

## LETTERS

## Silicon in the Earth's core

R. Bastian Georg<sup>1,2</sup>, Alex N. Halliday<sup>1</sup>, Edwin A. Schauble<sup>3</sup> & Ben C. Reynolds<sup>2</sup>

Small isotopic differences between the silicate minerals in planets may have developed as a result of processes associated with core formation, or from evaporative losses during accretion as the planets were built up. Basalts from the Earth and the Moon do indeed appear to have iron isotopic compositions that are slightly heavy relative to those from Mars, Vesta and primitive undifferentiated meteorites<sup>1–4</sup> (chondrites). Explanations for these differences have included evaporation during the ‘giant impact’ that created the Moon (when a Mars-sized body collided with the young Earth). However, lithium<sup>5</sup> and magnesium<sup>6</sup>, lighter elements with comparable volatility<sup>7–9</sup>, reveal no such differences, rendering evaporation unlikely as an explanation. Here we show that the silicon isotopic compositions of basaltic rocks from the Earth and the Moon are also distinctly heavy. A likely cause is that silicon is one of the light elements in the Earth's core. We show that both the direction and magnitude of the silicon isotopic effect are in accord with current theory<sup>10</sup> based on the stiffness of bonding in metal and silicate. The similar isotopic composition of the bulk silicate Earth and the Moon is consistent with the recent proposal<sup>11</sup> that there was large-scale isotopic equilibration during the giant impact. We conclude that Si was already incorporated as a light element in the Earth's core before the Moon formed.

We have measured the Si isotopic compositions for 44 meteorites and lunar and terrestrial samples (Table 1) using high-resolution multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS)<sup>12</sup>. The data are plotted on a conventional three-isotope diagram (Fig. 1) and are consistent with a mass-dependent fractionation line with a slope of  $\delta^{29}\text{Si} = 0.5178 \times \delta^{30}\text{Si}$ . There are no resolvable nucleosynthetic isotopic anomalies. A similar level of nucleosynthetic homogeneity has been reported for many other elements, such as magnesium<sup>6</sup>, and contrasts with the widespread non-mass-dependent heterogeneity in oxygen<sup>13</sup>.

The range of Si isotopic compositions for meteorites is small (Table 1). The means are  $\delta^{30}\text{Si} = -0.58 \pm 0.06\text{‰}$  and  $\delta^{29}\text{Si} = -0.30 \pm 0.03\text{‰}$  ( $\pm 1$  standard deviation, s.d.). It is clear from our data that the Solar System as sampled by chondrites is close to being uniform isotopically; the same applies to basaltic achondrites from Mars and Vesta. The possible exceptions are enstatite chondrites and aubrites, which provide a hint of slightly lighter Si. There is no indication of any significant isotopic effect associated with basaltic partial melting.

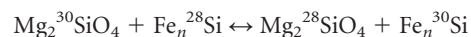
The data for the Earth and the Moon are heavy relative to these meteorite values. The four lunar samples are indistinguishable from each other and give a mean  $\delta^{30}\text{Si}$  of  $-0.31 \pm 0.03\text{‰}$ . The average  $\delta^{30}\text{Si}$  of samples from the terrestrial mantle is  $-0.38 \pm 0.06\text{‰}$ . The few data for clinopyroxene and olivine in mantle xenoliths are similar to the data for basalts, endorsing the view from the meteorite work and the predictions from theory<sup>10</sup> that Si isotope fractionation during partial melting is small. Our data are in excellent agreement with previous estimates for the composition of the bulk silicate Earth (BSE) of  $\delta^{30}\text{Si} = -0.4\text{‰}$  based on averages for mafic and ultramafic rocks<sup>14</sup>, as well as with previously reported data for the Moon<sup>15,16</sup> and

meteorites<sup>17</sup> (see Methods). However, the analytical uncertainties in these other studies are too large to resolve differences.

