

Oxygen origins

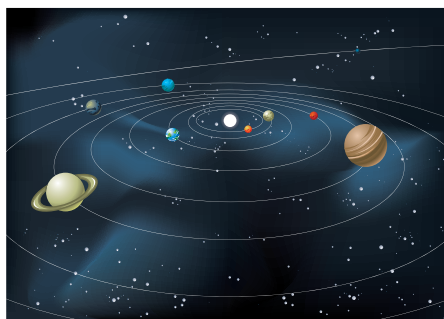
Oxygen has contributed to our understanding of the evolution of life on Earth by providing invaluable clues to geological processes — yet it still holds the key to some unsolved mysteries, as **Mark H. Thiemens** explains.

Long before oxygen bars made it cool, element number 8 was somewhat magical. In the nucleus, there exist levels that when filled provide additional nuclear stability beyond that expected from normal binding-energy considerations, much like the filled shells of the noble gases for electrons. These nuclear ‘magic numbers’ occur at proton or neutron numbers of 2, 8, 20, 28, 50, 82 and 126. Consequently, oxygen’s most common isotope ($^{16}\text{O}_8$), with its eight protons and eight neutrons, is ‘doubly magic’. This accounts for its abundance — it is the third most abundant element in the universe after hydrogen and helium.

During nucleosynthesis, in which protons and neutrons organize to form atom nuclei in stars, three ^4He nuclei combine to form ^{12}C — a two-step process, with two ^4He nuclei forming ^8Be that in turn fuses with the third ^4He . ^{12}C is subsequently converted into ^{16}O by further fusion with another helium nucleus.

Positioned at group 16 and period 2 in the periodic table, oxygen is an unusually reactive non-metallic atom that forms compounds with nearly all other elements. Its cosmic abundance combined with its chemical properties lead to its participation in a range of processes that build or protect planets (as part of silicate material or through the allotrope ozone, respectively) construct living organisms (in DNA, proteins, lipids and carbohydrates), as well as serving metabolic roles (photosynthesis and respiration). It is ubiquitous in the Earth’s crust, mantle, atmosphere and surface water, and biological reservoirs that are connected through oxygen transfer. Carbon dioxide — a dominant greenhouse gas — is a major agent of the transfer between these reservoirs.

Since its original discovery by Carl Wilhelm Scheele in Uppsala in 1773, and publication by Joseph Priestley two years later, oxygen has had a long and interesting history. Lavoisier played a major role in the identification of the process by which



©ISTOCKPHOTO.COM/IKLR

oxidation or combustion occurs — and provided oxygen with its name, borrowing Greek roots (*oxys* and *-genes*) to refer to it as ‘creator of acids’ because he thought all acids contained oxygen. Oxygen’s role throughout the history of civilization is extensive, from energy production (whether hydrological or as a general fuel oxidant) to agriculture and as a component of textiles and ceramics, as well as many drugs.

Going back further in time, oxygen is intimately associated with the origin and evolution of life. In the Precambrian era, atmospheric oxygen levels were significantly lower than now, probably less than 0.1% of the current ones — although it is still difficult to quantify this with precision. Using multi-isotope measurements of sulfur¹ these low oxygen levels were estimated to have occurred between about 3.8 and 2.7 billion years ago. Only a little later — 2.2–2.5 billion years ago — the ‘Great Oxygenation Event’² occurred and oxygen levels abruptly rose, largely owing to activities of cyanobacteria producing noticeable changes in the redox state and distribution of oxygen in minerals, such as the globally pervasive banded iron formations.

Measurements of oxygen isotopes (^{16}O , ^{17}O and ^{18}O) have been crucial in resolving natural processes. Stemming from work in the Urey laboratory in the 1950s^{3,4} analyses of oceanic biological carbonates have been used to quantify the temperature change of the oceans over geological timescales. Similarly, the role of marine and terrestrial organisms in global photosynthesis,

respiration and their change over time was deduced from measurements of atmospheric oxygen — which depend on the difference in the ^{18}O to ^{16}O ratio between air and water (the Dole effect).

Since 1973, we have known that the oldest objects in the solar system — the calcium- and aluminium-rich inclusions of ‘carbonaceous chondritic’ meteorites — possess a multiple oxygen isotope distribution that is inconsistent with conventional isotope effects⁵. Experiments a decade later suggested that this might be because of processes such as photochemical isotope self-shielding, or chemical reactions that depend on symmetry factors rather than the conventional mass effect, which can produce a similar anomalous isotopic distribution⁶. Recently, however, measurements of solar wind samples collected⁷ by the spacecraft Genesis — which may reflect the dominant reservoir of oxygen in the solar system — have shown that their isotopic distribution is not similar to that of meteorites.

This means that the oxygen isotopic distribution of the Sun may potentially not reflect the original distribution of the isotopic reservoir of meteorites and stony planets. Consequently, the nebular source of that original distribution, and how these celestial bodies went on to produce the current meteorites and planets, remain unresolved. □

MARK H. THIEMENS is at the Department of Chemistry and Biochemistry, University California San Diego, La Jolla, California 92093-0356, USA.
e-mail: mthiemens@ucsd.edu.

References

1. Farquhar, J., Bao, H. & Thiemens, M. H. *Science* **289**, 756–758 (2000).
2. Holland, H. D. *Geochim. Cosmochim. Acta* **66**, 3811–3826 (2002).
3. Urey, H. C., Lowenstaam, H. A. & McKinney, C. R. *Bull. Geol. Soc. Am.* **62**, 399–416 (1951).
4. Epstein, S., Buchsbaum, D., Lowenstaam, H. & Urey, H. C. *Bull. Geol. Soc. Am.* **62**, 417–426 (1951).
5. Clayton, R. N., Grossman, L. & Mayeda, T. K. *Science* **182**, 485–488 (1973).
6. Thiemens, M. H. & Heidenreich III, J. E. *Science* **219**, 1073–1075 (1983).
7. McKeegan, K. D. *et al. Science* **332**, 1528–1532 (2011).

