

Non-chondritic sulphur isotope composition of the terrestrial mantle

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Core-mantle differentiation is the largest event experienced by a growing planet during its early history. Terrestrial core segregation imprinted the residual mantle composition by scavenging siderophile (iron-loving) elements such as tungsten, cobalt and sulphur. Cosmochemical constraints suggest that about 97% of Earth's sulphur should at present reside in the core¹, which implies that the residual silicate mantle should exhibit fractionated $^{34}\text{S}/^{32}\text{S}$ ratios according to the relevant metal-silicate partition coefficients², together with fractionated siderophile element abundances. However, Earth's mantle has long been thought to be both homogeneous and chondritic for $^{34}\text{S}/^{32}\text{S}$, similar to Canyon Diablo troilite^{3–6}, as it is for most siderophile elements. This belief was consistent with a mantle sulphur budget dominated by late-accreted chondritic components. Here we show that the mantle, as sampled by mid-ocean ridge basalts from the south Atlantic ridge, displays heterogeneous $^{34}\text{S}/^{32}\text{S}$ ratios, directly correlated to the strontium and neodymium isotope ratios $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$. These isotope trends are compatible with binary mixing between a low- $^{34}\text{S}/^{32}\text{S}$ ambient mantle and a high- $^{34}\text{S}/^{32}\text{S}$ recycled component that we infer to be subducted sediments. The depleted end-member is characterized by a significantly negative $\delta^{34}\text{S}$ of $-1.28 \pm 0.33\text{‰}$ that cannot reach a chondritic value even when surface sulphur (from continents, altered oceanic crust, sediments and oceans) is added. Such a non-chondritic $^{34}\text{S}/^{32}\text{S}$ ratio for the silicate Earth could be accounted for by a core-mantle differentiation record in which the core has a $^{34}\text{S}/^{32}\text{S}$ ratio slightly higher than that of chondrites ($\delta^{34}\text{S} = +0.07\text{‰}$). Despite evidence for late-vein addition of siderophile elements (and therefore sulphur) after core formation, our results imply that the mantle sulphur budget retains fingerprints of core-mantle differentiation.

Earlier reports of mid-ocean ridge basalts (MORBs) $\delta^{34}\text{S}$ (where $\delta^{34}\text{S} = [(^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{CDT}} - 1] \times 1,000$ and CDT is Canyon Diablo troilite) yielded values statistically indistinguishable from the reported chondrite average of $0.04 \pm 0.31\text{‰}$ (refs 3–6), consistent with a late-vein origin for sulphur in the mantle. This view has been recently questioned in a study using improved sulphur-extraction techniques⁷. Worldwide MORBs exhibit exclusively negative $\delta^{34}\text{S}$ ranging down to -1.9‰ , with an approximately 2‰ variability⁷. These observations raise questions as to whether the terrestrial mantle is chondritic in sulphur isotopes, but the mechanisms controlling MORB $^{34}\text{S}/^{32}\text{S}$ variability remain unclear.

To address these issues, we investigated the sulphur isotope composition of 23 glasses dredged on the South Atlantic ridge between 40° and 55° S. Previous radiogenic isotopes^{8–10}, noble gases^{11,12}, volatiles¹³, major-element¹⁴ and trace-element¹⁵ measurements on these basalts illustrate interactions of the Shona-Discovery hotspots with the ridge. Several of the typical mantle end-members feed the mantle source of the two plumes, including HIMU ('high- μ ' where $\mu = ^{238}\text{U}/^{204}\text{Pb}$), LOMU ('low- μ '), and enriched-mantle components. The samples analysed were chosen to reflect this geochemical variability and thus offer an opportunity to address $^{34}\text{S}/^{32}\text{S}$ variations with respect to these mantle heterogeneities.