The most obvious distinction between the Earth on the one hand and Mars and Vesta on the other is the size of the body, which would have led to higher average pressures of core formation<sup>18</sup>. This is a likely explanation for the heavier silicon isotopic composition of the BSE. It has long been recognized that the Earth's core must contain a significant amount of a light element, candidates for which have included hydrogen, carbon, silicon, sulphur and potassium. A key argument in favour of Si is the high Mg/Si ratio of the silicate Earth<sup>19,20</sup>. Recent experimental results<sup>21</sup> are consistent with  $\sim 5$  wt% Si in the core<sup>18</sup>, which corresponds to a Si deficiency of the BSE of 11%, in accord with its Mg/Si ratio<sup>20</sup>. The partitioning of Si into liquid iron is thought to be a high-temperature, high-pressure effect<sup>21</sup> that became important after the Earth had achieved 15% of its current mass<sup>18</sup>. Therefore, any resultant metal/silicate Si isotopic fractionation might not be present in smaller objects such as Vesta or Mars.

Some have proposed a ‘heterogeneous accretion’ of the Earth with an early reduced stage<sup>22</sup>. Silicon would then partition into metal even at low pressures. However, the absence of reduced chondritic meteorites with a chemical composition like that of the Earth has led to these models being largely abandoned. Either way, the isotope data provide evidence that Si is a light element in the core.

Silicon isotope fractionation during core formation is likely because enrichment of heavy isotopes is expected in the phase with the ‘stiffer’ bonds<sup>10</sup>, in this case the Si–O bonds in silicates. Sufficient independent constraints exist to provide first order confirmation of the direction and magnitude of such a fractionation. To estimate the likely equilibrium  $^{30}\text{Si}/^{28}\text{Si}$  fractionation between silicate and metal, one can examine the reaction:



In this reaction,  $^{30}\text{Si}$  substitution is expected to affect free energies primarily by lowering phonon frequencies<sup>23</sup>. The size of the isotopic energy shift is calculated by comparing the phonon density of states (PDOS) of each isotopologue. The PDOS of  $\text{Mg}_2\text{SiO}_4$  is calculated using a first principles model of the forsterite (olivine) structure based on density functional perturbation theory<sup>24,25</sup>. Olivine is the primary silicate phase in the upper 400 km of the Earth's mantle. The electronic structure is determined using norm-conserving pseudo-potentials and a gradient-corrected functional<sup>26</sup>. Phonon energies are sampled at one non-zero wave vector, and scaled by 1.043, based on comparison between measured and computed Raman- and infrared-active phonon frequencies (see, for example, ref. 27). Similar models of diopside, quartz and zircon suggest that  $^{30}\text{Si}/^{28}\text{Si}$  fractionation between silicates is  $<0.3\text{‰}$  above 1,000 °C.  $\text{Fe}_n\text{Si}$  is modelled by analogy with  $\text{Fe}_3\text{Si}$ , which has an atomic packing structure similar to the body-centred cubic phase of iron. The upper limit of the effect of isotope substitution on the phonon energy of  $\text{Fe}_3\text{Si}$  is estimated by assuming that silicon vibrates at the highest frequencies observed in

<sup>1</sup>Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3PR, UK. <sup>2</sup>Department of Earth Sciences, ETH Zentrum NW, Clausiusstrasse 25, CH-8092 Zürich, Switzerland. <sup>3</sup>Department of Earth and Space Sciences, University of California, Los Angeles, California 90095-1567, USA.

