

to the phylogenetic or phenotypic variability observed in the lab.

Martiny and co-workers filled this observational gap by providing a global-scale view of C:N:P variations in marine organic matter. With a compilation of both old and new observations, they identified patterns of C:N:P variability across a wide range of ocean biomes (Fig. 1). Their results demonstrated clear and coherent variations in organic matter stoichiometry. In the nutrient-starved subtropical gyres, organic matter C:N:P ratios were as high as 226:37:1, whereas in nutrient-rich high-latitude regions they were as low as 66:11:1, consistent with the conclusions drawn from culture experiments. Thus, the global-scale variations in organic matter C:N:P appear to reflect shifts in the composition of plankton communities: fast-growing plankton with low C:N:P such as diatoms dominate in nutrient-replete waters, while slow-growing plankton with high C:N:P survive in the deserts of the subtropical gyres. The patterns of C:P variability in organic matter observed by Martiny and co-workers were subsequently confirmed by inversions of global nutrient and carbon data¹¹, and by analyses of nutrient and oxygen data¹², adding to previous models that had demonstrated large regional variability in plankton N:P ratios^{13,14}.

The work of Martiny and co-workers ignited interest in the implications of flexible plankton C:N:P stoichiometry for the ocean's carbon cycle. Model simulations that included flexible C:P stoichiometry of phytoplankton did not show the high-latitude dominance of the biological pump that characterized previous constant-stoichiometry models¹⁵. Because low-latitude plankton have higher C:P ratios than their high-latitude counterparts, any changes in the delivery of nutrients to low-latitude oceans can have a much greater impact on the biological pump than comparable changes

in the high latitudes. Flexible plankton C:N:P stoichiometry also tends to buffer the biological pump response to climate change. As the oceans warm and become more stratified, nutrient supply to the surface ocean is cut off, and productivity declines. If the ratio of carbon to nutrients in the plankton increases in response, the productivity loss is counteracted¹⁶.

Anthropogenic climate change is affecting ocean ecosystems in ways that will cause substantial stoichiometric shifts in plankton. In addition to expansion of low-nutrient regions that favour survivalist plankton with high C:N:P ratios, warmer ocean temperatures promote higher C:P and N:P ratios of plankton^{17,18}, and enhance the activity of C-mobilizing enzymes, further contributing to increased C:N:P of plankton¹⁹. Rising CO₂ levels may also help shift plankton C:N and C:P ratios higher²⁰. The overall effects of climate change thus appear to favour a stoichiometric shift toward more C-rich and nutrient-poor organic matter (Fig. 1).

The effects of this stoichiometric shift will cascade into other elemental cycles, such as ocean oxygen and nitrogen cycling. Many regions of the ocean are subject to hypoxic or even anoxic conditions. Multiple forces conspire to push oxygen levels even lower, including rising temperatures, stagnating circulation and coastal eutrophication. If stoichiometric shifts make organic matter increasingly C-rich and nutrient-poor, this will exacerbate the deoxygenation problem as microbes consume more oxygen to metabolize nutrients. A higher plankton N:P ratio will also affect the balance of the ocean's nitrogen cycle: as nitrogen is drawn out of the surface ocean, the ecological niche of nitrogen-fixing phytoplankton will expand¹⁴, in turn pushing the total nitrogen inventory of the ocean higher (Fig. 1).

The interactions of these perturbations to elemental cycles are complex and difficult to predict. Thanks to the work of Martiny et al.¹ and others, we are beginning to develop a process-level understanding of plankton elemental composition that can be integrated into biogeochemical models, yielding more accurate predictions of ocean CO₂ uptake, ocean nutrient balance, and ocean deoxygenation. □

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ANNIVERSARY RETROSPECTIVE

Telltale tungsten and the Moon

Advances in high-precision isotopic analysis have provided key constraints on the origin and early evolution of the Earth and Moon. Measurements of the isotopes of tungsten provide the most stringent constraints on this history.

Kaveh Pahlevan

The Earth–Moon system is currently thought to have emerged from the impact of two planet-sized bodies towards the end of planetary accretion¹. Although this idea is now more than four

decades old^{2,3}, new tools to test, develop and interrogate the giant-impact hypothesis have come of age over the past decade. An isotopic resemblance for lunar and terrestrial rocks was recognized upon initial analysis

of the lunar samples returned by the Apollo program, but recent advances in analytical techniques have revealed the scope and magnitude of the isotopic similarities and differences between the Earth and

