

# Zinc isotopic evidence for the origin of the Moon

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**Volatiles elements have a fundamental role in the evolution of planets. But how budgets of volatiles were set in planets, and the nature and extent of volatile-depletion of planetary bodies during the earliest stages of Solar System formation remain poorly understood<sup>1,2</sup>. The Moon is considered to be volatile-depleted and so it has been predicted that volatile loss should have fractionated stable isotopes of moderately volatile elements<sup>3</sup>. One such element, zinc, exhibits strong isotopic fractionation during volatilization in planetary rocks<sup>4,5</sup>, but is hardly fractionated during terrestrial igneous processes<sup>6</sup>, making it a powerful tracer of the volatile histories of planets. Here we present high-precision zinc isotopic and abundance data which show that lunar magmatic rocks are enriched in the heavy isotopes of zinc and have lower zinc concentrations than terrestrial or Martian igneous rocks. Conversely, Earth and Mars have broadly chondritic zinc isotopic compositions. We show that these variations represent large-scale evaporation of zinc, most probably in the aftermath of the Moon-forming event, rather than small-scale evaporation processes during volcanism. Our results therefore represent evidence for volatile depletion of the Moon through evaporation, and are consistent with a giant impact origin for the Earth and Moon.**

The mode of origin of the Earth–Moon system that is most consistent with both physical and chemical constraints is through a giant impact between the proto-Earth and a Mars-sized body<sup>7,8</sup>. Depending on the Hf/W ratios of the bulk silicate Earth and Moon, this event is calculated to have occurred some 10–150 Myr after the formation of the first Solar System solids<sup>9,10</sup>. This highly energetic collision is predicted to have melted the impactor, with much of its core material being sequestered into Earth, while silicate material spun into an Earth-orbiting disk that later accreted to form the Moon<sup>11,12</sup>. Despite this cataclysmic mode of origin, and silicate vapour-phase models proposed to explain non-volatile stable isotope fractionation<sup>13</sup>, to date there have been no collateral heavy isotope enrichments found for moderately volatile elements (for example, K) in lunar or terrestrial rocks<sup>3</sup>.

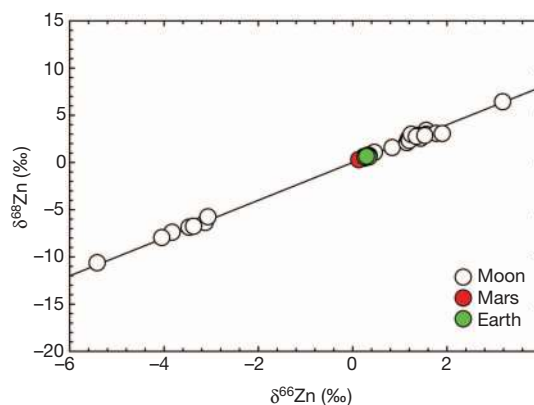
Zinc is more volatile than both K and Cl (ref. 14) under solar nebula conditions and exhibits limited isotopic fractionation during igneous processes<sup>6,15</sup>. On Earth, and in primitive meteorites such as chondrites, variations of  $\delta^{66}\text{Zn}$  (see Fig. 1 legend for definition) larger than 1‰ have only been observed in association with evaporation events<sup>4,16</sup>. Therefore any Zn isotopic fractionation, combined with differences in Zn concentrations between planetary igneous rocks from differentiated bodies such as Earth, the Moon and Mars, can reveal important differences in volatile depletion and replenishment events for these bodies.

Here we report high-precision Zn isotopic data for lunar basalts, Martian meteorites and terrestrial igneous rocks (see Methods, Supplementary Table 1 and Supplementary Information). Combined with previously published data for lunar rocks, terrestrial basalts, and carbonaceous, ordinary and enstatite chondrites, these new data allow us to establish the nature and extent of volatile depletion in Earth, the Moon and Mars. Fractionation between  $\delta^{66}\text{Zn}$  and  $\delta^{68}\text{Zn}$  is mass-dependent (Fig. 1), conforming to the expected mass-dependent mass-fractionation slope of two, hence only  $\delta^{66}\text{Zn}$  is discussed here

although  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$  and  $^{68}\text{Zn}$  intensities were precisely measured. Because terrestrial, Martian and lunar rocks all lie on the same mass-dependent mass-fractionation line, along with all classes of chondritic meteorites<sup>16,17</sup>, this implies that Zn from all of the analysed samples evolved from a single, isotopically homogeneous reservoir. This relationship presumably reflects Zn isotope homogeneity in the solar nebula before terrestrial planet formation and, thus, that all reported isotopic variations are due to mass-dependent fractionations. Spallogenic effects or secondary neutron capture would lead to non-mass-dependent behaviour.