**Table 1 | Silicon isotope compositions of samples from the Earth, Moon and meteorites**

Sample		$\delta^{30}\text{Si}$	2 s.e.	$\delta^{29}\text{Si}$	2 s.e.	n	$\text{SiO}_2$	Group average			
								(‰ relative to NBS-28)	(wt%)	$\delta^{30}\text{Si}$	1 s.d.
<b>Carbonaceous chondrites</b>											
Allende	CV3	-0.58	0.03	-0.29	0.03	39	35.4				
Orgueil	CI	-0.60	0.03	-0.30	0.01	40	22.2				
Murchison	CM2	-0.65	0.03	-0.34	0.03	33	29.7				
ALH 83108	CO3.5	-0.54	0.03	-0.29	0.02	11	34.9				
EET 92002	CK4	-0.53	0.02	-0.27	0.01	11	34.0				
Group average								-0.58	0.05	-0.30	0.03
<b>Ordinary chondrites</b>											
Cereseto	H5	-0.56	0.03	-0.29	0.02	22	34.4				
Cangas de Onis	H5	-0.55	0.03	-0.28	0.03	19	31.6				
Allegan	H5	-0.62	0.03	-0.33	0.03	28	42.1				
Bruderheim	L6	-0.56	0.03	-0.31	0.03	22	43.0				
Bath	H4	-0.51	0.03	-0.26	0.02	20	37.9				
Epinal	H5	-0.60	0.03	-0.32	0.02	22	37.4				
Group average								-0.57	0.04	-0.30	0.03
<b>Enstatite chondrites</b>											
Abee	EH4	-0.69	0.03	-0.36	0.01	11	46.5				
<b>Eucrites and diogenites</b>											
Sioux Country	Monomict eucrite	-0.52	0.04	-0.25	0.03	20	46.5				
Bouvante	Polymict eucrite	-0.53	0.03	-0.26	0.03	22	50.2				
Bereba	Monomict eucrite	-0.50	0.03	-0.26	0.02	22	52.8				
Juvinas	Monomict eucrite	-0.60	0.03	-0.28	0.02	25	50.5				
Pasamonte	Polymict eucrite	-0.66	0.02	-0.35	0.02	22	49.3				
Johnstown UB	Diogenite	-0.56	0.02	-0.32	0.01	11	54.4				
Group average								-0.56	0.06	-0.29	0.04
<b>Aubrites</b>											
ALH 84009	Aubrite	-0.70	0.03	-0.36	0.02	11	57.4				
<b>Chainpur (LL3.4) chondrules</b>											
XT-1	Chondrule	-0.61	0.04	-0.29	0.01	7	51.4				
XT-2	Chondrule	-0.46	0.04	-0.23	0.04	7	38.7				
XT-3	Chondrule	-0.48	0.02	-0.28	0.02	11	36.2				
XT-4	Chondrule	-0.24	0.04	-0.11	0.02	11	32.5				
XT-5	Chondrule	-0.75	0.02	-0.40	0.04	7	41.5				
Group average								-0.51	0.19	-0.26	0.11
<b>Martian meteorites</b>											
ALH 84001	Orthopyroxenite	-0.57	0.03	-0.30	0.02	12	54.7				
Zagami	Basalt	-0.55	0.03	-0.28	0.02	22	47.7				
Nakhla	Olivine clinopyroxenite	-0.64	0.02	-0.35	0.02	13	48.1				
Group average								-0.59	0.05	-0.31	0.04
<b>Lunar rocks</b>											
15555.115	Olivine-normal basalt	-0.32	0.03	-0.18	0.02	11	35.6				
70035.158	High-Ti basalt	-0.30	0.01	-0.16	0.02	11	41.4				
75075.17	High-Ti basalt	-0.35	0.02	-0.17	0.02	11	42.8				
77516.26	High-Ti basalt	-0.27	0.02	-0.14	0.01	11	33.8				
Group average								-0.31	0.03	-0.16	0.02
<b>Ocean island basalt</b>											
ICE-B1	Scoria Iceland	-0.35	0.04	-0.19	0.02	7	45.4				
ICE-B2	Basalt Iceland	-0.35	0.03	-0.21	0.01	9	43.9				
SH-6	Basalt St Helena	-0.31	0.03	-0.14	0.01	11	41.2				
LGG8	Basalt glass Loihi	-0.36	0.03	-0.16	0.01	7	43.9				
P-13	Basalt Principe	-0.49	0.04	-0.26	0.02	11	41.4				
<b>Mid-ocean ridge basalt glasses</b>											
A 127 / D5-5	Atlantic	-0.35	0.04	-0.20	0.01	11	44.5				
A 127 / D21-3	Atlantic	-0.51	0.02	-0.26	0.02	11	49.6				
R 93-7	East Pacific Rise	-0.39	0.02	-0.22	0.02	11	48.0				
<b>Cameroon line spinel lherzolites</b>											
C 235A	Olivine	-0.35	0.03	-0.16	0.02	9	NA				
C 235 A	Clinopyroxene	-0.41	0.03	-0.23	0.02	11	NA				
C 271 I	Olivine	-0.31	0.03	-0.14	0.03	11	NA				
C 271 I	Clinopyroxene	-0.42	0.04	-0.23	0.03	9	NA				
Group average (last 3 groups)								-0.38	0.06	-0.20	0.04

