

The earliest memories of life on Earth

John M. Hayes

How old is life on Earth? Its chemical traces may have been recognized in rocks from Greenland that are more than 3.8 billion years old, at least 300 million years older than any previous evidence.

ITSQAQ is Greenlandic for 'ancient thing'. The Itsaq Gneiss Complex, a geological region in southern West Greenland, is indeed ancient¹. And, importantly, it contains the metamorphosed remains of the Earth's oldest-known sediments, providing evidence that there was something like an ocean 3.85 billion years (Gyr) ago. Until now it has seemed that these sediments might be relics of a prebiotic world, but the article on page 55 of this issue² may well remove that option. Specifically, new analyses of the traces of organic carbon present in the sediments change our estimates of its ¹³C/¹²C ratio. The new value is within the range characteristic of biological debris from sediments 2.7 to 3.5 Gyr old.

In modern oceans, both carbonates and organic molecules are derived from CO₂ through precipitation and photosynthesis. Isotopic effects associated with these reaction pathways lead to an isotopic difference, or fractionation, of about 25 parts per thousand, with the organic materials being depleted in ¹³C relative to the carbonates. A similar isotopic signal persists, with some variations³, back through time to rocks that are 3.5 Gyr old.

The new finding seems to extend that record to the very bottom of our planet's sedimentary pile, crucially altering earlier views of these oldest sediments and leaving almost no time between the end of the 'late heavy bombardment' of bodies within the inner Solar System by giant meteorites and the first appearance of life. Two earlier papers published in this journal^{4,5} conclude that these asteroid impacts might have sterilized the planet as recently as 3.8 Gyr ago. It could follow that the 3.85-Gyr-old Itsaq organic material derives from biochemical processes that developed with breathing rapidly after the last large impact, or even that it is a product of a biota that was wiped out, then supplanted by our ancestors. Can this all be true?

Isotopic fractionations result from physical phenomena associated with chemical reactions. The task now is to determine whether the observed fractionations are due to biochemical processes, other low-temperature chemical reactions, or some post-depositional effect. The magnitude of the observed fractionations favours the biochemical alternative.

but does not fit perfectly. About half of the new analyses indicate fractionations larger than any in the next-oldest organic material, found in Australian rocks about 3.5 Gyr old, which also contain bacterium-like bodies and laminated sedimentary structures that resemble algal mats. These features are not considered a sure sign of life, but the carbon-isotope differences are roughly equal to those in

All previous analyses of such ancient materials have dealt only with bulk organic carbon, which shows all too well the hazards of an early birth. Any sediment that sits around for long is likely to be buried by still further sedimentation and then dragged into the crust's tectonic traffic. The Itsaq rocks were churned downwards within a billion years and heated to 500 °C at pressures of 5,000 at-



A chip off the old block. A geologist's hammer leans against the oldest-known sediments in the world, on the bleak Akilia island off the Greenland coast. Despite metamorphism, they show signs of ancient life.

still younger rocks that have compelling evidence for biology, so many investigators have proposed that life was present 3.5 Gyr ago and that it was controlling the redox chemistry of carbon at Earth's surface.

The new Itsaq data were gathered using an ion-microprobe mass spectrometer that can selectively analyse features as small as 20 μm. That selectivity has been used to examine carbon occluded in apatite grains (see Fig. 1 on page 56). Apatite, a phosphate mineral, is known for its biological associations, but there have been no previous measurements of the isotopic composition of organic carbon closely associated with it. Interpretations of the new data may evolve as points of comparison become available. Although the age of the samples and the tantalizing results command interest and prominent publication, the novelty should also inspire caution.

mospheres. From the point of view of anyone seeking to reconstruct details of their initial, low-temperature environment, they've been badly overcooked. Although some previously analysed samples contain as much as 2.5 per cent carbon⁶, it looked more like graphite than biological debris.

During graphitization, mobile chemical products wheeze or ooze from the geological pressure cooker wherever a vent can be found. If carbonate minerals are present, their carbon is thrown into the chemical m^êl^ée. In the process, isotopic evidence is first altered (as some carbon depleted in ¹³C is lost) then destroyed (as the residue exchanges carbon with metamorphic fluids^{7,8}). For this reason, results of earlier analyses of the Itsaq materials were set aside as they were received, because they showed the damage done by graphitization. When the authors examined bulk rather than apatite-

associated carbon, their results agreed with those of previous analyses.

What is missing is an understanding of why the apatite should act as a safe-deposit vault. Until that is known, other questions will claim attention. First, why are the $^{13}\text{C}/^{12}\text{C}$ ratios so variable and, in half of the cases, so low? Biological fractionation is usually very consistent, and ratios like those in the lower half of the present distribution do not appear for more than a billion years, when they are thought to be produced by methane-consuming bacteria. These organisms require oxygen, which fits well with other indicators of increasing oxygenation 2.7 Gyr ago, but not 3.85 Gyr ago. Second, is there a plausible non-biological cause for the fractionation, either an isotope effect associated with one of the infinite number of uninvestigated prebiotic chemical reactions, or some obscure post-depositional effect peculiar to microscopic inclusions in apatite? These are worries and long-shots. It's most likely that the new results are indeed evidence for life 3.85 billion years ago.

