

probability for muon-to-electron neutrino conversion would be the same as that for muon-to-electron antineutrino conversion. The T2K Collaboration has been able to study these oscillations with unprecedented precision, and has observed possible evidence of leptonic CP violation.

In the T2K experiment¹⁵, a neutrino beam is generated at the Japan Proton Accelerator Research Complex in Tokai. Here, highly accelerated protons hit a dense graphite target, producing large quantities of particles known as pions and kaons. These particles decay, giving rise to a neutrino beam (or an anti-neutrino beam, depending on the conditions used), which is monitored by two detectors 280 metres away.

The neutrinos subsequently travel through Earth without being stopped, but some are detected by the underground detector at the Kamioka Observatory 295 km away, deep beneath Japan's Mount Ikeno. The detector consists of 50,000 tonnes of ultrapure water surrounded by a vast array of light sensors. When a neutrino interacts with a neutron in the water, it can produce a muon or an electron, depending on its flavour. The T2K experiment detects the muons and electrons and discriminates between them, thereby identifying the flavour of the impinging neutrino and measuring the oscillation probability of muon-to-electron neutrino conversion.

The T2K Collaboration analysed data collected between 2009 and 2018, in both neutrino and antineutrino mode. By combining this with input from other neutrino-oscillation experiments, the researchers have disentangled the dependence of the conversion probability on various parameters and thus provide evidence of CP violation. The results exclude CP conservation (that is, they suggest that CP violation has occurred) at a 95% confidence level, and show that the CP-violating parameter is likely to be large. These results could be the first indications of the origin of the matter–antimatter asymmetry in our Universe.

The measurement is undeniably exciting. But extraordinary claims need extraordinary evidence – a confidence level of more than 99.9999% will be needed to be certain that leptonic CP violation has occurred. This requires a more precise measurement of the oscillation probability, with more intense beams, larger detectors and better-understood experimental features.

The next generation of large-scale, multi-purpose neutrino experiments is preparing for the challenge. The T2HK experiment in Japan¹⁶ is based on the same technology as T2K but will use the Hyper-Kamiokande detector, which will have ten times the mass of water and a more intense beam. Hyper-Kamiokande received official approval this February, and construction will start soon. And the

Deep Underground Neutrino Experiment¹⁷ (DUNE) will be based at the Sanford Lab in Lead, South Dakota; its technical-design report was published in February^{18,19}. DUNE will use a different detector technology consisting of four modules filled with several thousand tonnes of liquid argon, to detect an intense beam of neutrinos produced 1,300 km away at Fermilab in Batavia, Illinois. Smaller prototypes tested at CERN, Europe's particle-physics lab near Geneva, Switzerland, have demonstrated the feasibility of the large-scale DUNE detector. T2HK and DUNE therefore provide complementary techniques and measurements. They will probably give us a definitive answer in the quest for CP violation in the next 15 years.

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Geochemistry

Primordial nitrogen variations in the mantle

Rita Parai

A method for identifying atmospheric contamination of volcanic-gas samples reveals variations in the isotopic composition of nitrogen in the mantle, and provides a clearer view of the origins of this element in Earth's interior. **See p.367**

Earth's nitrogen-rich atmosphere contributes to the pleasant surface environment in which we live and breathe – but makes it very difficult to determine the nitrogen isotope composition of anything else. Pervasive atmospheric contamination of samples derived from Earth's mantle poses a formidable challenge to anyone investigating the origins and transport of volatile species, such as nitrogen and the noble gases, in the deep Earth. On page 367, Labidi *et al.*¹ report that they have used a 'clumped isotope' method to identify uncontaminated mantle nitrogen in volcanic-gas effusions and gases trapped in volcanic-rock samples. The relative abundances of isotopes in uncontaminated nitrogen vary among samples from different locations. The authors argue that these differences originate from Earth's formation and have survived approximately 4.5 billion years of mixing associated with mantle convection.

