

used photons to measure a related quantity, they too found a vindication for complex-valued quantum mechanics.<sup>2</sup>

Like Bell tests, the experiments are subject to some fine print. The measurements should be close enough to simultaneous to ensure that no classical information can pass between the observers that could influence their outcomes. And few enough of the measurement trials should go undetected to ensure that the correlation threshold is met not just by the detected trials, but by all of them. If either of those loopholes is not closed, it's

possible for quantum-like correlations to be mimicked not just by a real-valued theory but by a classical one. (See PHYSICS TODAY, December 2011, page 20.) Closing the loopholes in Bell tests themselves was a decades-long effort that came to fruition only in 2015. (See PHYSICS TODAY, January 2016, page 14.)

Neither Pan's nor Fan's group has yet closed the loopholes in their experiments. Technically, therefore, the jury is still out on whether real or complex numbers are the better descriptors of the quantum world. Still, it seems likely that

future students of quantum mechanics will have no choice but to continue to grapple with the mathematics of imaginary numbers.

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# Krypton isotopes tell the early story of Earth's life-giving elements

Since its infancy, our planet has accumulated volatiles from more than one source.

**T**he Galápagos Islands' extraordinary biodiversity famously helped inspire Charles Darwin to formulate his theory of the evolution of life on Earth. But the volcanic islands also offer a window into our planet's even deeper past. The volcanoes, including the one in figure 1, sit atop a mantle plume that channels deep-mantle material to Earth's surface. And the portion of the mantle tapped by the plume has been unusually stagnant over the planet's 4.5-billion-year history.

Over geologic time, Earth's crust and much of its mantle are in constant, albeit slow, motion, as tectonic plates are recycled from the crust to the mantle and back again. Like the churning of butter, the churning of the planet's thickest layer serves not to homogenize its components but to separate them based on their density, volatility, and chemical properties. As a result, almost nothing we encounter on Earth's surface bears any relation to the planet's average composition.

But some pockets of the mantle seem to have been immune to that mixing and have instead remained undisturbed by geological processes since at least the first 100 million years of the planet's history. (For more on the analysis that makes that conclusion possible, see PHYSICS TODAY, October 2010, page 16.) When bits of those primitive materials make their



**FIGURE 1. FERNANDINA VOLCANO** in the Galápagos Islands is one of several sites around the world where geoscientists can discern Earth's original composition. (Photo by tomowen/Shutterstock.com.)

way to the surface—as they do in the Galápagos, Iceland, and a few other volcanic regions—they provide scientists with a valuable look back in time to reveal what the infant planet was originally made of.

Now Sandrine Péron (a postdoc at the University of California, Davis, at the time she did the work, now at ETH Zürich) and colleagues have used a newly developed technique to analyze

some primordial mantle samples for their krypton, an element present only at the parts-per-trillion level.<sup>1</sup> The findings paint a picture not only of krypton itself but of carbon, hydrogen, nitrogen, and oxygen—all the building blocks of life.

## Mantle fingerprints

Early Earth was a hot place, as the young planet was frequently enduring energetic collisions with the planetesimals that it

hadn't yet cleared out of its orbit. The life-giving elements, on the other hand, tend to form compounds with low boiling points, such as methane, ammonia, and water. It wouldn't seem that those volatile substances would stick around long in such an environment—if they could even condense in the first place.

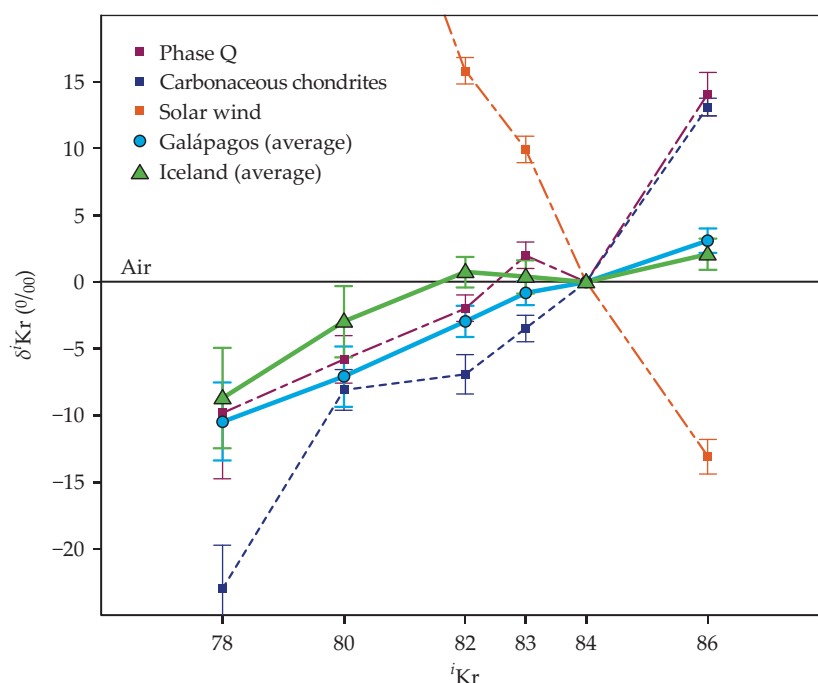
Clearly, Earth does have an abundance of volatile elements, and they had to have come from somewhere. They're not created in earthly nuclear reactions in appreciable amounts, so they must have either been part of the planet's original composition or been delivered later, perhaps by a comet. Knowing how Earth got its volatiles could help researchers understand how usual or unusual our planet's circumstances are—and perhaps how likely they are to have been replicated elsewhere in the universe.

