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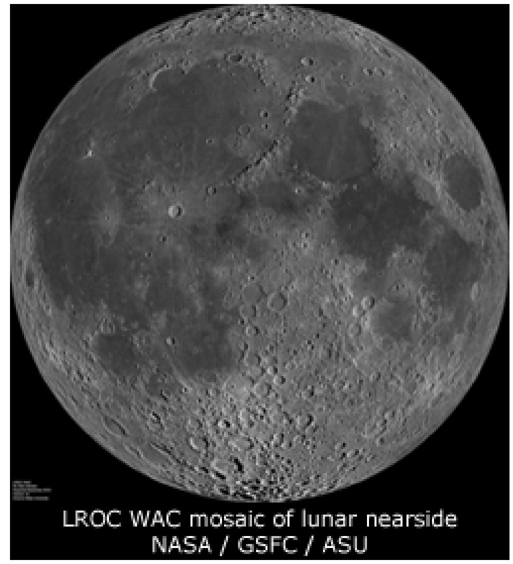
PSRD Discoveries



Headline Article

December 10, 2012

Zinc Isotopes Provide Clues to Volatile Loss During Moon Formation

--- Ratios of zinc isotopes indicate evaporation of zinc (and other volatiles) during formation of the Moon.

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Isotopic analyses of the oxygen and the **refractory** elements chromium, tungsten, and titanium show that Earth and Moon have the same isotopic compositions for these elements. In contrast, Randal Paniello and Frédéric Moynier (Washington University in St. Louis) and James Day (Scripps Institution of Oceanography, La Jolla) report from high-precision analyses of the isotopes of the **volatile** element zinc that the Moon differs significantly from Earth in the abundances of zinc isotopes. The authors ascribe this difference to evaporation processes during formation of the Moon by a giant impact. The refractory elements probably did not vaporize significantly during lunar formation, leaving their isotopic compositions unscathed by this significant event in Solar System history.

Reference:

- Paniello, R. C., Day, J. M. D., and Moynier, F. (2012) Zinc Isotopic Evidence for the Origin of the Moon, *Nature*, vol. 490, p. 376-379, doi: 10.1038/nature11507.
- **PSRDpresents:** Zinc Isotopes Provide Clues to Volatile Loss During Moon Formation --**Short Slide Summary** (with accompanying notes).

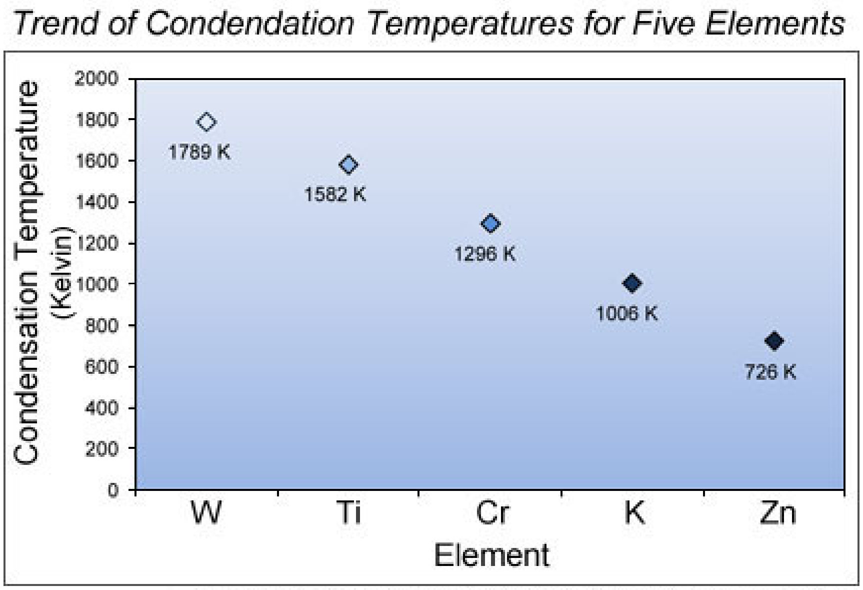
Indistinguishable Isotopic Compositions of Earth and Moon

Cosmochemists have known since the 1970s that Earth and Moon have the same oxygen isotopic compositions. They interpreted this to mean that the two bodies formed from a uniform reservoir in the inner Solar System. However, Kaveh Pahlevan and David Stevenson (Caltech) suggested that the uniformity of oxygen isotopes might have been caused by homogenization (equilibration) during the formation of the Moon by a giant impact (PSRD article: **Compositional Balancing Before Moon Formation**).