In our samples, sulphur occurs only in its reduced form, as commonly found in MORBs^{16–18}, and the sulphur content, from 642 to 1,388 parts per million (p.p.m.), correlates with the FeO content (Supplementary Fig. 3A), illustrating magmatic sulphide saturation¹⁶. The eruption depth of our samples precludes any significant sulphur degassing¹⁹, restricting the sulphur isotope discussion to primary magmatic considerations. $\delta^{34}\text{S}$ varies between -1.80‰ and $+1.05\text{‰}$, whereas both the quantifying mass-independent signatures $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (where $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1,000 \times [(\delta^{34}\text{S}/1,000 + 1)^{0.515} - 1]$ and $\Delta^{36}\text{S} = \delta^{36}\text{S} - 1,000 \times [(\delta^{34}\text{S}/1,000 + 1)^{1.889} - 1]$), are homogeneous and equal within uncertainty to those of Canyon Diablo troilite (Supplementary Table 1). Besides, $\delta^{34}\text{S}$ is remarkably correlated to source enrichment proxies such as $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 1). Seawater sulphate ($\delta^{34}\text{S} = +21\text{‰}$) assimilation by erupted basalts could result in an increase in $\delta^{34}\text{S}$; it would, however, scatter or erase any correlations between $\delta^{34}\text{S}$ and tracers that remain insensitive to seawater incorporation (such as $^{143}\text{Nd}/^{144}\text{Nd}$). It would also result in a relationship between $\delta^{34}\text{S}$ and proxies of seawater incorporation such as chlorine contents or Cl/K ratios, which is again not the case (Supplementary Fig. 4). Correlated $\delta^{34}\text{S}$ and radiogenic isotope enrichments thus reflect the variability of the MORB sources.

All the samples are saturated with immiscible sulphide¹⁶, and the extremely low osmium contents in the most primitive MORBs probably indicates that they were already sulphide-saturated during melting¹⁰. Such a saturation mechanism prevents us from constraining the sulphur contents of the mantle source, and because the fractionation factor between dissolved sulphur and magmatic sulphide might be significant, it raises the question of whether basalts can preserve the $^{34}\text{S}/^{32}\text{S}$ ratios of their mantle source. Those basalts investigated have such distinct differentiation and melting histories^{14,15} that the amount of sulphide left during both melting and differentiation is variable^{10,16}. If the high-temperature sulphur isotope fractionation during magmatic sulphide exsolution were significant, it would have erased the observed $\delta^{34}\text{S}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ trends (Fig. 1). The lack of correlation between $\delta^{34}\text{S}$ and sulphide segregation proxies indicates a fractionation factor, $\alpha_{\text{sulph-melt}}$, of between 1.0000 and 0.9995 ± 0.0005 , at most (Supplementary Information). The $\delta^{34}\text{S}$ of basalts hence provides direct information on mantle source composition, here displaying an average value of $-0.80 \pm 0.58\text{‰}$ (1σ).

The most ^{34}S -depleted samples correspond to depleted MORB and ^{34}S -enriched samples are related to the Discovery plume, whereas the Shona and LOMU basalts are of intermediate composition. Interestingly, samples from Shona and Discovery display similar $^3\text{He}/^4\text{He}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ (refs 11 and 12) but have different ^{34}S enrichments, suggesting that these isotopic systems are decoupled. Such a lack of correlation between noble gases and S isotopes suggests that the primitive mantle is sulphur-poor compared to the recycled components. Hence, characterization of the primordial sulphur cannot be directly achieved from the present data set.

Our results can be explored in two ways. First, the south Atlantic depleted mantle has an average $\delta^{34}\text{S}$ of $-1.28 \pm 0.33\text{‰}$ (error is 1σ ,

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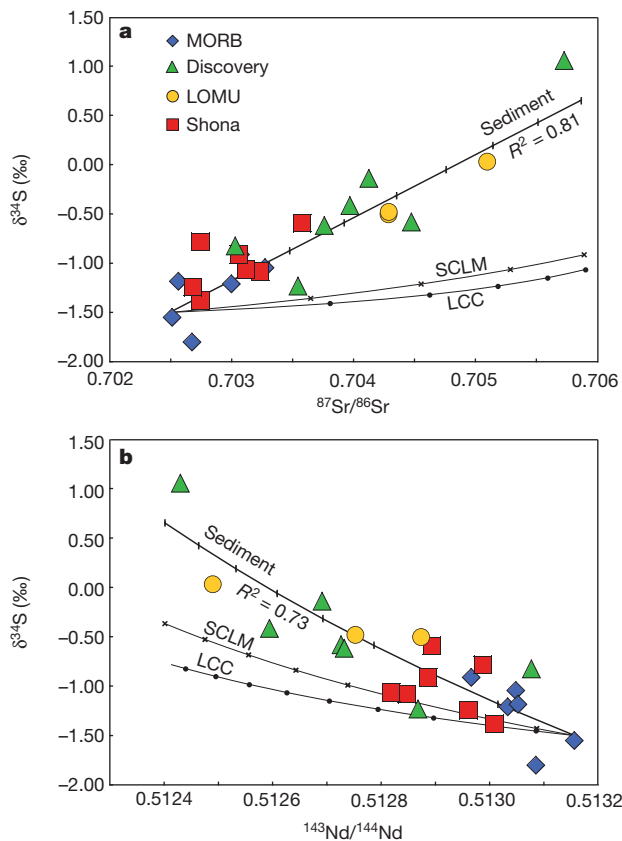