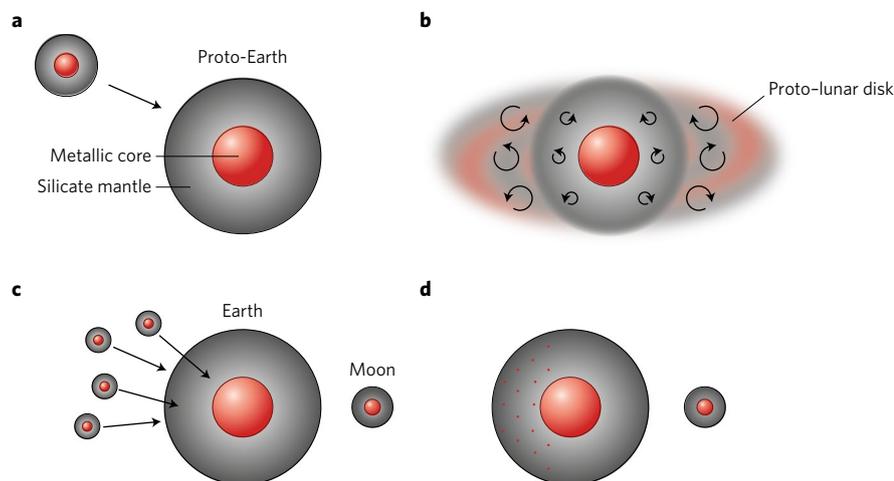


Fig. 1 | A view of the evolution of the Earth–Moon system as revealed by high precision isotope measurements. **a**, The Moon-forming giant impact between a differentiated Earth and impactor. **b**, Post-impact isotopic equilibration of the post-impact Earth and the vaporized proto-lunar disk through mixing of a silicate vapour atmosphere. **c**, Preferential late accretion of differentiated bodies onto the Earth following lunar accretion. **d**, The Earth–Moon system with a small tungsten isotopic offset.

Moon. The flood of new high-precision isotopic data has presented challenges to leading hypotheses of Moon formation and motivated new proposals of processes accompanying lunar origin that can reconcile the observed isotopic signatures. In particular, high-precision measurements of tungsten (W) reported in *Nature* in 2007⁴ and 2015^{5,6} have stirred the debate over how the Earth–Moon system evolved.

When lunar samples were first returned by the Apollo missions and analysed, a general isotopic similarity between Earth's mantle and the Moon suggested that the two bodies formed from similar material⁷. It was hypothesized that the similarity could be explained by an off-centre giant impact of a Mars-sized impactor onto the proto-Earth in which the Moon formed from material vaporized from Earth mantle and emplaced into orbit. In such a scenario, the Moon would be expected to be depleted in volatile elements relative to the Earth's mantle, but similar in isotopic composition for more refractory elements. However, in numerical simulations of this canonical giant-impact scenario, the debris disk is sourced mainly from the impacting body, whereas the Earth's mantle is sourced mainly from the proto-Earth. Since all planetary bodies from which we have samples show isotopic differences, it is commonly assumed that the proto-Earth and the impactor were isotopically distinct as well. Therefore, it was expected that a difference in the isotopic compositions of the Earth and Moon would ultimately be resolved with improvements in analytical precision.

Impressive analytical advances have been achieved, yet for several isotope systems, the Earth and Moon remain apparently identical to a precision difficult to explain by the canonical giant-impact process alone. Oxygen isotopic measurements are extremely similar relative to observed differences between planetary reservoirs. For instance, the difference in oxygen isotopes between Earth and Moon is less than a few percent of the difference between Earth and Mars^{8,9}. Such a high-precision match, like that observed for titanium isotopes¹⁰, is suggestive of a common source for terrestrial and lunar mantle material.

There is also a match for silicon isotopes. Silicon, however, can be sequestered into planetary cores with lighter isotopes preferentially partitioning into metals¹¹, resulting in isotopically-heavy mantles. Silicon isotope fractionation depends on the pressure and temperature conditions of core formation. Although it is unknown if substantial silicon is sequestered in Earth's core, the silicon isotopic identity of the Earth and Moon — again offset from Mars — suggests that the Moon formed from the Earth after the Earth's core had formed. However, despite the high precision of the measurements, the interpretation of the match in O, Ti and Si isotopes is ambiguous: it is also conceivable that the Earth and Moon were built independently, but from the same planetary building blocks.

Growing evidence for an apparent genetic link between lunar and terrestrial matter has been accompanied by an evolving and broadening debate about its origin — a

debate that has been energized by isotopic measurements of tungsten. Although each element conveys unique information, tungsten yields particularly strict constraints on the events accompanying lunar origin: ¹⁸²W is a decay product of ¹⁸²Hf (hafnium), and the tungsten isotopic composition of lunar and terrestrial samples record the relative behaviour of hafnium and tungsten during the first 60 million years of Solar System history — spanning core formation in the Earth and in the putative Moon-forming impactor. Moreover, because tungsten has affinities for metals but hafnium does not, core formation will result in isotopic heterogeneity. Even after ¹⁸²Hf becomes extinct, tungsten isotopes remain as tracers of geochemical equilibration expected during global differentiation events, such as the Moon-forming event. Unlike oxygen, titanium and silicon isotopes, the isotopes of tungsten would necessarily be affected by these planetary events, so any isotopic similarity between Earth and Moon materials cannot be explained by simply being sourced from the same precursors. Tungsten thus attains special significance in unravelling the lunar origin story.