Low-Ti lunar mare basalts, including the mare basalt meteorite LaPaz Icefield (LAP) 02205, span a range in  $\delta^{66}\text{Zn}$  of  $-3.13\text{‰}$  to  $+1.56\text{‰}$  (Fig. 2). Sample 12018 is isotopically light ( $\delta^{66}\text{Zn} = -3.10 \pm 0.03\text{‰}$ ,  $n = 2$ ) when compared with the other 11 low-Ti mare basalt samples measured. If sample 12018 is excluded from the comparison, we find a limited range in  $\delta^{66}\text{Zn}$  for low-Ti mare basalts of  $+0.84\text{‰}$  to  $+1.56\text{‰}$ , with a mean of  $+1.31 \pm 0.13\text{‰}$ . The mean  $\delta^{66}\text{Zn}$  for low-Ti mare basalts is identical, within the uncertainties, to that derived for high-Ti mare basalts ( $\delta^{66}\text{Zn} = +1.39 \pm 0.31\text{‰}$ ;  $n = 8$ ), and excluding the isotopically light sample 10017 ( $\delta^{66}\text{Zn} = -5.42\text{‰}$ ; ref. 18). Zinc concentrations in mare basalts range from 0.6 to 12 p.p.m., and are lower than concentrations of Zn measured in lunar soils (average = 25 p.p.m.), or in lunar pyroclastic glass beads (129 to 231 p.p.m.).

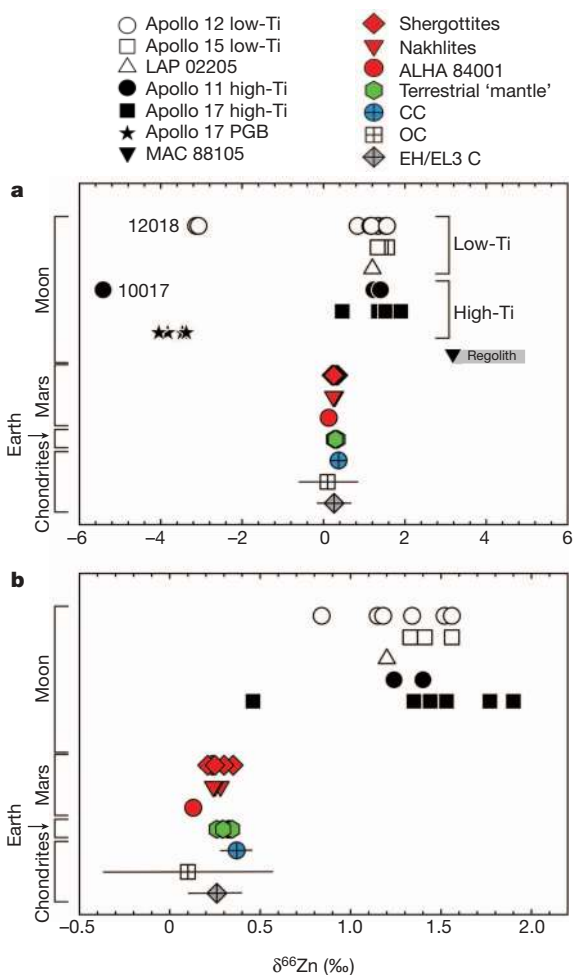
Martian SNC (Shergotty–Nakhla–Chassigny) meteorites span a limited range in  $\delta^{66}\text{Zn}$  ( $+0.13\text{‰}$  to  $+0.35\text{‰}$ ), with an average  $\delta^{66}\text{Zn}$  of  $+0.25 \pm 0.03\text{‰}$  ( $n = 10$ ) (Fig. 2). Measured values of  $\delta^{66}\text{Zn}$  are slightly higher in Mg-rich shergottites (for example, Elephant Moraine 79001, Allan Hills (ALHA) 77005), than in more evolved shergottites, nakhlites and ALH 84001, which has the lowest  $\delta^{66}\text{Zn}$  composition of Martian meteorites. The average Zn isotopic composition of Martian meteorites ( $+0.25 \pm 0.03\text{‰}$ ) is identical to the



**Figure 1** |  $\delta^{68}\text{Zn}$  versus  $\delta^{66}\text{Zn}$  for lunar, terrestrial and Martian samples. All of the samples fall on the mass-dependent mass-fractionation line of slope 2. Analytical uncertainties ( $2\sigma$ ) are smaller than the data marker size.  $\delta^X\text{Zn} = [(^X\text{Zn}/^{64}\text{Zn})_{\text{sample}} / (^X\text{Zn}/^{64}\text{Zn})_{\text{JMC Lyon standard}} - 1] \times 1,000$ , where  $X = 66$  or  $68$ .