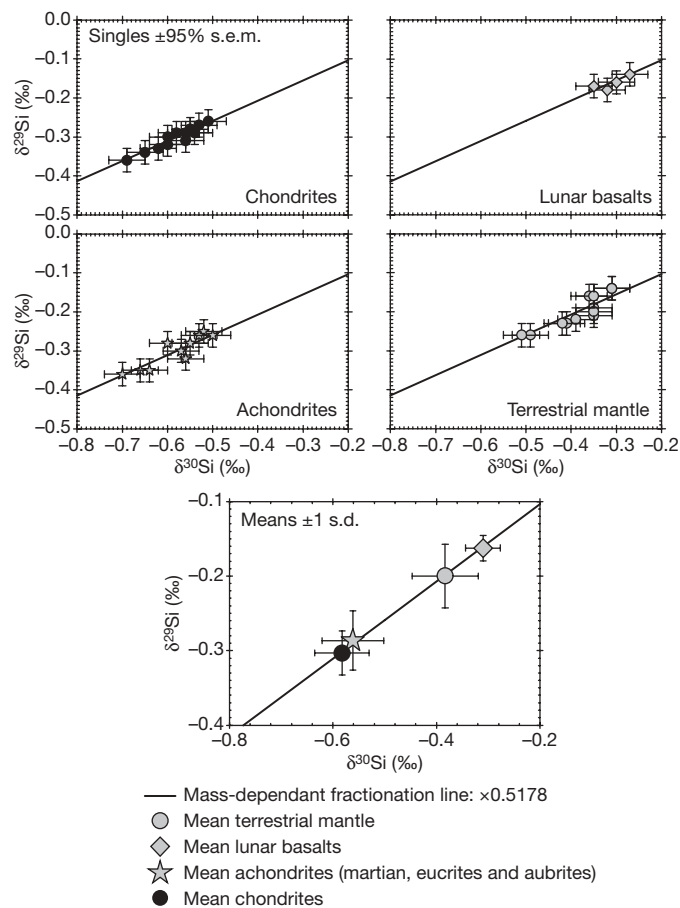
All data represent whole rock analyses, except for chondrules and spinel lherzolite mineral separates. The uncertainties on  $\text{SiO}_2$  wt% are  $\pm 3\%$ . Silicon isotopic compositions are reported in parts per thousand of the deviations of the  $^{30}\text{Si}/^{28}\text{Si}$  ( $J = 30,29$ ) of the sample relative to the international reference material NBS-28 (ref. 12). Each sample was measured at least 11 times, resulting in an average limiting precision of 0.04‰ and 0.03‰ (2 s.e.) for  $\delta^{30}\text{Si}$  and  $\delta^{29}\text{Si}$ , respectively. The 5 carbonaceous chondrites, 6 ordinary chondrites, 6 HED basaltic achondrites thought to come from Vesta and 3 martian meteorites display identical mean  $\delta^{30}\text{Si}$  ( $\pm 1$  s.d.) of  $-0.58 \pm 0.05\%$ ,  $-0.57 \pm 0.04\%$ ,  $-0.56 \pm 0.06\%$  and  $-0.59 \pm 0.05\%$ . Even the 5 chondrules, though spanning a considerable range that implicates small scale heterogeneity, yield an identical average of  $-0.51 \pm 0.19\%$ . The one enstatite chondrite yields a  $\delta^{30}\text{Si}$  of  $-0.69 \pm 0.03\%$  (2 s.e.) at the most negative end of the range found for bulk meteorites. An aubrite (a class of meteorite considered to represent the achondritic derivative of enstatite chondrites) yields an identical value of  $-0.70 \pm 0.03\%$ . The four lunar samples are indistinguishable from each other and give a mean  $\delta^{30}\text{Si}$  of  $-0.31 \pm 0.03\%$ , which is significantly different from the meteorite value. On the basis of the samples analysed here, the terrestrial mantle has an average  $\delta^{30}\text{Si}$  of  $-0.38 \pm 0.06\%$ , slightly lighter than the lunar data but heavier than the meteorite values. NA, not available.

the structure (10 THz; ref. 28). This gives a rough lower bound of 3.6‰ for the  $^{30}\text{Si}/^{28}\text{Si}$  fractionation between silicate and metal at 1,000 °C, and 2.7‰ at 1,200 °C (Fig. 2).