That's where krypton comes in. As a gaseous element, it's physically similar to other volatiles, so it's likely to have condensed and degassed along with them. And its six naturally occurring isotopes are present in different ratios in different possible sources. If a particular sample of krypton has an isotopic composition matching what's found in the solar wind, for example, that's at least circumstantial evidence that the krypton came from the Sun.

The challenge in working with krypton is that there's so little of it. The element itself is rare enough, but its least abundant isotopes are two to three orders of magnitude rarer still: A typical 4 g sample of mantle material could have just a few hundred thousand atoms of  $^{78}\text{Kr}$ . Moreover, it's subject to contamination. The gas entrained in volcanic rock could be bubbles of the original mantle gas, or it could be air that made its way into the lava after an eruption. Any given sample likely contains unknown amounts of both, and previous efforts to analyze mantle krypton have been stymied by the atmospheric contamination.

Péron developed a way around that problem.<sup>2</sup> She'd crush the sample a bit at a time, and she'd separately analyze the gas released at each step. If it showed signs of having been contaminated by air, she'd exclude it from the measurement. Otherwise, she'd keep it.

But Péron couldn't make that determination by looking at the krypton alone. Too little is released at each stage to separately analyze, and without knowing



**FIGURE 2. THE ISOTOPIC MAKEUP** of krypton can be used to trace its source. The krypton found in mantle samples from Iceland and the Galápagos Islands differs from that of air. But the levels of five of the six isotopes closely match those of phase Q, a carbonaceous material found in meteorites. The deficiency of  $^{86}\text{Kr}$  in the mantle follows a pattern of similar anomalies observed in other elements; it could be a sign that the protoplanetary disk that formed the solar system was not well mixed. (Adapted from ref. 1.)

the mantle krypton composition, it's not possible to know how much, if any, atmospheric krypton is present. Instead, she turned to the more abundant neon. With only three natural isotopes, neon is less effective at distinguishing among many possible sources. But the isotopic composition of mantle neon and atmospheric neon are both well known, and they're significantly different. Only if the neon released at a crushing step matched the expected mantle composition would Péron keep the krypton released in the same step.

### Volatile two-step

The stepwise analysis takes a long time—about a week for a single sample—and requires throwing away half to two-thirds of the data. But it gives a better estimate of the primordial mantle's krypton composition than has been possible before.

The results of Péron and colleagues' measurements are shown in figure 2. Their Galápagos and Iceland measurements reassuringly match one another. On the other hand, the mantle krypton is distinctly different from that of air. The difference means two things. First, the

krypton in the mantle definitely isn't just recycled atmospheric krypton. Second and conversely, the krypton in the air—and by extension, other volatiles—can't have come solely from the degassing of the primordial mantle. Later in its history, Earth must have received another delivery of volatiles from somewhere else.

In five of the six isotopes—all but  $^{86}\text{Kr}$ —the new mantle measurements are a reasonable match to a class of meteorites called chondrites, which are thought to represent the original building blocks of the solar system. Figure 2 shows the krypton isotopic composition of two chondritic references: average carbonaceous chondrites (chondrites that originated from the outer solar system, where volatiles could more easily condense) and phase Q, a poorly characterized material that carries most of the heavy noble gases found in many types of meteorites.

But the krypton in Earth's mantle couldn't have come directly from either of those sources because the  $^{86}\text{Kr}$  levels don't match. The discrepancy is a bit of a puzzle, but it's also a clue. Similar anomalies—specifically, a deficit in the mantle



of an element's most neutron-rich isotope—have been observed for at least eight other elements, including calcium, titanium, and nickel. Krypton, however, is the first volatile element found to follow the pattern.

Neutron-rich isotopes form in stars mostly through the r-process, or rapid neutron capture, as opposed to the s-process, or slow neutron capture. The protoplanetary disk that formed the solar system likely drew on the remains of a few different stars—some with more vigorous r-processes than others. If the

stars' contributions weren't well mixed, the part of the disk that formed into Earth could have been relatively enriched in s-process matter. Moreover, the fact that krypton shows the same anomaly as other elements seems to indicate that Earth acquired its early dose of krypton and other volatiles at the same time, and from the same source, as it accreted its nonvolatile elements.

