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GEOCHEMISTRY

Sulphur from heaven and hell

Fingerprints of sulphur isotopes in rocks from the ridge beneath the Atlantic Ocean suggest that a substantial fraction of sulphur at Earth's surface is left over from the formation of the planet's core. SEE LETTER P.208

NICOLAS DAUPHAS

The relative abundances and isotopic signatures of sulphur found in rocks exhumed from Earth's mantle act as fingerprints of how and where our planet acquired its complement of this biochemically important element. Textbooks say that Earth's sulphur has the same isotopic composition as chondrites, a type of meteorite that is thought to best represent the building blocks of terrestrial planets. With dashes of audacity and insight, Labidi and co-workers[1] question this assumption in a paper on page 208 of this issue. They report measurements of rocks derived from Earth's mantle that reveal isotopic patterns unlike any others previously reported, with implications for how the planet formed*.

Most of us take Earth's chemical composition for granted, but unique circumstances may have been at play in delivering the right mix of elements for life to develop and flourish. For example, this is true of the noble metals needed in the electronic devices used to print or display this page. It is also true of sulphur, which is found in the amino acids cysteine and methionine and represents around 0.2% of our body weight. These elements and a few others

*This article and the paper under discussion[1] were published online on 4 September 2013.

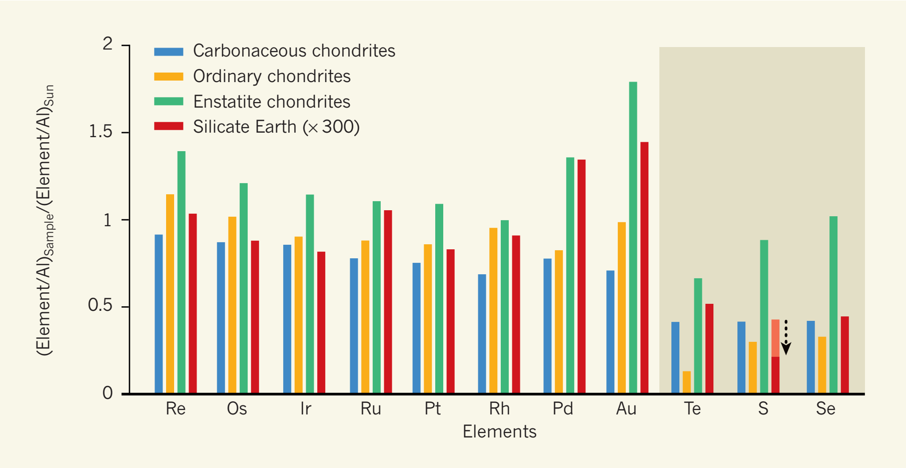

Figure 1 | Abundances of elements in Earth's mantle and in chondritic meteorites. The elements shown have strong affinities with metallic iron[9,11,12] and are in order of increasing volatility. Shaded region indicates elements that are not noble metals. Data are normalized to the abundance of aluminium (Al), because this element was neither lost to space during Earth's accretion nor scavenged by metallic iron during core formation. The data are also normalized to solar abundances to prevent them from spanning many orders of magnitude. The 'silicate Earth' pattern shows abundances in the mantle, and has been multiplied by a factor of 300 to allow easy comparison with the chondrite data. The depicted elements are thought to have segregated into Earth's core as the planet formed, but were subsequently replenished in the mantle by the accretion of chondritic material — which is why these elements are found in proportions similar to those of chondrites. However, Labidi *et al.*[1] suggest that about half or more of the sulphur in Earth's mantle may be left over from core formation (black arrow), with the remainder coming from chondrites; the upper part (light red) for sulphur represents the total abundance of the element in the mantle, and the lower part indicates the abundance left over from core formation.

have strong affinities for metallic iron — so much so that when Earth's metallic, iron-rich core formed, it scavenged all these elements, leaving behind a rocky mantle barren of sulphur, selenium, tellurium and noble metals. The prevailing view regarding the origin of these elements is that they were replenished in the mantle by a rain of asteroids from the heavens, known as the late veneer[2–5]. This late accretion of meteoritic material may also have delivered a fraction of the elements needed for life (hydrogen, carbon and nitrogen), as well as prebiotic organic molecules that could have served as the seeds for life.