Figure 1 | $\delta^{34}\text{S}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$. Strontium and neodymium isotope data are from ref. 8. Sulphur-isotope uncertainties are estimated on the basis of replicate analysis for all samples, and are all within symbol sizes. The samples define a binary mixing relationship between a depleted-mantle and an enriched-mantle endmember. Mixing trends with sub-continental lithospheric mantle (SCLM) and lower continental crust (LCC) are also shown, illustrating that mixing with sediments account better for the geochemical composition of our samples. **a**, $\delta^{34}\text{S}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$. **b**, $\delta^{34}\text{S}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$. $\delta^{34}\text{S}$ is defined in the main text; the CDT standard is used. R , correlation coefficient. Data used for the mixing calculation is as follows, from refs 22–27 and Supplementary ref. 37. For depleted mantle, $\delta^{34}\text{S} = -1.5\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7025$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.513156$, $\text{Sr} = 11.3$ p.p.m., $\text{Nd} = 1.12$ p.p.m. and $\text{S} = 200$ p.p.m. For LCC, $\delta^{34}\text{S} = +3\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7080$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.511600$, $\text{Sr} = 348$ p.p.m., $\text{Nd} = 11$ p.p.m. and $\text{S} = 408$ p.p.m. For SCLM, $\delta^{34}\text{S} = +3\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7100$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.511663$, $\text{Sr} = 49$ p.p.m., $\text{Nd} = 2.67$ p.p.m. and $\text{S} = 157$ p.p.m. For the sediment, $\delta^{34}\text{S} = +10\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7203$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.511170$, $\text{Sr} = 327$ p.p.m., $\text{Nd} = 27$ p.p.m. and $\text{S} = 5,700$ p.p.m. Markers on the fits are separated by 0.1%, 1.0% and 4.0% for sediment, LCC and SCLM, respectively.

$n = 6$), defining a mean value consistently distinct from chondrites. We note that an extrapolation of Sr–Nd–S isotope trends to most depleted compositions would lead to a depleted-mantle endmember as low as -1.80‰ (Fig. 1). Second, the nature of classical mantle endmembers can be addressed. Whereas it is commonly accepted that HIMU features reflect the occurrence of subducted oceanic crust in plume sources²⁰, the enriched-mantle and LOMU cases remain much debated. In the south Atlantic mantle, a significant contribution of continental material has been invoked to account for the LOMU endmember, including either delaminated subcontinental lithospheric mantle^{8,9} or lower continental crust¹⁰. In S–Sr and S–Nd isotope spaces, however, the samples lie on a linear trend regardless of their locations or type of anomalies (Fig. 1), highlighting binary mixing between depleted mantle ($\delta^{34}\text{S} = -1.28\text{‰}$ or lower) and the enriched-mantle-type endmember ($\delta^{34}\text{S} = +1.05\text{‰}$ or higher).

Both LOMU basalts (having the lowest $^{206}\text{Pb}/^{204}\text{Pb}$) and Shona samples (HIMU-type⁸, having the highest $^{206}\text{Pb}/^{204}\text{Pb}$) cannot be distinguished from the other samples in the observed trends (Fig. 1). This

lack of correlation between $\delta^{34}\text{S}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ (Supplementary Fig. 5), together with the preservation of the trends between $\delta^{34}\text{S}$ and Sr–Nd isotopes, argue in favour of relatively sulphur-poor HIMU and LOMU endmembers, overprinted by the contribution of a sulphur-rich enriched-mantle component. In this view, recycled oceanic crust carrying the radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is inferred to be relatively sulphur-depleted, consistent with its required high U/Pb. Sulphides are indeed the main Pb carrier in the oceanic crust²¹ and any Pb loss along subduction should occur through a concomitant sulphur loss.

