

# Earth's Early Atmosphere

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There is considerable evidence that before 2400 million years ago, oxygen was at best a minor component (less than 1%) of Earth's atmosphere. The subsequent onset of "red beds" (sediments with a red color from iron oxidation) and oxidized "paleosols" (soil horizons) and the disappearance of detrital pyrite, uraninite, and siderite have been attributed to the rise of oxygen (1, 2). But not all geologists accept this evidence. It has, for example, been argued that the oxygen content was at least 50% of the present atmospheric concentration throughout the last 4000 million years (3).

The recent discovery of mass-independent fractionation in the isotopic composition of sulfur in sedimentary iron sulfides (pyrite) and sulfates makes a change in the oxygen content of the atmosphere between 2400 to 2100 million years ago almost inevitable (4–7). The rate of chemical reactions usually depends on the mass of the atoms or molecules involved, and thus changes slightly for isotopically substituted but otherwise identical molecules. Only one natural process is known to produce mass-independent sulfur isotope effects: atmospheric photochemical reactions in the absence of ozone or oxygen, which shield the atmosphere from the ultraviolet (UV) radiation required for the reactions.

On page 2369 of this issue, Farquhar *et al.* (8) provide further evidence that the Archean atmosphere had, if anything, only traces of oxygen. They report mass-independent sulfur isotope variation in sulfide inclusions of diamonds from the Orapa kimberlite mine in Botswana. The material must have been transported by subduction from Earth's early atmosphere and hydrosphere into the mantle, where it has been sampled more recently in the form of diamonds brought to the surface by explosive volcanism.

Clues to the composition of the Archean ocean and atmosphere are provided by Habicht *et al.* on page 2372 (9). The authors estimate the sulfate concentration in Archean oceans on the basis of fractionation experiments on sulfate-reducing bacteria cultures. They conclude that methanogenic bacteria are the most likely

candidate for mineralization of organic matter during the Archean (3800 to 2500 million years ago). The global activity of these bacteria must have increased the methane content of the atmosphere substantially. At this time, Earth might have looked like Titan (see the figure), Saturn's largest moon, with its thick, hazy atmosphere consisting mostly of nitrogen (94%) and methane. The hazy color of Titan's atmosphere may originate from large organic molecules formed by photochemical processes, despite surface temperatures far below the melting point of water.

Mass-independent sulfur isotope fractionation can be produced experimentally by photodissociation of SO<sub>2</sub> with UV light of 190 to 220 nm (10). In this range, O<sub>2</sub> and ozone absorb strongly. A few percent of today's atmospheric oxygen concentration would be sufficient to eliminate UV light at these wavelengths from the lower atmosphere. The mass-independent sulfur isotope effects in Archean sulfides and sulfates thus provide evidence for an atmosphere containing at best traces of oxygen. It is inconsistent with models that assume the existence of a UV shield or of UV-labile greenhouse gases such as ammonia in the lower atmosphere early in Earth history (11).

The mass-independent sulfur isotope signature of the inclusions studied by Farquhar *et al.* furthermore provides compelling evidence that material from Earth's surface has been transported into the mantle. Mantle processes such as melting, crystallization, and hydrothermal processing all obey mass-dependent fractionation laws. Therefore, the data indicate that the diamonds did not form only by processes that are internal to the mantle, ending a long debate about their origin (12–14).

However, it is not just the mass-independent fractionation effects in sulfur that provide important information. Bacterial reduction of sulfate and sulfur causes

mass-dependent sulfur isotope fractionation. Present-day sedimentary sulfides are commonly depleted in <sup>34</sup>S by 45 to 70‰ compared with sulfate sulfur in ocean water. In contrast, Archean sedimentary pyrites before 2500 million years ago show much less depletion (~10‰).

It has been proposed that the limited <sup>34</sup>S depletion in Archean sedimentary pyrites is due to low sulfate concentration in Archean oceans (15, 16). Habicht *et al.* have investigated this question in a fractionation experiment on bacterial cultures. At high sulfate concentration, the sulfate-reducing bacteria fractionate sulfur isotopes by more than 30‰. Below about 200 μM sulfate, the fractionation is less than 10‰, as is typical for sedimentary pyrites before 2500 million years ago. The estimated sulfate content of ~200 μM is lower than previously thought by a factor of 5 and lower than today's sulfate concentration of the oceans by a factor of ~100.

Why is a low sulfate concentration of Archean oceans exciting? Standard models for the evolution of the Sun predict that 4500 million years ago, when Earth was newly formed, the Sun was 30% less luminous than

it is today. Therefore, the mean surface temperature during the Archean should have been below the freezing point of seawater (11, 17). It is, however, well known from the geological record that liquid water was present on Earth from at least 3500 million years ago.

This "faint young sun paradox" could be solved if the greenhouse effect was larger in the past. If sulfate was rare in Archean oceans, then sulfur-reducing bacteria cannot have contributed much to the mineralization of organic matter.

Organic matter must have been processed through another metabolism—such as ancient methanogenic bacteria, which would have produced substantial amounts of methane that would have partly accumulated in the atmosphere (18).