There are two stable nitrogen isotopes,

¹⁴N and ¹⁵N, and their relative abundances are expressed as $\delta^{15}\text{N}$ values – the parts per thousand deviation of the ¹⁵N/¹⁴N ratio from a standard value. The nitrogen isotopic compositions of mantle-derived samples can provide insight into a wide range of topics, from the mix of planetary building blocks that brought volatile species to Earth during its formation², to the transport of atmospheric nitrogen into the mantle through the sinking of tectonic plates over time³.

Apart from the proportions of ¹⁴N and ¹⁵N in a sample, the way that isotopes are distributed between molecules also provides information. An isotopologue is a molecule that has a specific combination of isotopes of its constituent elements. For example, diatomic nitrogen molecules (N₂, which constitute about 78% of the atmosphere by volume) can incorporate either ¹⁴N or ¹⁵N, yielding three possible isotopologues: ¹⁴N¹⁴N, ¹⁴N¹⁵N and ¹⁵N¹⁵N. Because the vast majority of nitrogen is

^{14}N , the most common isotopologue is $^{14}\text{N}^{14}\text{N}$. Substitution of a single ^{15}N for ^{14}N is rare; a doubly substituted isotopologue ($^{15}\text{N}^{15}\text{N}$) is rarer still. A random distribution of ^{14}N and ^{15}N between N_2 molecules produces a specific mixture of the three isotopologues. Any measured deviation from the expected proportion of $^{15}\text{N}^{15}\text{N}$ is described as a clumped-isotope anomaly.

Earth's atmospheric N_2 exhibits a well-resolved clumped-isotope anomaly⁴, and Labidi *et al.* used this signature to identify atmospheric contamination of volcanic gases. The authors established that mantle N_2 has no clumped-isotope anomaly by analysing nitrogen released from unusually gas-rich samples of mid-ocean ridge basalt, confirming the expectation that magmatic gases have a random distribution of isotopes among N_2 isotopologues. With this information in hand, the authors examined nitrogen isotope compositions in hydrothermal gases sampled from Yellowstone National Park in the United States, Iceland and other volcanic localities. They identified the nitrogen isotope compositions of the mantle sampled at locations at which trends showing varying degrees of atmospheric contamination were evident.

In previous studies^{3,5} of nitrogen in mantle-derived gases, systematic variations among measured nitrogen and noble-gas compositions were sought to identify atmospheric contamination, but contradictory signatures were sometimes observed – some metrics indicated that there was contamination, whereas others suggested there was none. Labidi and colleagues show that data that might have been interpreted as mantle compositions on the basis of relationships between nitrogen and noble gases are, in fact, affected by atmospheric N_2 contamination.

Their study also indicates that $\delta^{15}\text{N}$ variations are produced in atmospheric N_2 as it circulates through hydrothermal systems. However, the processes that generate such changes in the bulk proportions of ^{14}N and ^{15}N do not redistribute isotopes among isotopologues, so that the atmospheric clumped-isotope anomaly is preserved – which means that any contamination remains identifiable. There is no place for atmospheric N_2 to hide if one is looking through a clumped-isotope lens.

An important feature of the authors' analytical approach is that it is not necessary to measure pure, uncontaminated magmatic gas to estimate the mantle composition. Even if multiple atmospheric contaminants are present, evidence of mixing trends in the data can be used to identify the mantle $\delta^{15}\text{N}$ value of magmatic gas, which has no clumped-isotope anomaly. Labidi *et al.* report a mantle $\delta^{15}\text{N}$ value for the potentially deep-seated^{6,7} Yellowstone mantle plume that is distinct from those determined for mid-ocean ridge basalts.