The mixing trends being linear, the enriched-mantle component must be enriched in sulphur in the same way as it is enriched in strontium and neodymium. This allows a reliable estimate of its S/Sr and S/Nd, broadly equal to that of the depleted mantle. For simplicity, only the S/Sr ratio is used in the following. Taking 200 ± 40 p.p.m. (ref. 22) for sulphur and 11.3 p.p.m. (ref. 15) for strontium in depleted mantle, we obtain an S/Sr value for enriched mantle of 17 ± 4 . Both delaminated lithospheric mantle and lower continental crust have been suggested to account for enriched-mantle-type signals, especially in south Atlantic basalts^{8–10}. These reservoirs are, however, relatively sulphur-poor compared to incompatible trace elements, yielding S/Sr ratios of 3.2 ± 2.0 (ref. 23) and 0.8 ± 0.3 (ref. 24), respectively, that are low compared to the required value of 17 ± 4 (see above). Any occurrence of such a component in the south Atlantic mantle would have led to highly curved mixing relationships in S–Sr isotope space, especially given the range of $^{87}\text{Sr}/^{86}\text{Sr}$ displayed by the samples (Fig. 1a).

Alternatively, sediment may be a good candidate: sediments are enriched in trace elements²⁵ and can bear significant amounts of sulphur. In particular, many sediments deposited one to two billion years ago during the Proterozoic eon formed under reduced conditions and usually contain more than 1% of sulphur pyrite²⁶. A subducted sediment containing a realistic sulphur content of $5,700 \pm 1,000$ p.p.m. would satisfy the S/Sr of the enriched-mantle component. The fact that our estimate for recycled sediment falls within large uncertainties of non-subducted sediments suggests only moderate devolatilization, if any, during recycling (Supplementary Information). The best fits to our data are obtained for sediment having a $\delta^{34}\text{S}$ of $+10 \pm 3\text{‰}$, consistent with sediments one to two billion years old with an average $\delta^{34}\text{S}$ of $+5 \pm 10\text{‰}$ (ref. 27). This Proterozoic age for subducted sediments is also consistent with the observed lack of $\Delta^{33}\text{S}$ variability²⁸ best-fitted with a $\Delta^{33}\text{S}$ of $+0.06 \pm 0.03\text{‰}$ (Supplementary Fig. 6).

If subducted sediments are major ^{34}S carriers to the deep mantle, the depleted mantle is shown here to be significantly ^{34}S -depleted with respect to chondrites. This low $^{34}\text{S}/^{32}\text{S}$ ratio has fundamental implications for our understanding of the origin and processes affecting moderately volatile elements in the terrestrial mantle. In the following, we use the $-1.28 \pm 0.33\text{‰}$ depleted MORB average as the representative $\delta^{34}\text{S}$ of the depleted mantle, but further studies are needed to refine this value. Such a negative estimate allows us to discard a purely late-vein origin for sulphur in the mantle, because this scenario requires a strictly chondritic $^{34}\text{S}/^{32}\text{S}$ ratio for depleted mantle. According to the kinetic theory of gases, partial evaporation of sulphur during accretion could have modified the $^{34}\text{S}/^{32}\text{S}$ ratio of the accreted Earth, leaving the residual terrestrial mantle enriched in ^{34}S relative to chondrites. This would be at odds with the observed depletion in ^{34}S . Finally, assuming that the depleted mantle represents 25%–80% of the whole mantle²⁹, the complementary surface reservoirs (continents, oceans and altered oceanic crust) would need to have an average $\delta^{34}\text{S}$ of between $+8\text{‰}$ and $+25\text{‰}$ to balance the non-chondritic $\delta^{34}\text{S}$ of the depleted mantle. Current estimates, however, yield average $\delta^{34}\text{S}$ values of $-0.4 \pm 3.0\text{‰}$ (ref. 30) for the bulk surface reservoirs, a value that is far from being reconcilable with the above requirement, and emphasizing the non-chondritic character of the bulk silicate Earth.