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**Figure 2 | Zinc isotopic composition of terrestrial, lunar, Martian and chondritic samples.** CC, carbonaceous chondrite; OC, ordinary chondrite; EH/EL3 C, enstatite chondrite; PGB, pyroclastic glass beads. Data for chondrites and Earth represent an average of the different samples measured so far (refs 4, 6, 16, 17 and Methods); error bars,  $2\sigma$ . For Martian meteorites and lunar samples, each data point represents one sample;  $2\sigma$  on the  $\delta^{66}\text{Zn}$  is 0.05‰.

average measured  $\delta^{66}\text{Zn}$  composition of terrestrial igneous rocks ( $+0.27 \pm 0.10\%$ ). Zinc concentrations in shergottite meteorites are higher than for lunar mare basalts at between 41 and 130 p.p.m., and Zn concentrations in nakhlite meteorites lie within the range of shergottite meteorites at between 61.5 and 89 p.p.m. (Supplementary Information); Martian igneous rock Zn concentrations are therefore similar to terrestrial basaltic lavas (typically 70 to 100 p.p.m.; see the GERM database at <http://earthref.org/GERM/>).

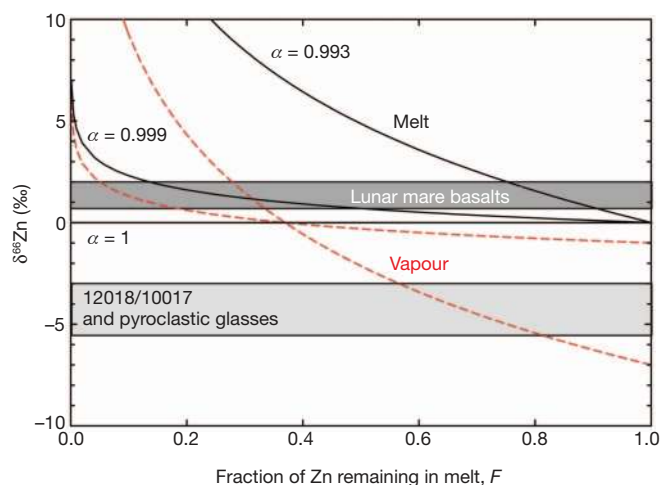
The range of  $\delta^{66}\text{Zn}$  values measured for lunar rocks are bracketed by the low  $\delta^{66}\text{Zn}$  values of 12018 ( $-3.10 \pm 0.03\%$ ), 10017 ( $-5.42\%$ ) and pyroclastic glass beads ( $-2.9\%$  to  $-4.2\%$ ), and by the high  $\delta^{66}\text{Zn}$  values of MacAlpine Hills (MAC) 88105 ( $\delta^{66}\text{Zn} + 3.18\%$ ) that we have measured. MAC 88105 is a lunar anorthositic regolith breccia meteorite<sup>19</sup>, and has a  $\delta^{66}\text{Zn}$  value similar to lunar regolith and soil samples from the Apollo 14, 15, 16 and 17 sites ( $+2.6\%$  to  $+5.6\%$ ) (Fig. 2). The high  $\delta^{66}\text{Zn}$  of the regolith and soil samples reflect both sputtering effects and impact gardening of the lunar regolith<sup>4,18</sup>, and do not represent primary magmatic compositions, so will not be considered further.

The isotopically light Zn values measured for 10017, 12018 and pyroclastic glass beads are not associated with petrology, mineralogy or cosmic ray exposure ages (see Supplementary Information). Previously, light Zn isotope enrichment in pyroclastic glass beads has been attributed to Zn evaporation during fire-fountaining, with condensation of isotopically light Zn on the surfaces of the ejected beads<sup>4</sup>, as also

proposed for  $^{32}\text{S}$  enrichments<sup>20</sup>. These observations appear to be supported by increased Zn concentrations on the exterior portions of the pyroclastic glass beads, relative to interior portions (see, for example, refs 18, 21). Vapour loss should increase the  $\delta^{66}\text{Zn}$  value of the residual magma and this process can be modelled assuming exhalative evaporation of Zn as  $\text{ZnCl}_2$  on the Moon (for example, ref. 21); in contrast, Zn is evaporated as  $\text{Zn}^{2+}$  on Earth (see, for example, ref. 22) with essentially no fractionation between vapour and melt (that is,  $\alpha = 1$ ; see below).