Measurement of indigenous tungsten isotopes in lunar samples is hampered by the exposure to cosmic rays that results in heterogeneous compositions. Until recently, tungsten isotopic measurements had been used primarily as chronometers for early lunar differentiation. A decade ago, improved analytical techniques permitted the indigenous tungsten isotopic composition to be extracted from lunar samples⁴ revealing that diverse lunar rocks have identical indigenous tungsten isotopic compositions. This suggests differentiation of the lunar interior occurred after the ¹⁸²Hf had been used up, and thus relatively late Moon formation. Moreover, the tungsten isotopic composition of lunar materials is nearly identical that of Earth's mantle.

Like other known isotopes systems, the tungsten similarity supports a terrestrial origin of lunar material. But, since the tungsten isotopic system is so sensitive to core formation conditions and timing, the compositions of proto-Earth mantle and impacting body were probably distinct. Even if they were identical, metal-silicate equilibration in the post-impact Earth and debris disk would be expected to lead to tungsten isotopic heterogeneity in the absence of system-wide mixing. The isotopic similarity in tungsten thus supports equilibration of the terrestrial magma ocean and the proto-lunar disk in the aftermath of the giant impact (Fig. 1), as has also been proposed for oxygen¹².

The Moon-forming impact event is thought to have been a relatively late event that occurred towards the end of Earth formation, but planetary accretion continued after the Moon formed. Indeed, such late accretion has been invoked to explain the abundance of highly siderophile elements in the Earth's mantle, due to the fact that such elements would have partitioned almost entirely into the core during planetary differentiation. Following the initial measurements of the indigenous tungsten composition of lunar rocks, it was predicted that the delivery of highly siderophile elements, such as tungsten, to the Earth's mantle by late accretion would have produced an offset between the tungsten isotopic compositions of the silicate Earth and Moon^{13,14}. In 2015, two independent sets of measurements at high precision^{5,6} found a small offset — only about 25 ppm — between terrestrial and lunar samples, consistent with late accretion to an initially isotopically homogeneous Earth and Moon.

The small offset in tungsten's isotopic composition implies that the composition of the Earth and Moon immediately after Moon formation was incredibly similar: any differences would require even higher precision to observe. Although the isotopic similarity of Earth and Moon is consistent

with the giant-impact hypothesis, isotopic equivalence poses problems. If the Moon formed via impact of two planetary bodies, where is the isotopic evidence for the second body? Even if the two impacting bodies were isotopically indistinguishable, an isotopically identical Earth and Moon is not an inevitable or even likely outcome of a single giant impact event: metal–silicate equilibration would be expected to cause observable offsets in the silicate mantles of the Earth and Moon. Efficient mixing of Earth and Moon materials in the aftermath of the impact may be required.

The implications of the close, but not perfect, match in tungsten isotopes between the Earth and Moon are inspiring a new generation of models of both Moon formation and late accretion that aim to meet the refined constraints. For example, writing in *Nature Geoscience*, Marchi and colleagues¹⁵ propose that late accretionary impacts of large differentiated bodies — in which highly siderophile elements are sequestered in the planetesimal cores — can explain tungsten isotopic compositions of Earth and Moon materials. A decade of revelations of the isotopic identity of the Earth and Moon has challenged the canonical giant impact hypothesis of Earth–Moon formation, but has inspired

collaborations between isotope geochemists and impact modellers to address the many open questions. □

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ANNIVERSARY RETROSPECTIVE

Regional climate goes global

A compilation of hundreds of palaeoclimate records highlighted the extent of regional variability during the past 2,000 years, and therein the uniqueness of recent warming.

Helen McGregor

When it comes to climate change it is most often the global picture that captures the headlines: 2017 shaping up to be one of the warmest years on record; average global temperature rise of almost 1°C since 1880 CE (ref. ¹); atmospheric CO₂ has reached 403 ppm (ref. ²). But arguably it is how the global changes manifest at the local and regional scale that matters. Different temperatures, synoptic patterns and extremes that occur on the decadal-to-seasonal scale will most affect our day-to-day lives. In this context, the paper from the PAGES 2k Consortium³ published in *Nature Geoscience* in 2013 represents an important advance in understanding how both regional and global climate has varied over the past 2000 years.

Reconstructing regional (and global) climate back in time is a huge undertaking, which relies on climate proxies as diverse as tree rings, ice cores, speleothems and corals, as well as historical records. These proxy records are not evenly distributed, and not all span the full 2,000-year period. In around 2009 the Past Global Changes 2k (PAGES2k) Network formed to draw on the expertise of hundreds of palaeoclimate scientists with in-depth knowledge of the strengths and limitations of the various proxy records. From a total of 511 individual records, seven regional temperature syntheses were published — one for each continent except Africa and one for the Arctic region — and these efforts were assembled in the 2013 paper (Fig. 1). The PAGES 2k Consortium

found that the six continents studied, the Arctic region and the majority of individual records cooled over the millennia prior to 1900 CE. However, the rate of cooling varied across the regions and there was considerable variability at the multi-decadal scale. In all regions except Antarctica the cooling trend was reversed by warming over the past from the mid-nineteenth century.

These regional differences gave some clues to the drivers of the multi-decadal climate change. Changes in solar irradiance (for example, sunspot cycles); aerosols from volcanic eruptions; land-cover changes; changes in the Earth's orbit around the sun; and CO₂ levels are all known to force climate to change. These factors were all shown to be involved