In contrast to immiscible sulphide exsolution, sulphur dissolution into metal from silicate could fractionate the $^{34}\text{S}/^{32}\text{S}$ ratio owing to the distinct molecular environment of sulphur in a silicate versus a metallic liquid (and distinct vibrational partition functions). One likely possibility

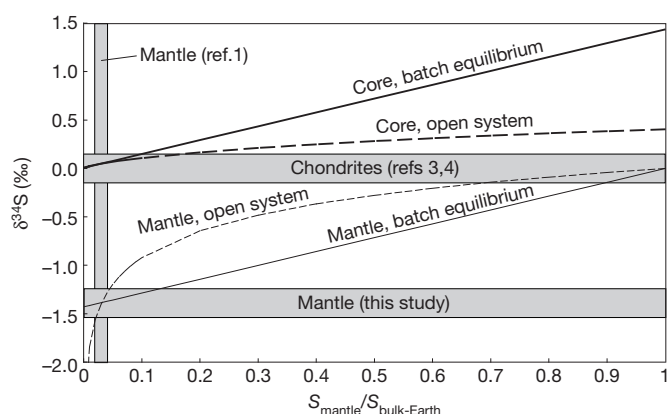


Figure 2 | Core-mantle sulphur partitioning model in batch equilibrium or open system. The $\delta^{34}\text{S}$ of the mantle is plotted against the sulphur content of the mantle S_{mantle} divided by the sulphur content of the bulk Earth $S_{\text{bulk-Earth}}$. According to ref. 1, S_{mantle} represents less than 3% of $S_{\text{bulk-Earth}}$. The sulphur isotope composition of chondrites (refs 3 and 4) and mantle (this study) values are both plotted, allowing a clear visualization of the sulphur isotope shift between these two reservoirs. Sulphur isotope and sulphur abundance observations coincide at an anchor point constraining the core-mantle fractionation. Under batch equilibrium, core $\delta^{34}\text{S}$ is +1.26‰ higher than the silicate value ($\alpha_{\text{core-mantle}} = 1.00130$). In an open system model, the core is treated as a cumulative product and $\alpha_{\text{core-mantle}}$ of 1.00035 is sufficient to explain the shift between mantle and chondrites.

involves the dissolution of sulphur in its metallic form (S^0) in the core, given that stable isotope fractionation theory predicts the more oxidized compound to be ^{34}S -enriched compared to sulphur dissolved as S^{2-} in the silicate mantle. The $\alpha_{\text{core-mantle}}$ can be inferred from a chondritic bulk Earth (that is, mantle and core) by combining the distribution of sulphur in the bulk Earth (ref. 1) and the re-evaluated $^{34}\text{S}/^{32}\text{S}$ of the mantle (this study), leading to a $\alpha_{\text{core-mantle}}$ of 1.00130 for a batch-equilibrium or 1.00035 for an open-system sulphur incorporation into the core (Fig. 2). In all cases, the core $\delta^{34}\text{S}$ is expected to be +0.07‰, almost indistinguishable from that of chondrites and iron meteorites, because this reservoir would contain most of the terrestrial sulphur¹.

Only Shahar *et al.*² experimentally addressed the $^{34}\text{S}/^{32}\text{S}$ fractionation between metal and silicate at high temperature, and estimated a $\alpha_{\text{core-mantle}}$ of 1.00220 ± 0.0014 at 1,850 °C (ref. 2). For 97% of the sulphur occurring in the core¹, such an estimate should lead to a mantle $\delta^{34}\text{S}$ of -2.10 ± 1.40 ‰, under batch-equilibrium fractionation. This value, despite a significant overlap, seems slightly lower than our observation. Because stable isotope fractionations scale with temperature T as $1/T^2$, such distinct estimates could reflect a core segregation occurring at a temperature higher than 1,850 °C: the average temperature for core-mantle segregation remains highly debated, with values up to 3,300 °C (ref. 31). Alternatively, such a distinction may require the involvement of ‘hybrid models’, as suggested for highly siderophile elements³¹, in which a fraction of the mantle sulphur is a fractionated leftover from core-mantle equilibrium, whereas the other fraction would have been delivered during the late-accretionary stage. For a $\alpha_{\text{core-mantle}}$ of 1.00220 (ref. 2), the proportion of late-accreted sulphur (that is, with chondritic $^{34}\text{S}/^{32}\text{S}$) in the mantle would reach approximately 40% of mantle sulphur, after batch-equilibrium core segregation.