More recently, cosmochemists have shown that the isotopes of other elements are also the same in Earth and Moon. The prominent ones are all refractory elements that condense at high temperature in the **solar nebula**, so presumably behave in similar fashion during lunar formation. The key elements are tungsten (W, described by Mathieu Touboul and colleagues in 2007), titanium (Ti, Junjun Zhang and colleagues in 2012), and chromium (Cr, Gunter Lugmair and

Alexander Shukolykov in 1998). We described the titanium isotopic work in the PSRD article: **Titanium Isotopes Provide Clues to Lunar Origin**. The important point about the refractory nature of these elements is that the high-temperature processing that occurred during lunar formation might not have led to significant differences in isotopic composition, or that the large impactor and the proto-Earth were compositionally similar, or that, contrary to models for lunar origin, the Moon formed mostly from the Earth, not the impactor.

In any case, Randal Paniello and colleagues looked at a significantly more volatile element, zinc (Zn), to see if it conforms to the trend set by the refractory elements. The elements and their **condensation** temperatures (a measure of how refractory they are) appear in the diagram below.



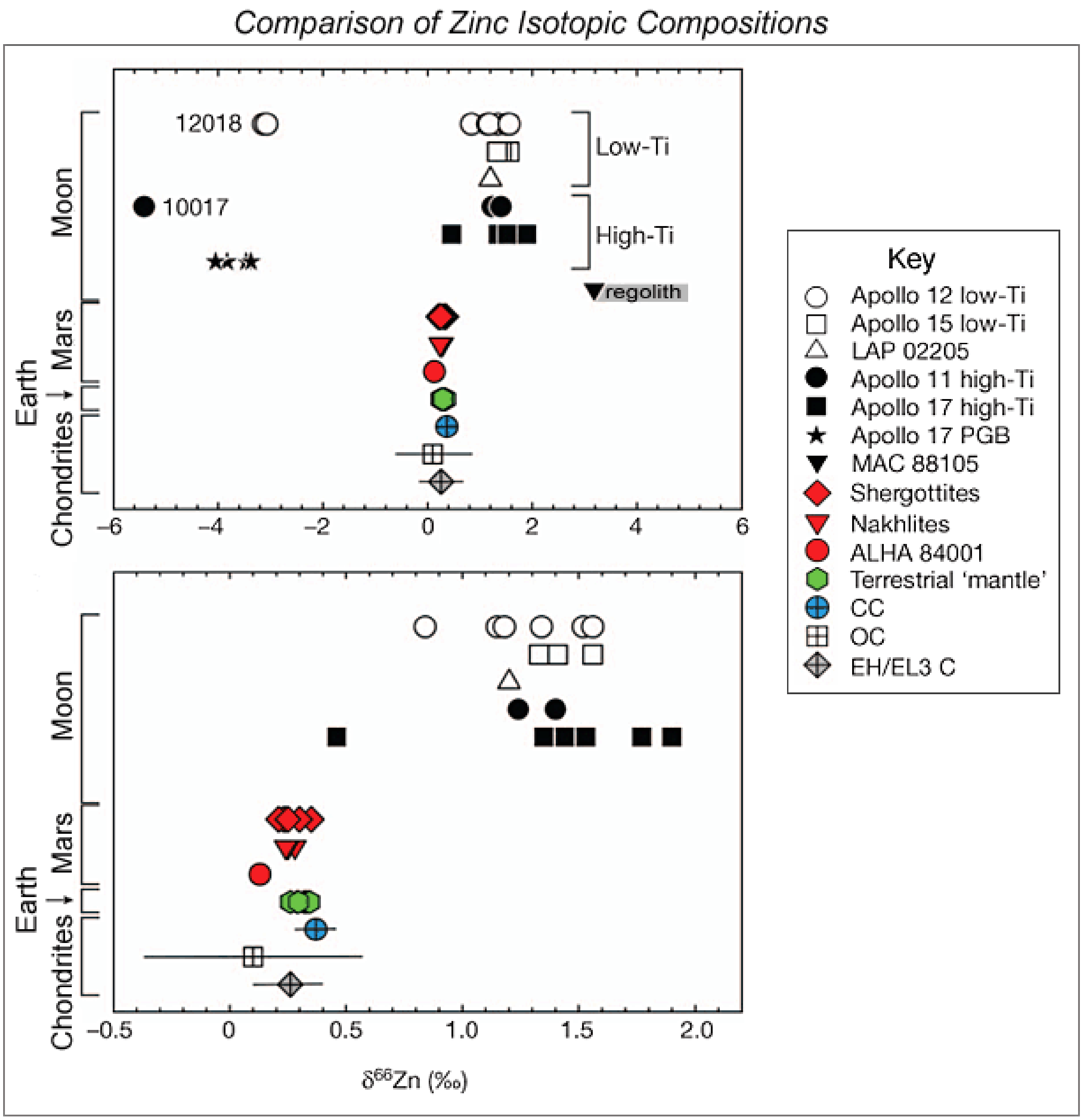
(Courtesy of Katharina Lodders, Washington University in St. Louis.)