For volatilization of a liquid into a vacuum, fractionation between vapour and melt during Rayleigh distillation (differential distillation) leads to:  $\delta_{\text{final}} = \delta_{\text{initial}} + [(1,000 + \delta_{\text{initial}})(F^{\alpha-1}) - 1]$ , where  $F$  is the fraction of Zn remaining in the melt, and  $\delta_{\text{initial}}$  and  $\delta_{\text{final}}$  are the  $\delta^{66}\text{Zn}$  of the initial and final liquid, respectively. The value of  $\alpha$  can be approximated as the square-root of the mass number of the light isotopologue over that of the mass number of the heavy isotopologue of the vaporizing species; for  $\text{ZnCl}_2$ , the  $\alpha$  value is 0.993. Extreme fractionations of Zn isotopes in the melt and associated vapour phase are computed for low remaining Zn in the melt fraction, and fractionations greater than those measured for lunar rocks can be calculated; such fractionations could possibly reflect incomplete evaporation to low melt fractions, or the competing effect of diffusion rates being insufficient to maintain isotopic homogeneity in melts on the Moon (this latter effect is exemplified as a lower  $\alpha$  value of 0.999; Fig. 3). These calculations demonstrate that isotopically light vapour conforming to those measured in 12018, 10017 and pyroclastic glass beads can also be achieved by evaporation and re-deposition of  $\text{ZnCl}_2$  from lunar melts. We therefore exclude these isotopically light samples from the planetary comparisons made between Earth, the Moon and Mars.

As demonstrated above, Zn isotopes can be strongly fractionated during high-temperature evaporative processes, and an important distinction to be made is how and when Zn isotopic fractionation occurred between different planetary basalts. For example, there is a clear difference in the Zn isotopic composition of lunar mare basalts relative to Martian and terrestrial rocks, but with no corresponding differences between terrestrial and Martian rocks. Zinc isotopic compositions for the majority of mare basalts (0.7–1.9‰) can be attained from between 10% to >90% evaporative loss of Zn using the different  $\alpha$  values shown in Fig. 3, whereas terrestrial and Martian samples do not require significant evaporative loss. Therefore, the conditions responsible for Zn isotopic fractionation in lunar rocks do not appear to have existed, or have been overprinted, for terrestrial and Martian igneous rocks.



**Figure 3 | Zinc isotopic fractionation as a function of the fraction of Zn remaining during open-system Rayleigh distillation.** Results are shown for three different fractionation factors ( $\alpha$ ) between vapour and melt versus the range of Zn isotopic compositions measured for lunar samples. The two grey areas represent the  $\delta^{66}\text{Zn}$  ranges of lunar mare basalts and the 12018/10017/pyroclastic glasses.

There is strong evidence that 'planet-scale' evaporation of Zn during the Moon-forming event, rather than 'localized-scale' evaporation processes during volcanic eruption into hard vacuum (as suggested for Cl isotopes<sup>23</sup>), is responsible for the Zn isotopic character of mare basalts. The limited range in Zn isotopic compositions and systematically low Zn abundances for 19 of the 21 studied mare basalts, combined with the identical  $\delta^{66}\text{Zn}$  values for low- and high-Ti mare basalts, support a large-scale planetary volatile depletion process. Low-Ti mare basalts are the predominant form of basalt exposed on the lunar surface (~90%; ref. 24), and their prevalence over high-Ti mare basalts is consistent with magma ocean crystallization models that indicate >78% of the lunar mantle would be dominated by olivine and orthopyroxene, whereas ilmenite-rich cumulates formed after 95% crystallization<sup>25</sup>. Thus, low-Ti mare basalts are often considered more representative of lunar mantle composition than high-Ti mare basalts (for example, ref. 26) and so the identical Zn isotopic composition of low- and high-Ti mare basalts points towards identical processes acting on both basalt types, despite conspicuously differing modes of origin and lunar mantle sources.

The evidence for extreme volatile depletion of the Moon from Zn isotopes and Zn abundance contrasts with the greater Zn abundance and broadly chondritic Zn isotopic compositions of Earth and Mars. The simplest explanation for these differences is that conditions during or after formation of the Moon may have led to more extensive volatile loss and Zn isotopic fractionation than experienced by Earth or Mars. The Zn isotopic homogeneity in lunar materials suggests that this would have to result from a large-scale process rather than from small-scale processes, or from hydrodynamic escape<sup>15</sup>. Given these lines of evidence, the most likely large-scale event to explain evaporative Zn isotopic fractionation would be a wholesale melting event associated with the formation of the Moon. The Zn isotope data therefore support existing dynamical models that argue for a giant impact event as the origin of the Earth–Moon system<sup>11,12,27</sup>.

