and modern *Volvox* is far from exact, but nonetheless reflects a similar grade of organization.