The late-veneer hypothesis for the origin of Earth's sulphur is supported by strong observational evidence. First, laboratory experiments to reproduce the conditions of core–mantle segregation indicate that sulphur, selenium, tellurium and the noble metals are efficiently scavenged into metallic iron. Second, these elements are present in the mantle in proportions similar to those found in chondrites (Fig. 1). And third, the isotopic composition of sulphur in mantle rocks is identical to that of chondrites[6,7]. It is this third point that Labidi *et al.* call into question. They find that the ratio of sulphur-34 to sulphur-32 in Earth's mantle is 0.13% lower than that of chondrites.

To arrive at this conclusion, the authors used an analytical technique that provides a more complete recovery of sulphur from rock samples than has previously been possible. The difference in sulphur isotopic ratios that they infer between Earth's mantle and meteorites corresponds approximately to the difference measured in laboratory experiments when sulphur is partitioned between (core-like) metal and (mantle-like) silicate. An appealing possibility is therefore that a large fraction (maybe half or more) of the sulphur in Earth's mantle originated in the bowels of the Earth — that is, it is left over from core formation. If correct, there is no need to invoke unique circumstances to explain the presence of sulphur at Earth's surface. Furthermore, this element should be ubiquitous in Earth-like planets, raising the possibility of one day detecting sulphur-bearing molecules in the atmospheres of such extrasolar planets.

A difficulty with a dynamically active planet such as Earth is that geological processes, for example partial melting of the interior to form magmas and recycling of surface rocks into the interior at subduction zones, can blur isotopic signals and complicate interpretations. For instance, Labidi and co-workers identify the isotopic signatures of two distinct sulphur-containing components in rocks formed by melting of the mantle. One has a sulphur-isotope composition distinct from that of chondrites, which they interpret to be representative of the mantle. The other has a sulphur-isotope composition similar to that of chondrites, but the authors ascribe it to recycling of sulphur from sediments. This interpretation is reasonable, but a question lingers as to whether or not these components are representative of their mantle sources. During magma formation and extraction from the mantle, considerable amounts of sulphide minerals can remain behind at the magma's source, potentially affecting the sulphur isotopic ratios of magma-derived rocks[8]. Labidi *et al.* argue against this interpretation of their results, but insufficient experimental data are available on sulphur-isotope partitioning between sulphide and silicate melts to definitely rule out this possibility.

The relative abundances of selenium, sulphur and tellurium in the mantle have been used to gain insight into the nature of the late veneer[9]. These relative abundances best match the composition of carbonaceous chondrites (Fig. 1), suggesting that Earth received a late veneer of material rich in volatile compounds and organic molecules. Other isotopic evidence[10] suggests that the nature of the meteoritic material accreted by Earth was not very different before and after the completion of core formation. If Labidi and colleagues are correct and a substantial fraction of sulphur in the mantle is left over from core formation, this undermines the argument for a volatile-rich later veneer.

However, one is left wondering whether the good match between the selenium/sulphur and tellurium/sulphur ratios of chondrites and those of Earth can be coincidental. Labidi and co-workers' measurements are of the highest quality and will endure, but the same can be said of another study[9], published earlier this year, the conclusions of which contradict the present findings. The questions raised by these two conflicting studies will undoubtedly stimulate further discussion and experiments. ■

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NATURE

50 Years Ago

Prof. L. Egyed has recently summarized a number of hypotheses concerning the expansion of the Earth, and has suggested that the Earth's radius is expanding at a rate of 0.5–1.0 mm per year. There appears to be a remarkably close agreement between the rate of increase of the Earth's radius and that of the universe according to Hubble's law. Using the at present accepted value for Hubble's constant, $H = 100$ km/s/megaparsec, which is 1.65×10^{-4} mm per year per mile, and substituting the value of the Earth's radius in the Hubble equation, $v = RH$, we obtain a radial expansion for the Earth of 0.66 mm per year. While this agreement may be fortuitous it may suggest a fundamental concordance between expansion processes in the Earth's core and those responsible for the expansion of the universe.
From *Nature* 14 September 1963

100 Years Ago

In a paper on the psychology of insects, read before the General Malarial Committee at Madras in November, 1912, Prof. Howlett, after giving an account of experiments carried out by him on the response of insects to stimuli, comes to the conclusion that insects are to be regarded "not as intelligent beings consciously shaping a path through life, but as being in a sort of active hypnotic trance." It is claimed that this view of insect-psychology opens up great possibilities in the study of insect carriers of disease, since "it is no intelligent foe we have to fight, but a mere battalion of somnambulists." If we discover the stimuli or particular conditions which determine the actions of an insect, we can apply them to its undoing.
From *Nature* 11 September 1913