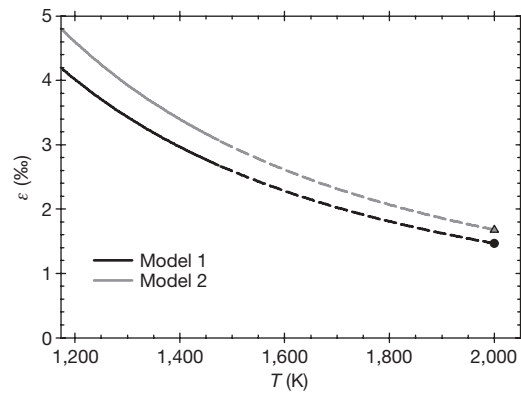
An alternative calculation assumes that silicon oscillates at a frequency corresponding to the root mean square of the total PDOS of  $\text{Fe}_3\text{Si}$  (~7.5 THz), providing a lower limit of the isotope substitution energy. This provides evidence that the maximum fractionation is 4.1‰ at 1,000 °C (3.1‰ at 1,200 °C). In both calculations, silicate is the high- $^{30}\text{Si}/^{28}\text{Si}$  phase. The models considered here give isotope effects ( $\epsilon$  in ‰, where  $\epsilon = 1,000 \times \ln \alpha_{\text{silicate-metal}}$  and  $\alpha_{\text{silicate-metal}} = (^{30}\text{Si}/^{28}\text{Si})_{\text{silicate}} / (^{30}\text{Si}/^{28}\text{Si})_{\text{metal}}$ ) of about 1.7 and 1.5 at ~2,000 K (Fig. 2). However, the calculated fractionation factors can only be extrapolated to such higher temperatures if one assumes that the Fe–Si bonding environment does not change greatly on melting.

Pressure could also change the fractionation. All models are calculated at  $\sim 10^5$  Pa pressure, under the assumption of harmonic phonon oscillation. Equilibration of metal in the presence of high-pressure silicate phases (for example,  $\text{MgSiO}_3$ -perovskite)<sup>21</sup> might be expected to cause less isotopic fractionation, owing to longer, more ionic Si–O bonds in octahedral coordination sites.

These preliminary estimates can be compared with the fractionation factors calculated from the Si isotope data (Fig. 3). Assuming  $\delta^{30}\text{Si}$  for the total Earth of  $-0.58$ ‰ (average chondrites) and for the BSE of  $-0.38$ ‰, one can use the BSE Si deficiency of 11% (ref. 20)



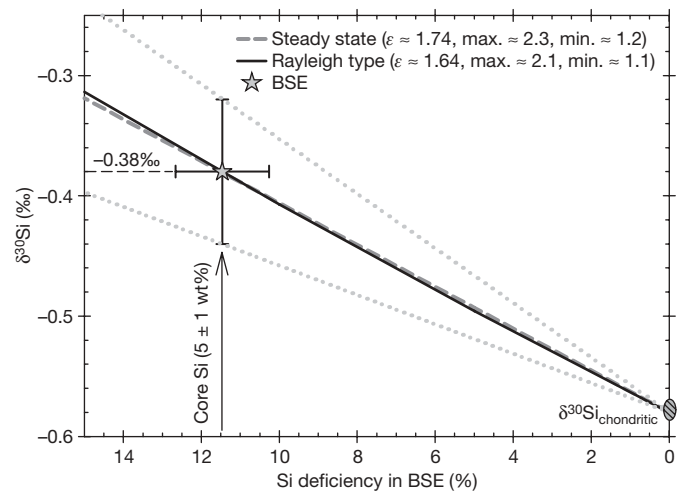
**Figure 1 | Silicon isotopic compositions of different Solar System objects.** Three-isotope plots showing the data given in Table 1, and divided to illustrate the similarities and differences between reservoirs. It can be seen that all of the data plot on the same mass-dependent fractionation line, consistent with a single homogeneous inner Solar System Si isotopic reservoir. The means and standard deviations for each type are shown in the bottom panel. Chondrites and achondrites are indistinguishable but different from mantle samples from the Earth, which overlap with the data for lunar basalts.