Condensation temperatures (in Kelvin) for the refractory elements tungsten (W), titanium (Ti), and chromium (Cr), and for the moderately volatile elements potassium (K) and zinc (Zn). The isotopic compositions of W, Ti, and Cr are virtually the same in the Moon and Earth, whereas Zn isotopic composition (as shown by Randal Paniello and colleagues) are distinctly different (see below). Inexplicably, the isotopic composition of K is the same throughout the sampled Solar System. The condensation temperatures are calculated from the thermodynamic properties of the elements and compounds they form and assume that the condensation takes place in the solar nebula at a pressure of 1/10,000 atmospheres. The temperatures were calculated by Katharina Lodders (Washington University in St. Louis).

Zinc Isotopes

As usual for isotopic measurements, analysis of the zinc isotopes involved a sequence of chemical steps to separate the zinc from the rest of the rock, and then measurements in a mass spectrometer. Paniello and colleagues did the measurements using an inductively coupled plasma-mass spectrometer in the Isotope Geochemistry Laboratory at Washington University in St. Louis. The instrument allows several isotopes to be analyzed simultaneously, enhancing the precision of the analyses.

The results are shown in the diagram below, and compared to those for terrestrial samples, Martian meteorites, and assorted groups of **chondrites** (primitive meteorites). The data for Martian meteorites are also a new, important contribution by Paniello and colleagues. The diagram shows data reported as $\delta^{66}Zn$, geochemists' favorite way to express isotopic composition. It is simply the ratio of zinc-66 to zinc-64, divided by the same ratio in a standard (a well-characterized terrestrial sample), multiplied by 1000. One (1) is subtracted from the ratio of the ratios before the multiplication by 1000 takes place to show deviations from the terrestrial standard. If $\delta^{66}Zn$ is zero, the ratio is the same as in Earth, if negative the zinc isotopes are lighter than in Earth (the ratio is lower than in Earth), and if positive zinc isotopes are heavier than in Earth (the ratio is higher than in Earth).