At that stage, the most obvious implication of such a core-mantle differentiation record is that sulphur and elements of comparable volatilities (such as zinc, fluorine and lead) must have been present to some extent before the late-accretion event. This is a robust and independent constraint that will help to build more consistent models of timing for the origin of moderately volatile elements in Earth’s mantle.

METHODS SUMMARY

Samples were analysed following the protocol described in ref. 7. Glassy rims of basalts were handpicked under a binocular microscope and if needed, cleaned

through a sonication in 99.9% ethanol. For each sample, about 300 mg was crushed to a fine powder (<100 µm) and dissolved in a 29 N HF + 2.1 M CrCl_2 solution. Under these conditions, sulphur is released as H_2S and subsequently trapped as precipitated Ag_2S . Sulphur extraction yields are $101 \pm 4\%$ for the 23 samples analysed in this study.

Weighed aliquots of silver sulphide were wrapped in aluminium foil and placed in Ni-reaction bombs for fluorination with purified F_2 at 250 °C overnight. The SF_6 produced was then purified using both cryogenic separation and gas chromatography. The purified SF_6 was then quantified and analysed using a dual-inlet ThermoFinnigan MAT 253 mass spectrometer where $m/z = 127^+$, 128^+ , 129^+ and 131^+ ion beams are monitored. All the samples were replicated, yielding a ± 0.1 , ± 0.005 and ± 0.1 ‰ uncertainty for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, respectively, consistent with the basal internal standards processed in ref. 7.

Online Content Any additional Methods, Extended Data display items and Source Data are available in the online version of the paper; references unique to these sections appear only in the online paper.

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Supplementary Information is available in the online version of the paper.

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Author Contributions J.L. performed sulphur isotope measurements. J.L. and M.M. performed sample preparation. P.C. conceived the project. J.L. took the lead in writing the paper, with substantial contributions from P.C. and M.M.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to J.L. (labidi@ipgp.fr).

METHODS

Sample selection and preparation. Studied samples were chosen according to their degree of glassiness. They were cleaned in 99.9% ethanol to remove any room dust from the samples. Phenocrysts were removed under a binocular microscope or by magnetic separation, when needed. Samples were then crushed to a grain size smaller than 63 μm .

Electron microprobe measurement. Sulphur contents of MORB glasses were determined by electron micro-probe (EMP) analyses on polished sections with a Cameca SX100 at the CAMPARIS facility (Pierre et Marie Curie University). The analytical conditions used were 15 kV accelerating voltage, 100 nA sample current, 20 μm beam size, and 60 s counting time for each point. Ten spots were analysed on each polished section, the calculated mean value being taken as the sulphur content of the sample and the standard deviation of each series of measurements being taken as the 1σ uncertainty (around 25 p.p.m.).

A natural pyrite was used as a standard. Results were additionally calibrated using two reference samples: sample JDF D2 (high-sulphur-content standard, with 1,400 p.p.m. sulphur) and ED DR11 1–9 (low-sulphur-content standard, with 731 p.p.m. sulphur). These two standards were analysed alternately every 3 or 4 samples. For chlorine contents (see Supplementary Information), the analytical conditions used were 25 kV accelerating voltage, 500 nA sample current, 20 μm beam size, 100 s counting time for each point. A natural scapolite was used as a standard. In addition, results were systematically calibrated using one reference sample: the south Atlantic ridge sample EW9309 41D-1, for which the chlorine amount has been chemically determined at 55 ± 12 p.p.m. (ref. 32). Ten spots were analysed on each polished section. The calculated mean value was taken as the chlorine content of the sample and the standard deviation of each series of measurements is taken as the 1σ uncertainty (10 p.p.m.).

Sulphur extraction for isotope determination. Sulphur isotope measurement of sulphide inclusions in 300–400 mg of glass separates were performed after chemical extraction, by gas source isotope ratio mass spectrometry at the Stable Isotope

Laboratory at the Institut de Physique du Globe de Paris. Powdered samples were transferred to a Teflon apparatus like that in ref. 7, where they underwent sub-boiling HF–Cr(II) sulphur extraction. Sulphur released in this process as H_2S was trapped as silver sulphide, which was washed, dried and wrapped in clean Al foil. The sulphur-content measurement performed via the EMP value represents the bulk sulphur content of the sample, compared to our chemical extraction protocol, which is strictly specific to reduced sulphur (see details in ref. 7). Chemical extraction yields (that is, the ratio of chemically extracted reduced sulphur to sulphur determined by EMP) averaged $101 \pm 4\%$ (1σ , $n = 23$). Such a good match with EMP data supports the absence of significant amounts of oxidized sulphur in these basalts, in agreement with synchrotron spectroscopic results in worldwide samples¹⁸.