Whereas Zn abundances and isotopic compositions for Earth, the Moon and Mars provide compelling evidence for evaporative loss of volatile elements during lunar formation, they also provide important insights into planetary volatile inventories. In the case of the Moon, studies have shown that pyroclastic glass beads have elevated volatile contents, and contain water<sup>28</sup>, suggesting a volatile-rich reservoir in the lunar interior. However, a study of Cl isotopes<sup>23</sup> suggests a volatile-depleted Moon, and our results for Zn isotopes suggest that the source regions of mare basalts are strongly volatile-depleted. In contrast with mare basalts, the elevated Zn abundances and light  $\delta^{66}\text{Zn}$  values of lunar pyroclastic glasses are possibly consistent with derivation from a localized volatile-rich mantle reservoir within the Moon. For Mars, the identical Zn isotopic composition of Martian meteorites and terrestrial igneous rocks, combined with the elevated estimate of Zn abundance in the Martian mantle<sup>29</sup>, suggests a volatile-rich planet. Thus, Zn isotopic data for Earth, Mars and the Moon place fundamental constraints on planetary accretion, pointing to evaporative loss during the Moon-forming event but that evaporative loss of volatiles in Earth and Mars did not occur, or has been over-printed by later events.

## METHODS SUMMARY

Fragments (each of 500–1,000 mg) were leached in double-distilled water for 300 s in an ultrasonic bath. After removal from the water and drying, sample fragments were crushed to a homogeneous fine powder using an agate mortar and pestle. Samples were dissolved in a 4:1 mixture of ultra-pure HF/HNO<sub>3</sub> in Teflon beakers for four days. Zinc purification was achieved using anion-exchange chromatography using procedures described previously<sup>4</sup>, with recovery of  $99 \pm 1\%$ . Zinc was purified by anion-exchange chromatography. The samples were loaded in 1.5 M HBr on 0.25-ml AG-1X8 (200–400 mesh) ion-exchange columns and Zn was collected in 0.5 M HNO<sub>3</sub>. The Zn fraction was further purified by eluting the samples twice on a 100- $\mu\text{l}$  column with the same eluting solutions. Blanks were <10 ng and represent less than 1% of total measured Zn. Zinc isotopic compositions were measured on the ThermoElectron Neptune Plus multi collector-inductively coupled plasma-mass spectrometer housed at the Isotope Geochemistry Laboratory,

Washington University, St Louis. The Faraday cups were positioned to collect masses 62, 63, 64, 65, 66, 67 and 68. Possible <sup>64</sup>Ni isobaric interferences were controlled and corrected by measuring the intensity of the <sup>62</sup>Ni peak. A solution containing 500 p.p.b. Zn in 0.1 M HNO<sub>3</sub> was prepared for isotopic analysis. Isotopic ratios of Zn in all samples were analysed using a spray chamber combined with a 100  $\mu\text{l min}^{-1}$  PFA nebulizer. One block of 30 ratios, in which the integration time of one scan was 10 s, was measured for each sample. The background was corrected by subtracting the on-peak zero intensities from a blank solution. The instrumental mass bias was corrected by bracketing each of the samples with standards. External precision based on the JMC Lyon Zn standard was 0.05‰ per a.m.u. ( $2\sigma$ ).

**Full Methods** and any associated references are available in the online version of the paper.

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

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**Author Contributions** R.C.P. and F.M. performed zinc isotope and abundance measurements. All authors wrote the Letter and contributed to discussion and interpretation of results in the manuscript.

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## METHODS

We used methods for the purification and isotopic measurement of Zn described previously<sup>4,5,16,18,30,31</sup>. Briefly, 500–1,000 mg sample fragments were leached in double-distilled water for 300 s in an ultrasonic bath. After removal from the water and drying, sample fragments were crushed to a homogeneous fine powder using an agate mortar and pestle. Samples were dissolved in a 4:1 mixture of ultra-pure HF/HNO<sub>3</sub> in Teflon beakers for four days. Zinc purification was achieved using anion-exchange chromatography using procedures described previously<sup>4</sup>, with recovery of 99 ± 1%. Zinc was purified by anion-exchange chromatography. The samples were loaded in 1.5 M HBr on 0.25-ml AG-1X8 (200–400 mesh) ion-exchange columns and Zn was collected in 0.5 M HNO<sub>3</sub>. The Zn fraction was further purified by eluting the samples twice on a 100- $\mu$ l column with the same eluting solutions. Blanks were <10 ng and represent less than 1% of total measured Zn. Zinc isotopic compositions were measured on the ThermoElectron Neptune Plus multi collector-inductively coupled plasma-mass spectrometer housed at the Isotope Geochemistry Laboratory, Washington University, St Louis (see Supplementary Table 2 for parameters). The Faraday cups were positioned to collect the masses 62, 63, 64, 65, 66, 67 and 68. Possible <sup>64</sup>Ni isobaric interferences were controlled and corrected by measuring the intensity of the <sup>62</sup>Ni peak. A solution containing 500 p.p.b. Zn in 0.1 M HNO<sub>3</sub> was prepared for isotopic analysis. Isotopic ratios of Zn in all samples were analysed using a spray chamber combined with a 100  $\mu$ l min<sup>-1</sup> PFA nebuliser. One block of 30 ratios, in which the integration time of one scan was 10 s, was measured for each sample. The background was corrected by subtracting the on-peak zero intensities from a blank solution. The instrumental mass bias was corrected by bracketing each of the samples with standards. External precision based on the JMC Lyon Zn standard was 0.05‰ per a.m.u. (2 $\sigma$ ).