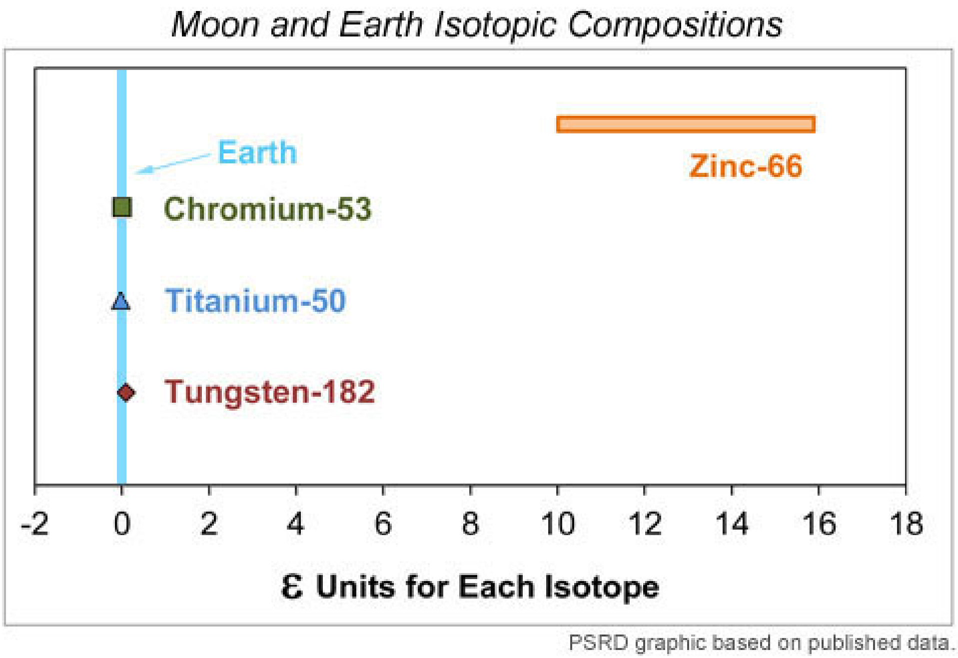


(Paniello *et al.*, 2012, *Nature*, v. 490, p. 376-397, doi:10.1038/nature11507.)

Zinc isotopic composition expressed as $\delta^{66}Zn$ in lunar samples (and lunar meteorites LAP 02205 and MAC 88105) measured by Randal Paniello and colleagues, compared to samples of the terrestrial mantle, Martian meteorites, and carbonaceous chondrites (CC), ordinary chondrites (OC) and enstatite chondrites (EH/EL3 C). The top diagram has an expanded scale compared to the lower one and shows that three lunar sample types plot at much lower values than the other planetary materials. Most lunar samples have heavier zinc (higher $\delta^{66}Zn$) than do the Earth, Mars, and chondrites. This suggests that zinc isotopes were uniform throughout the Solar System, even during formation of Earth and Mars, but that processes operating during formation of the Moon enriched zinc in ^{66}Zn over ^{64}Zn. Paniello and his colleagues suggest that evaporation during formation of the Moon caused that enrichment. It is not clear why the three lunar samples with low $\delta^{66}Zn$ are so different from other lunar samples. Error bars are shown in a few cases, but in most the analytical uncertainty is the size of the symbols in the lower diagram.

The data clearly show that most lunar samples measured have distinctly higher $\delta^{66}Zn$ than the other planetary materials. Earth and Mars likely averaged numerous planetesimals during their **accretion**. The isotopic compositions of the planetesimals were probably similar anyway, as shown by the narrow range in $\delta^{66}Zn$ of chondrites. The Earth-Mars similarity, reported for the first time by Paniello and coauthors, shows that planetary accretion did not in general separate (fractionate) one isotope of an element from another. Paniello and colleagues argue that the big difference between most of the Solar System and the Moon must reflect conditions during formation of the Moon, which planetary scientists believe was a giant impact involving a large, possibly Mars-sized impactor, smashing into a stillaccreting Earth. In fact, the giant impact was the last big accretion event in Earth's construction, and it led to formation of the Moon.

The clear fractionation of the zinc isotopes compared to the uniformity in the isotopes of W, Ti, and Cr are shown in the diagram below. W, Ti, and Cr isotopic compositions are strikingly similar to those of Earth. In the diagram, the isotopic differences are expressed in epsilon units, which are calculated by multiplying by 10,000 rather than 1000 to get delta units. Thus, their lunar values differ from those of Earth by only a few parts in ten thousand. The zinc data are plotted in the diagram in epsilon units, emphasizing that they are markedly different in Earth and Moon.



Deviation in the ratios of $^{53}Cr/^{52}Cr$, $^{50}Ti/^{47}Ti$, $^{182}W/^{184}W$, and $^{66}Zn/^{64}Zn$ in the Moon compared to Earth, in parts per ten thousand (epsilon units). Only lunar data with elevated values (see diagram above) are plotted here. The large difference between Earth and Moon suggests a process that efficiently fractionated the heavier zinc isotope from the lighter one, likely the energetic Moon-forming giant impact.