**Figure 2 | Theoretical fractionation of silicon isotopes between silicate and metal as a function of temperature.** Equilibrium  $^{30}\text{Si}/^{28}\text{Si}$  fractionation ( $\epsilon = 1,000 \ln \alpha_{\text{silicate-metal}}$ ) between silicate and metal is estimated from lattice-dynamics modelling of  $\text{Mg}_2\text{SiO}_4$ -olivine and body-centred cubic  $\text{Fe}_3\text{Si}$ . The lower (black) curve is calculated assuming Si-atom vibration at 10 THz in the  $\text{Fe}_3\text{Si}$  structure. The upper (grey) curve assumes Si-atom vibration at 7.5 THz in  $\text{Fe}_3\text{Si}$ . The dashed curves at temperatures above 1,200 °C (1,473 K) indicate extrapolation beyond the 1 atm melting point of  $\text{Fe}_3\text{Si}$ .

and a bulk core concentration of 5 wt% Si (ref. 18) to determine the fractionation factor. Both steady-state and Rayleigh-type models can be investigated, and these yield isotope effects ( $\epsilon$ ) of 1.74‰ and 1.64‰, respectively (Fig. 3), in excellent agreement with our first order calculations (Fig. 2).

There are parallels between the results presented here for Si and those previously reported for Fe. Basalts from the silicate Earth and Moon have Fe that is isotopically heavy by at least 30 p.p.m. per atomic mass unit relative to that of basalts from Mars and Vesta<sup>1–4</sup>, which is in turn identical to data for chondrites<sup>1,4</sup>. The pattern is therefore analogous to that found for Si. Whether the mechanisms



**Figure 3 | Fractionation of silicon isotopes by core formation calculated from the composition of the bulk silicate Earth (BSE).** Isotope enrichment factors ( $\epsilon$ ) derived from the measured Si isotope data, as shown for a Rayleigh-type (solid line) or steady-state (dashed line) fractionation scenario. The modelling shows that an enrichment factor of 1.74 (steady state) or 1.65 (Rayleigh type) would suffice to produce the  $\delta^{30}\text{Si}_{\text{BSE}}$  of  $-0.38$ ‰ (star), starting with a  $\delta^{30}\text{Si}_{\text{chondritic}}$  of  $-0.58$ ‰ and taking the Si deficiency of the BSE into account. This would require the core to have ~5% of Si by mass. The isotope effects obtained from the measured data are in good agreement with theoretical predictions for metal–silicate fractionation at temperatures of ~2,000 K. Dotted lines indicate lower and upper limits for  $\epsilon$ . The error bars on  $\delta^{30}\text{Si}_{\text{BSE}}$  (star) indicate  $\pm 1$  wt% Si within the Earth's core and  $\pm 1$  s.d. on  $\delta^{30}\text{Si}$ , respectively.

are related is unclear. It is for example debated whether the effect may not reflect a different style of melting on Earth<sup>4</sup>. However, this would not explain the lunar data. One explanation to consider is that the heavier Fe is also a high-pressure effect but resulting from self-oxidation by perovskite–metal fractionation<sup>3,18</sup>. Formation of ferric iron can lead to heavier Fe isotopic compositions<sup>29</sup> in oxides and silicates, and this might explain the difference relative to Mars and Vesta, which are both of a size at which little or no perovskite would be stable.

A first order calculation of the expected effect can be made by assuming that perovskite–metal fractionation is the same as that of haematite–metal, that the lower-mantle silicate assemblage comprises a 50:50 mixture of periclase and perovskite, and that the fractionation is increased by high-pressure high-spin to low-spin transitions (see Supplementary Discussion). This gives a net  $\epsilon^{57/54}\text{Fe}$  (metal/silicate) of  $-0.04\%$ , which can be compared with a fractionation factor calculated from the effect in the BSE, assuming that all of the silicate and all of the metal formed in isotopic equilibrium, of  $-0.12\%$ . These are sufficiently close in terms of magnitude and sign to be interesting, but the model is simplistic and further work is needed before firm conclusions can be drawn (see Supplementary Discussion).