Even small amounts of methane in the atmosphere would have been sufficient to keep temperatures comfortable for early life, because methane is 23 times as efficient as carbon dioxide as a greenhouse gas. If Habicht *et al.* (9) are right, oxygen



**Distant relative?** On 12 November 1980, Voyager 1 recorded this view looking across the edge of Titan from a distance of about 22,000 km. Seen in false color, Titan's hazy atmosphere appears orange with further layers of blue haze suspended above. It may provide clues to Earth's early atmosphere and perhaps life-bearing chemistry. The Huygens probe on the Cassini spacecraft should provide further insights in 2005.

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may have left the most widely recognized imprint in the geological record, but the biogenic accumulation of methane in the Archean atmosphere may have been more important, protecting life from freezing.

The idea of a methane greenhouse is not new, but Habicht *et al.* (9) present the first model that is conclusive with respect to the residence time of methane in the atmosphere. Today, the residence time of methane is about 10 years, but in an Archean anoxic environment it might have been 10,000 years (19). This time scale requires a continuous supply of methane to keep the methane greenhouse going. Methanogenic bacteria could have provided a continuous flow of methane, building up a high methane concentration in the atmosphere as long as the ocean sulfate concentration remained low.

The studies of Habicht *et al.* (9) and Farquhar *et al.* (8) impose important constraints on the Archean sulfur cycle. The discovery of mass-independent sulfur isotope effects in sulfide inclusions makes an

oxygen-free atmosphere, flooded by UV light, a virtual certainty. Low sulfate concentration in the oceans seems to be essential for an early methane greenhouse.

However, to achieve a conclusive picture of the Archean environment, an independent proxy for atmospheric methane is needed. We must also improve our understanding of how the oxidation of the oceans relates to the rise of oxygen in the atmosphere. Iron and molybdenum isotopes may provide information about changing condition in the oceans. Another source of information may be the Cassini-Huygens mission (now on its way to Saturn), which will provide detailed insights into the composition of Titan's atmosphere. Titan could hold answers to Earth's evolution and may even provide tantalizing clues of life-bearing chemistry.

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#### PERSPECTIVES: HUMAN GENETICS

## Mapping Human History

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**T**he DNA of modern humans contains a record of the travels and encounters of our ancestors. The genotypes of people living today are the result of ancient human migrations, the continuous appearance of new mutations, selection by climate and infection for genetic alleles that conferred a survival advantage, and mating patterns determined by cultural norms. By sampling genotypes from people across the globe, geneticists have reconstructed the major features of our history: our ancient African origin, migrations out of Africa, movements and settlements throughout Eurasia and Oceania, and peopling of the Americas (1–5). As genomic technology has improved, these analyses of genotype have successively incorporated new markers: blood groups (2), protein polymorphisms (2), mitochondrial DNA sequences (1), Y chromosome haplotypes (3), and highly variable nuclear microsatellite markers (4, 5).

The most recent contribution to this literature is by Rosenberg *et al.* (6) on page 2381 of this issue. These investigators explored the genetic structure of human pop-

ulations using highly variable markers on the human autosomes of individuals from different parts of the world. The genotyped markers were microsatellite short tandem repeat sequences that do not encode any expressed genes and are generally selectively neutral. The populations studied were defined by geography, language, and culture, and participating individuals were well rooted in their populations, with several generations of ancestors known to have lived in the same locale as the participant. Genotypes from more than a thousand individuals were evaluated by a statistical method that defines clusters of people on the basis of genetic similarity at multiple loci, without using prior information about ancestry. In this method, individuals are assigned to clusters probabilistically (5, 7). Individuals may have significant probabilities of membership in more than one cluster due either to genetic similarities of groups or to ancestral intergroup matings. The world map (see the figure) illustrates variation at one microsatellite marker in 12 populations. This marker has four common alleles, each of which appears in all populations. Rare alleles are shared by fewer populations. Few alleles are unique to only one population. No allele is population specific.

Previous genetic analyses of human

history have consistently suggested that most human genetic variation is due to differences among individuals within populations rather than to differences among populations (4, 8). The Rosenberg *et al.* analysis of many more markers and many more people confirms this result: 93 to 95% of genetic variation is due to genetic differences among individuals who are members of the same population and only 3 to 5% of genetic variation is due to differences among the major population groups.

The power of the method lies in the construction of clusters on the basis of accumulated small differences in allele frequencies across many markers and many people. Statistical clustering of genotypes—composed of 4682 alleles from 377 markers in 1056 individuals from 52 populations—yields groups corresponding to major geographic regions of the world [see figure 1 in (6)]. Creation of two clusters reflects ancient human origins in Africa and rapid expansion throughout Eurasia, and migrations to the Americas from East Asia. Creation of five clusters yields groups corresponding to five major geographic regions of the world: Africa, Eurasia (Europe, the Middle East, Central and South Asia), East Asia, Oceania, and America. There is excellent agreement between membership of individuals in these clusters and their self-identified regions of origin. Similar results were obtained by the same statistical approach based on fewer populations and fewer markers [Table 2 of (5)].

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