The use of an ion microprobe to measure carbon isotopes is new. The probe works by firing caesium-ion bullets into a polished chip to break up crystals and molecules at its surface. Negative ions (C^- in this case) are extracted and accelerated, and the isotopes are electromagnetically separated by a mass spectrometer. It is assumed that any instrumental effects biasing the ratio observed from the thin films of carbon within the mineral matrices can be removed by comparison with a reference sample of pure graphite. Tests indicating consistency with results of conventional analyses are impressive, but more documentation of the probe's suitability for carbon-isotope analyses will be welcomed. As soon as that is available, curators of collections of martian meteorites and of ancient microfossils should start getting in line. □

John M. Hayes is at the Woods Hole Oceanographic Institution, MS8, 360 Woods Hole Road, Woods Hole, Massachusetts 02543-1539, USA.

1. Nutman, A. P., McGregor, V. R., Friend, C. L. R., Bennett, V. C. & Kinny, P. D. *Precamb. Res.* **78**, 1–39 (1996).
2. Mojzsis, S. J. et al. *Nature* **384**, 55–59 (1996).
3. Hayes, J. M. in *Early Life on Earth* (ed. Bengtson, S.) 220–236 (Columbia Univ. Press, New York, 1994).
4. Maher, K. A. & Stevenson, D. J. *Nature* **331**, 612–614 (1988).
5. Sleep, N. H., Zahnle, K. J., Kasting, J. F. & Morowitz, H. J. *Nature* **342**, 139–142 (1989).
6. Hayes, J. M., Kaplan, I. R. & Wedeking, K. W. in *The Earth's Earliest Biosphere: Its Origin and Evolution* (ed. Schopf, J. W.) 93–134 (Princeton Univ. Press, 1983).
7. Wedeking, K. W. & Hayes, J. M. in *Advances in Organic Geochemistry* (ed. Bjoroy, M.) 546–553 (Wiley, New York, 1983).
8. Schidlowski, M. & Aharon, P. in *Early Organic Evolution* (eds Schidlowski, M., Golubic, S., Kimberley, M. M., McKirdy, D. M. & Trudinger, P. A.) 147–175 (Springer, Berlin, 1992).

X-ray lenses near reality

Jerome Hastings

X-RAY sources have already evolved from the original sealed vacuum tubes into sophisticated electron-storage rings, and free-electron X-ray lasers may be just beyond the horizon. These advances promise intense, highly parallel and tunable photon beams. To focus and manipulate this radiation, a variety of X-ray optical devices have been developed, ranging from concentrators, in the form of tapered capillaries¹, to Fresnel zone plates². But a dream of X-ray opticians for some time has been to make a *refractive*

beams prohibits such applications.

The existing optics fall into a few categories: reflecting optics such as grazing-incidence X-ray mirrors; tapered capillaries; and various types of Fresnel zone plates. Refractive lenses, routinely used in visible-light optics, had been thought to be impractical at X-ray wavelengths. In the X-ray regime, the difference in the index of refraction between air and ordinary materials is tiny — typically of the order of 10^{-6} — which appeared to present an insurmountable problem. To maximize the effect, heavy-element materials were proposed, but they have high absorption. Light elements do not, but with their low refractive-index decrement they would have long focal length and thus provide little practical focusing of the X-ray source.



The European Synchrotron Radiation Facility in Grenoble, France. Compound refractive lenses may soon make its intense X-ray beams much more effective.

lens, the X-ray equivalent of conventional optics for visible light. On page 49 of this issue³, Anatoly Snigirev and colleagues describe the first significant step towards that goal. This should allow us to reach a submicrometre focus with much greater efficiency than before.

The desire in a multitude of scientific disciplines for intense submicrometre X-ray beams has driven the construction of new electron-storage-ring X-ray sources in Europe (the European Synchrotron Radiation Facility in Grenoble, France), the United States (the Advanced Photon Source in Argonne, Illinois) and Japan (the Spring-8 Project in Harima). The objective is to perform the various 'standard' X-ray analytical techniques of diffraction and spectroscopy on individual particles or grains.

These measurements could provide information about the atomic and electronic structure of systems of chemical, biological and technological interest, ranging from the characterization of an individual grain in a commercial catalyst to measuring the strain in the metallic interconnections of large integrated circuits. But the limited ability of available X-ray optics to focus the X-ray

Snigirev and colleagues³ have now proposed and demonstrated a compound refractive lens for hard (14 keV) X-rays that overcomes the difficulties of earlier schemes. A series of N refractive lenses has a focal length shorter than a single lens by a factor of N , and, in aluminium, absorption is slight for X-ray wavelengths below one ångström, so a series of tens to hundreds of lenses can be used. The authors made their lens by simply drilling small round holes in an aluminium block (see Figs 1 and 3 on pages 49 and 50, respectively).

This 'crude' technology permitted a demonstration of their ideas and showed the potential for future optics. With more sophisticated fabrication techniques, one can imagine extending these lenses from cylinders to spheres to provide focusing in two dimensions. Such lenses should then be commonplace at synchrotron sources, and the full potential of the X-ray beams already available will be realized. This development bodes well for the future of synchrotron-based microanalytical techniques that are impossible today but should be standard in the future. □

Jerome Hastings is at the Brookhaven National Laboratory, 75 Brookhaven Avenue, Building 725, Upton, New York 11973, USA.

1. Bilderback, D. H. & Thiel, D. J. *Rev. Sci. Instrum.* **66**, 2059–2063 (1995).
2. Lai, B. et al. *Rev. Sci. Instrum.* **66**, 2287–2289 (1995).
3. Snigirev, A., Kohn, V., Snigireva, I. & Lengeler, B. *Nature* **384**, 49–51 (1996).