Sample selection for this study was designed to complement and expand the existing high-precision Zn isotopic data available for the Moon (for example, refs 4, 18), and to investigate the Zn isotopic composition of Mars. Previous Zn isotopic studies of the Moon have focused on high-Ti mare basalts, high-Ti pyroclastic glass beads, and lunar soils. We have expanded the high-precision data set through the analysis of seven Apollo 12 and four Apollo 15 low-Ti mare basalts. We have also measured LaPaz Icefield (LAP) 02205, a low-Ti mare basalt meteorite with possible association to Apollo 12 mare basalts (for example, ref. 32), and MacAlpine Hills (MAC) 88105, an anorthositic regolith breccia paired with MAC 88104 (for example, refs 19, 33). From the available Martian Shergotty-Nakhla-Chassigny (SNC) meteorite suite, we measured Zn isotopic compositions in six shergottites (Shergotty, Zagami, Los Angeles, Elephant Moraine (EETA) 79001, Allan Hills (ALHA) 77005, Sayh al Uhaymir (SaU) 008), three nakhlites (Nakhla, Lafayette, Miller Range (MIL) 03346) and the orthopyroxenite ALHA 84001. We also prepared a terrestrial granite (G-2, a granite from Sullivan Quarry, Rhode Island, USA) and basalt (BCR-1, from the Columbia River region, Oregon, USA) for comparison with Martian and lunar samples.

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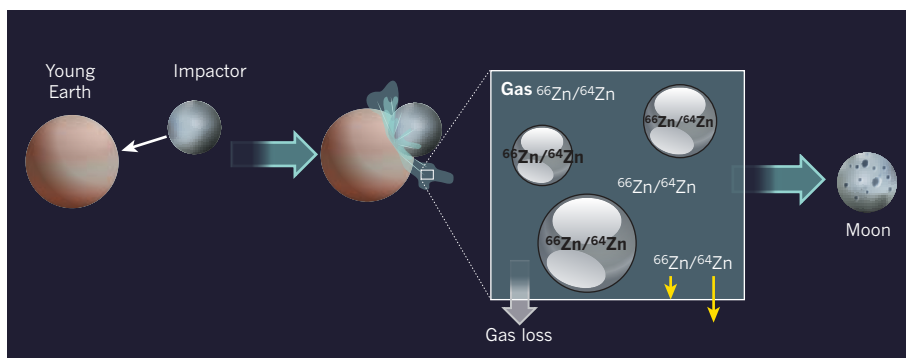
## Galvanized lunacy

The finding that magmatic material from the Moon is more enriched in the heavy isotopes of zinc than its terrestrial and Martian analogues prompts fresh thinking about the origin of our natural satellite. [SEE LETTER P.376](#)

TIM ELLIOTT

Like the perfect Martini, the Moon has a reputation for being dry. Most obviously, it lacks oceans on its surface, other than those of crystallized magma. Recent evidence suggests, however, that the Moon has a touch of damp. Several studies have found concentrations of water much higher than expected in lunar minerals<sup>1,2</sup> and quenched magma<sup>3,4</sup>. From these observations, it has been suggested that the interior of the Moon may contain similar concentrations of water to those in Earth's mantle. Yet it is difficult to make accurate measurements of water, and rather few samples are amenable to robust analysis. Instead, the abundances of less analytically challenging volatile elements can be studied as proxies for water, allowing investigation of a wider and probably more representative range of lunar materials. In this issue, Paniello and colleagues<sup>5</sup> provide a new perspective on the history of the Moon's volatile elements, based on zinc and, in particular, its isotopic composition. They show that the Moon has a distinctly heavier Zn isotopic composition than Earth, consistent with the satellite having experienced a marked depletion in volatiles.