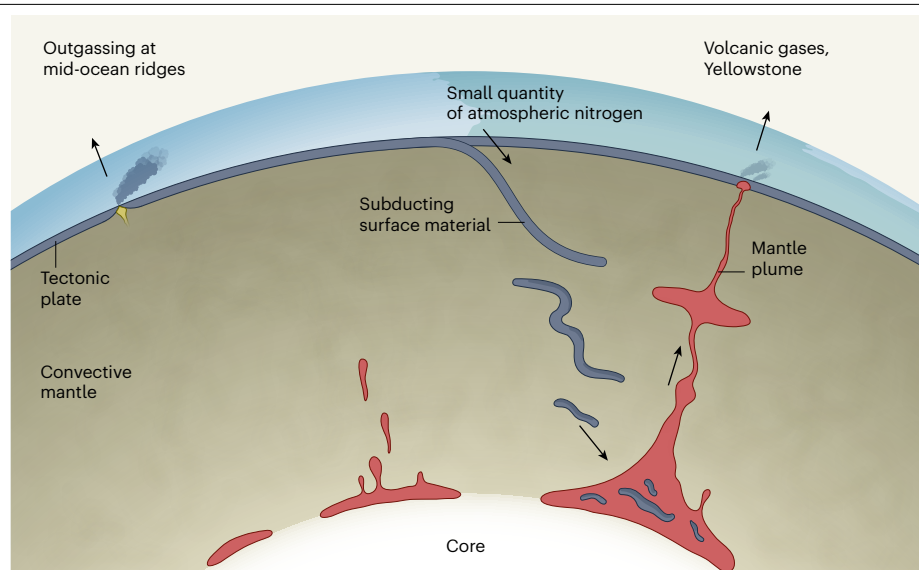


Figure 1 | Nitrogen in the deep Earth. Labidi *et al.*¹ report a new method for identifying contamination of volcanic gases by nitrogen from the atmosphere. The authors find that the nitrogen isotope composition of gases extracted from mid-ocean ridge basalts, which sample the convective mantle, is different from that of volcanic gas from Yellowstone National Park in the United States, which is thought to sample an upwelling mantle plume that originates in the deep mantle. By modelling transport of surface nitrogen into the mantle through subduction (the process in which one tectonic plate dives beneath another and descends into the mantle) and nitrogen loss (outgassing) from the mantle, the authors argue that only a limited amount of nitrogen from Earth's surface has been incorporated into the mantle. They conclude that the observed variations in mantle nitrogen isotope compositions reflect differences that originated early in Earth's history.

With uncertainties regarding atmospheric contamination eliminated, nitrogen isotope variations in the mantle can be interpreted in the context of Earth's formation, differentiation into distinct layers, and the long-term coevolution of the deep Earth and surface owing to plate tectonics (Fig. 1).

To test whether nitrogen exchange between the surface and mantle over time explains their results, Labidi and co-workers developed a mathematical model of nitrogen evolution in the mantle. Intriguingly, the results suggest that there has been a net loss of nitrogen from the convective mantle over most of Earth's history, and little incorporation of surface nitrogen into the mantle. This contrasts with previously reported evidence of substantial incorporation of atmospheric xenon into the mantle^{8,9}. Given the limited role of surface nitrogen in the mantle, the authors argue that the observed nitrogen isotope variations are a remnant from Earth's formation and early differentiation, when volatile species were delivered to the growing Earth as it separated into the core, mantle, crust and atmosphere.

Evidence that early-formed mantle heterogeneities survive in the modern mantle has come from studies of signatures formed by rapidly decaying radioactive isotopes that decayed within the first 100 million years of Earth's history^{8,10}. It will be challenging to confirm that the nitrogen isotope variations identified by Labidi *et al.* arose early in Earth's evolution, given that neither of the element's

two isotopes is produced by radioactive decay and that surface signatures might have a confounding role, however limited. Determination of $\delta^{15}\text{N}$ values at other plume localities, including regions thought to be influenced by the recycling of surface materials¹¹, would provide an interesting test of the authors' primordial hypothesis. The application of clumped-isotope analysis reported by Labidi *et al.* provides an exciting method for such future studies – we now have an improved tool with which to view the origins and evolution of volatile species in the mantle.

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