If that explanation is right, then there should be some meteorites—remnants of the same part of the protoplanetary disk that formed Earth—that show the same

$^{86}\text{Kr}$  deficit as the mantle does. None have yet been found, but data on krypton isotopes in meteorites are sparse. Péron's next plan is to turn her analysis technique to different types of meteorites to see whether she can find any with a krypton composition that matches Earth's in all six isotopes.

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# Laser pulses probe quantum beats

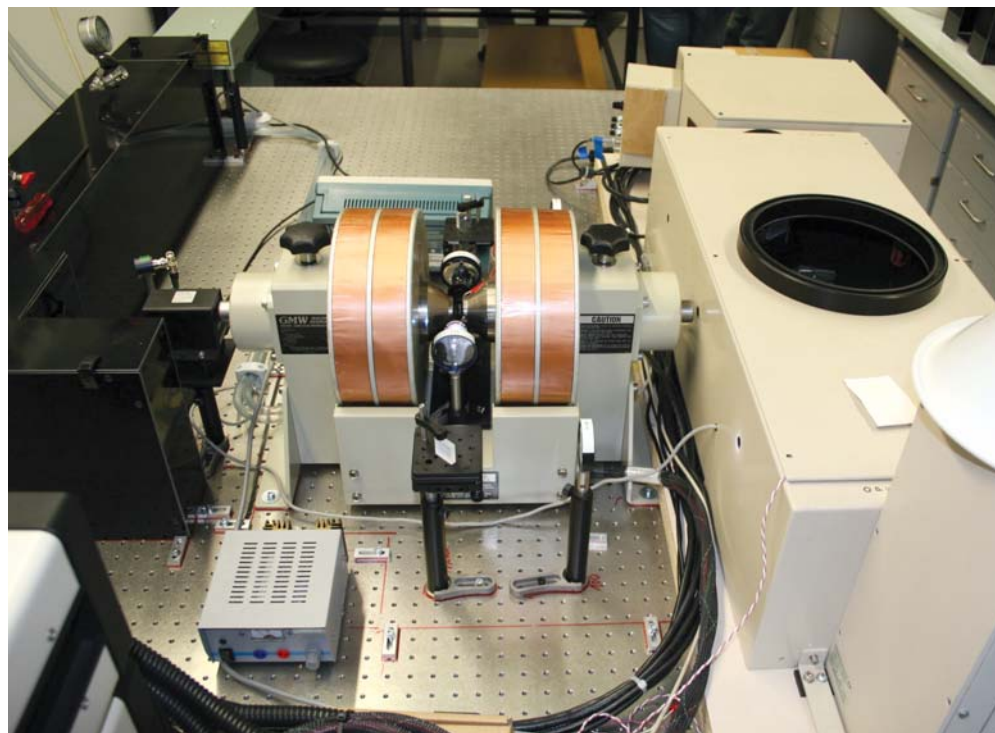
States of nearly equal energy underlie physiological processes, but studying them directly has been a challenge.

**C**ryptochromes are a class of light-sensitive proteins found in many organisms. In animals, they're an integral part of the circadian clock: the collection of biochemical oscillations that align physiology with the day–night cycle.<sup>1</sup> A network of positive and negative feedback loops in gene expression and protein production couple those oscillations to downstream processes. For example, they link external light and temperature conditions to levels of hormones that stimulate hunger and sleepiness.

The involvement of cryptochromes in circadian clocks is well established; they're part of a negative feedback loop that suppresses transcription. But much about them remains poorly understood—for example, their structures are not well characterized, and the light-reactive proteins participate in cycles that don't have light as an input.

Cryptochromes are also the only biomolecules other than chlorophylls that are known to host so-called radical pairs. When a photon hits a cryptochrome, it can excite an electron that hops along the molecule from an electron donor to an electron acceptor—areas with low and high electron affinities, respectively. The mobile electron leaves behind another electron, but the electrons' spins remain entangled despite the separation.

The paired electrons exist in a singlet



**FIGURE 1. TWO ELECTROMAGNET COILS** flank a sample chamber containing a solution of photoactive molecules. The surrounding optics direct a pair of laser pulses at the sample to manipulate the molecules' spin dynamics. (Courtesy of Michael Moos.)

state before the excitation because they must have opposite spins per the Pauli exclusion principle. And they usually remain that way afterward. But when conditions are just right, the electrons undergo quantum beats: oscillations between singlet and triplet states. The frequency of the beats is determined by the electron spins' magnetic environment, which is dominated by the magnetic nuclei in the molecule, and the electrons'

state can affect which reaction pathways are available to the molecule.

Unfortunately, the beats are tricky to study: The states' nearly equal energies make them indistinguishable by optical spectroscopy techniques. But Christoph Lambert and his graduate students David Mims and Jonathan Herpich (University of Würzburg, Germany), in collaboration with theoreticians Ulrich Steiner (University of Konstanz, Germany) and Nikita