From our everyday experience, we would not consider Zn to be volatile: there is generally little swooning from its vapours. However, in cosmochemistry, elements that condense at relatively low temperatures (less than about 1,000 °C) from a tenuous gas, as Zn does, are termed volatile. The abundance of these volatile elements varies greatly between planetary bodies — which can be sampled by means of meteorites — but the origin of this variability remains poorly understood. From the first analyses of samples returned by the Apollo missions, it has been clear that the Moon has very low abundances of volatile elements. Yet it is a considerable challenge to translate elemental concentrations measured in the erupted, but now cooled, magmas (melts) at the surface, into a global volatile inventory for the Moon. The power of isotopic measurements, such as those made by Paniello *et al.*, is that isotopes, unlike elements, are not significantly fractionated from each other during magmatic processes, and so erupted melts should faithfully record



**Figure 1 | Zinc isotope enrichment during Moon formation.** The diagram illustrates some of the general processes that could have generated a Moon that has a low abundance of volatile elements but is enriched in the heavy isotopes of zinc, as Paniello and colleagues' study indicates<sup>5</sup>. A collision between the young Earth and another planetary body produces the debris from which the Moon formed. The debris consists of silicate melt (spheres) and gas, some of which is lost to the surrounding environment. In chemical equilibrium, the melt phase will invariably have an abundance of the zinc-66 isotope relative to that of zinc-64 ( $^{66}\text{Zn}/^{64}\text{Zn}$ ) that is higher (black lettering) than that of the gas. Any gas loss from the system will thus result in a Moon both isotopically heavier than the starting composition of the debris and with a lower abundance of Zn. The mechanism of gas loss itself can also contribute to heavy-isotope enrichment of the debris. The lighter isotope  $^{64}\text{Zn}$  has a higher mean velocity than the heavier  $^{66}\text{Zn}$ , and so can preferentially escape the gravitational bond to the Moon (yellow arrows).

the composition of their deeper sources.

Using this isotopic approach, the authors show that the abundance ratio of Zn isotopes with mass numbers 66 and 64 ( $^{66}\text{Zn}/^{64}\text{Zn}$ ) is nearly constant for a range of lunar magma types, including those thought to be most representative of the interior. Therefore, the results provide a well-constrained value of this ratio for the Moon as a whole. Most significantly, Paniello *et al.* find that this value is markedly higher — by about 1.5 parts per 1,000 — than that of Earth, Mars and primitive meteorites, which are believed to be the building blocks of the rocky planets. This difference may seem minor, but in terms of isotopic differences between planetary bodies, it is huge.

The exact mechanism by which the Zn isotopic composition of the Moon became heavier than that of Earth is unclear; however, most processes of volatile loss that can be envisaged predict this as an outcome. For example, during condensation of the Moon from a cloud of gas and melt, the heavy isotopes of Zn should have preferentially partitioned into the melt phase (Fig. 1). If the gas phase never fully accreted onto the Moon, the Moon would be left poor in volatiles, but

also enriched in the heavy isotopes of volatile elements such as Zn. This diagnostic isotopic signature of volatile depletion has long been sought in lunar samples, and thus its eventual documentation by Paniello *et al.* is notable. Indeed, it was a major surprise that such an effect was not found in a high-precision isotope study<sup>6</sup> of the volatile element potassium almost 20 years ago.

More recently, researchers have reported<sup>7</sup> distinct isotopic differences between lunar and terrestrial chlorine, perhaps a more familiar volatile element. However, the lunar chlorine isotopic composition is not constant, and its trend to heavy values is argued to reflect variable loss of gas from magmas during magma eruption, rather than the interior composition of the Moon<sup>7</sup>. A more complete understanding of planetary volatile evolution requires an explanation of the contrasts in the isotopic signatures of these supposed chemical brethren. Of potential importance in this quest are better estimates of element volatilities under the specific conditions in which the Moon formed. Paniello *et al.* follow a traditional approach of assuming elemental condensation temperatures calculated for a hydrogen-rich, 'nebular' environment<sup>8</sup>. These values are appropriate

for the conditions of the earliest Solar System but not for the accretion of the Moon from a silicate-rich debris disk (Fig. 1).

Paniello and colleagues' new Zn isotope data may also contribute to the reawakened discussion of the very mechanism by which the Moon formed. A theory known as the giant-impact hypothesis — according to which our natural satellite is the outcome of reassembled debris from a collision between the proto-Earth and another planetary body — has dominated recent thinking about lunar genesis. In particular, an oblique-impact scenario was shown<sup>9</sup> to reproduce many of the physical and chemical attributes of the Moon. However, this model predicts that the Moon should be comprised predominantly of material from the colliding impactor rather than the target proto-Earth. Instead, the Moon has

proven to be embarrassingly similar to Earth in several isotopic characteristics<sup>10–12</sup>, seemingly requiring it to be derived almost wholly from Earth. Models have thus investigated mechanisms by which the isotopic composition of the Earth and Moon could have become homogenized after the impact<sup>13</sup>. The notable differences in Zn isotopic composition between Earth and Moon documented by Paniello *et al.* may be more readily reconciled with an entirely new model for Moon formation, in which the impactor hits a rapidly spinning proto-Earth<sup>14</sup>. This flurry of recent developments emphasizes a waxing interest in our ever-puzzling satellite. ■