Why would a giant impact fractionate the zinc isotopes? A related question is why did it not fractionate the isotopes of tungsten, titanium, and chromium? The answer may simply be that the impressively energetic Moon-forming event melted and vaporized substantial amounts of Earth and the impactor. This led to loss of many volatile elements and fractionation of their isotopes. + of volatile elements from the molten material could have fractionated the zinc isotopes, assuming that the gaseous envelop around the proto-Earth did not condense completely before the Moon formed. Isotopes fractionate during evaporation by a process called Rayleigh distillation, with the lighter isotope entering the gas (evaporating) more readily than the heavier isotopes. This explains the enrichment in the heavier isotope ^{66}Zn (higher $\delta^{66}Zn$) in the lunar samples. The refractory elements W, Ti, and Cr did not participate in this fractionation fest because, well, they're refractory—they tend to remain in solids or liquids (magma) rather than leaking into the gas. The fact that the Moon is clearly depleted compared to the Earth in elemental zinc and other volatile elements supports this idea.

Nagging Questions

As usual in cosmochemistry, there are a few nagging questions. One is why some of those lunar samples have low $\delta^{66}Zn$. Two of the samples are typical basalts from the lunar maria (10017 and 12018), not notably different from their lithologic compatriots that have high $\delta^{66}Zn$. The third sample (four analyses) is the Apollo 17 orange glass, the product of an explosive eruption billions of years ago. Paniello and coworkers note that this sample might have lost zinc initially when it erupted, but then a significant fraction of it condensed back onto glassy beads. They present some evaporation calculations that show this is reasonable. However, it is not clear that this process can explain the low $\delta^{66}Zn$ in the two typical lava flows from the maria. Perhaps additional detailed work on the distribution of zinc in these samples is warranted.

Another annoying question is why another relatively volatile element, potassium (K), does not differ in its isotopic composition in the Moon and Earth. In fact, Munir Humayun and Robert Clayton (University of Chicago) showed that all Solar System materials have the same $^{41}K/^{39}K$. No fractionation, in spite of the K concentration varying substantially throughout the Solar System. If the Moon lost volatile elements by fractionation during the giant impact, why did K isotopes not separate from each other while Zn did?

The answer to these questions might lie in additional sample analyses (and probably acquisition of additional samples) and comparison of the isotopes of other elements, such as chlorine (which Paniello and coworkers single out) and elements that are even more volatile than zinc. The trouble is that those highly volatile elements are present in very tiny concentrations (parts per billion). That might not be a permanent problem as history shows that cosmochemists and geochemists continually improve the accuracy, precision, and detection limits of isotope analyses.

Additional Resources

Links open in a new window.

- **PSRDpresents:** Zinc Isotopes Provide Clues to Volatile Loss During Moon Formation --**Short Slide Summary** (with accompanying notes).

- Lugmair, G. W. and Shukolyukov, A. (1998) Early Solar System Timescales According to ^{53}Mn-^{53}Cr Systematics, *Geochimica et Cosmochimica Acta,* vol. 62, pp. 2863-2886. [**NASA ADS link**]
- Paniello, R. C., Day, J. M. D., and Moynier, F. (2012) Zinc Isotopic Evidence for the Origin of the Moon, *Nature,* vol. 490, p. 376-379, doi: 10.1038/nature11507. [**NASA ADS link**]
- Touboul, M., Kleine, T., Bourdon, B., Palme, H., and Wieler, R. (2007) Late Formation and Prolonged Differentiation of the Moon Inferred from W Isotopes in Lunar Metals, *Nature,* vol. 450, p. 1206-1209. [**NASA ADS link**]
- Washington University in St. Louis Newsroom article by Diana Lutz (October 17, 2012) Moon Was Created in Giant Smashup. **http://news.wustl.edu/news/Pages/24148.aspx**
- Washington University in St. Louis, Inductively Coupled Plasma-Mass Spectrometer in the Isotope Geochemistry Laboratory (**ICP-MS**).
- Zhang, J., Dauphas, N., Davis, A. M., Leya, I., and Fedkin, A. (2012) The Proto-Earth as a Significant Source of Lunar Material, *Nature Geoscience,* vol. 5(4), p. 251-255, doi:10.1038/ngeo1429. [**NASA ADS link**]