As with Fe, the other explanation to consider for the heavy Si in the BSE is partial loss during high-temperature condensation/evaporation. Magnesium and Si have similar condensation temperatures, whereas Li is more volatile<sup>7</sup>. Evaporation experiments show that Si and Mg have similar volatility, with a stronger isotopic fractionation of Mg (ref. 8). Calcium aluminium refractory inclusions (CAIs) are natural evaporation residues and demonstrate the same thing<sup>9</sup>, with Si isotopic fractionations that are only half as extreme as those of Mg, exactly as predicted by experiments<sup>8</sup>. Therefore, available theoretical, experimental and observational evidence suggests that isotope fractionation resulting from partial condensation/evaporation causes similar, if not larger, effects for the lighter element Mg. However, no effects are found for either Li or Mg.

High-pressure core formation explains the Si isotopic composition of the BSE, but leaves the question of how the Moon acquired a similar composition. The Earth and Moon yield oxygen isotopic compositions that are irresolvable at very high precision<sup>30</sup>, despite widespread Solar System heterogeneity<sup>13</sup>. It was thought that this reflected a similar provenance of material making up the Earth and the planet that struck it in the giant impact, Theia<sup>30</sup>. The unlikelihood of this has recently been pointed out<sup>11</sup>, and it has been argued that a more viable explanation is that, following the enormously energetic giant impact, the vapour cloud from which the Moon condensed would have had sufficient time to isotopically equilibrate with the proto-Earth<sup>11</sup>, leading to identical isotopic compositions. This would also explain the Fe and Si isotopic similarities between the Earth and Moon, and it means that the mechanisms that generated these effects for the Earth need not have been operational on the Moon. In fact, the isotopic similarity of the Moon represents powerful vindication of the new equilibration model<sup>11</sup>, which in turn provides evidence that Si was already partitioned into the Earth's core before the giant impact. Future work with isotopic measurements on the products of high-pressure experiments should permit elucidation of the conditions of core formation at the time of this last major event in the accretion of the Earth.

## METHODS

All samples were dissolved using an alkaline flux and were subsequently transferred into a weakly acidic HCl solution. Silicon was quantitatively separated from the silicate cation matrix by ion exchange chromatography on BioRad columns packed with 1.8 ml DOWEX 50W-X12 (200–400 mesh). A detailed description of the fusion and ion exchange procedures is given elsewhere<sup>12</sup>. Silicon isotope data were acquired using the high-resolution Nu Instruments Nu1700 MC-ICPMS (ETH Zürich). Eleven samples were processed twice through the chemical procedure, and were analysed during different sessions more than two months apart. Data accuracy during sample runs was monitored using IRMM-018 and a second batch of NBS-28. The high level of

reproducibility is demonstrated by three different splits of one terrestrial bulk silicate rock sample, which has been processed through the entire procedure, including fusion and column chemistry. The three independent procedural repeats give an average  $\delta^{30}\text{Si}$  value of  $-0.17 \pm 0.10\%$  ( $\pm 2$  s.d.,  $n = 30$ ) and an average  $\delta^{29}\text{Si}$  value of  $-0.10 \pm 0.10\%$  ( $\pm 2$  s.d.,  $n = 30$ ). Our meteorite results are fully consistent with previously reported less precise data<sup>17</sup>. However, comparisons with still older data are more difficult. Not only are earlier data less precise<sup>15,16</sup>, they were also measured relative to a different standard, the Cal Tech Rose Quartz Standard (RQS), and not relative to NBS-28 as used here. When RQS was initially calibrated, it was found to be  $-0.28 \pm 0.18\%$  on the NBS-28 scale<sup>17</sup>. However, our own high-precision measurements of the RQS yield  $\delta^{30}\text{Si}$  of  $-0.02 \pm 0.10\%$  ( $\pm 2$  s.d.,  $n = 17$ ), rendering older and newer data directly comparable.

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**Supplementary Information** is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

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