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## CANCER THERAPY

# Tumours switch to resist

**Tumour cells can respond to targeted immune-cell therapies by losing proteins that mark them as being cancerous. Subverting this resistance mechanism may lead to more durable cancer-treatment strategies. SEE LETTER P.412**

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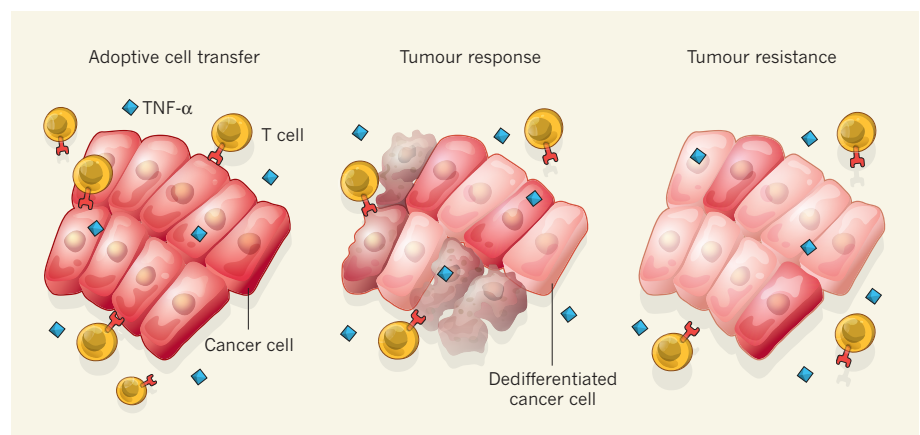
Decades of research have yielded methods for cancer treatment that can be more specifically tailored to a patient's cancer than broader strategies such as radiotherapy or chemotherapy. However, these methods — which include immunotherapy and therapies targeted at cancer-causing genes — are dogged by the problem of acquired resistance, in which many patients initially respond to the treatment but subsequently become unresponsive and experience relapse. Resistance is commonly thought to arise from the proliferation of a small proportion of resistant cells in a mixed tumour-cell population. But on page 412 of this issue, Landsberg *et al.*<sup>1</sup> show, using a mouse model of melanoma, that resistance to a promising form of immunotherapy can develop when cancer cells change their protein-expression profile in response to treatment\*.

Cancer immunotherapies are designed to initiate or boost a person's immune response to a tumour. One way of doing this is by adoptive cell transfer (ACT), in which patients receive transfusions of immune cells called T cells that target cancer-specific antigens (an antigen is a substance that elicits responses from

the B cells and T cells of the immune system). By contrast, oncogene-targeted therapies work by reducing the function of certain mutated proteins that are overactivated in tumour cells. Although much progress has been made in determining why patients relapse with oncogene-targeted therapies, little is known

about the mechanisms underlying acquired resistance in patients receiving ACT. However, there is generally a high initial response rate to ACT, so understanding what then happens to lead to resistance is a challenge worthy of investigation.

The most common sources of tumour-antigen-specific cells for ACT are tumour-infiltrating lymphocytes (TILs) or blood T cells that are isolated from the patient and modified before being reintroduced. In the case of TILs, which already have tumour specificity, this involves expanding the cell population and activating the cells. In therapies using blood T cells, which are initially not tumour specific, the cells' antigen receptors are first genetically engineered to recognize tumour antigens<sup>2</sup>. Tumour responses tend to last longer in TIL-based ACT, probably because each TIL preparation might target several tumour antigens simultaneously<sup>3</sup>. However, TILs can be isolated



**Figure 1 | Escape by dedifferentiation.** Cancer cells express certain antigens that are not expressed by non-cancerous cells (red colour on cells indicates antigen expression). Adoptive cell transfer is a type of immunotherapy in which immune cells called T cells with receptors that specifically recognize these defining antigens are transferred into patients, where they initiate an immune response that kills the cancer cells. Landsberg *et al.*<sup>1</sup> show that, in the process of cancer-cell killing, the tumour-infiltrating T cells release the inflammatory molecule TNF- $\alpha$ , which causes some of the tumour cells to stop expressing of some of their cancer-specific antigens. These 'dedifferentiated' cancer cells are no longer recognized by the T cells, resulting in resistance to the therapy and tumour regrowth.

\*This article and the paper under discussion<sup>1</sup> were published online on 10 October 2012.