The sulphur isotope measurements were then performed using a dual-inlet MAT 253 gas-source mass spectrometer. Weighed silver sulphide wrapped in aluminium foil was placed into Ni-reaction bombs for fluorination with 250 torr of purified F_2 at 250 °C overnight. The produced SF_6 was then purified from impurities in a vacuum line using cryogenic methods and subsequently by gas chromatography separation. Purified SF_6 was then quantified and analysed in the mass spectrometer, where $m/z = 127+$, $128+$, $129+$ and $131+$ ion beams are monitored. The quality of the measurements was estimated on the basis of long-term reproducibility for IAEA reference materials. Repeated analyses gave $\delta^{34}\text{S} = -0.29 \pm 0.04\text{‰}$, $\Delta^{33}\text{S} = +0.082 \pm 0.004\text{‰}$, $\Delta^{36}\text{S} = -0.91 \pm 0.11\text{‰}$ for IAEA S1 (all errors are 1σ , $n = 43$) and $\delta^{34}\text{S} = +22.33 \pm 0.06\text{‰}$, $\Delta^{33}\text{S} = +0.030 \pm 0.006\text{‰}$, $\Delta^{36}\text{S} = -0.17 \pm 0.07\text{‰}$ for IAEA S2 (all errors are 1σ , $n = 20$). These values are in agreement with data reported by other laboratories worldwide.

For each MORB glass sample, the sulphur isotope measurement was duplicated and the standard deviation between the two duplicates was taken as the 1σ external uncertainty. The standard $\delta^{34}\text{S}$ uncertainty is 0.01‰–0.15‰, whereas it is approximately 0.010‰ and 0.100‰ for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, respectively.

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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-workers¹ 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 discussion¹ were published online on 4 September 2013.

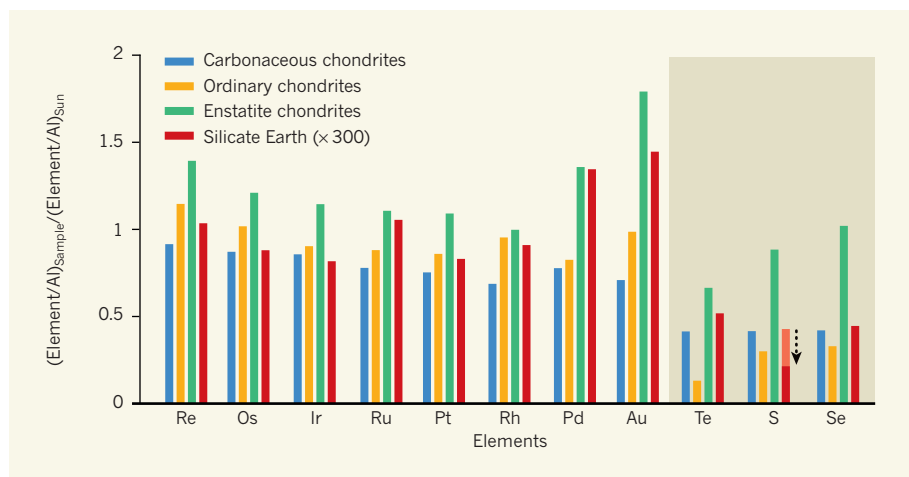


Figure 1 | Abundances of elements in Earth's mantle and in chondritic meteorites. The elements shown have strong affinities with metallic iron^{9,11,12} and are in order of increasing volatility. Shaded region indicates elements that are not noble metals. Data are normalized to the abundance of aluminium (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.



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, $H = 100 \text{ km/s/megaparsec}$, which is $1.65 \times 10^{-4} \text{ mm per year per mile}$, 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

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 rocks⁸. 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 veneer⁹. 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 evidence¹⁰ 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 study⁹, 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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