Xenon isotopes tell the story of volatile recycling

in the mantle

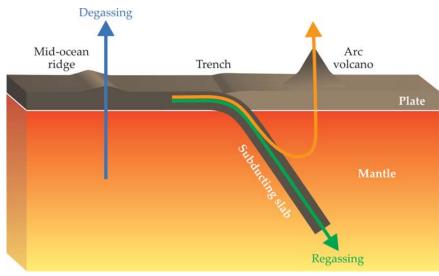
The mantle today reprocesses volatile substances from the crust and surface. But for billions of years, that wasn't the case.

he water that cycles through Earth's oceans, lakes, and atmosphere is just a portion of the water on this planet. A vast amount of water—as much as 2.5 times the mass of all surface reservoirs—is dispersed, molecule by molecule, in the mantle, where it influences mineral material properties and thus geological dynamics (see the article by Marc Hirschmann and David Kohlstedt, Physics Today, March 2012, page 40).

On time scales of millions to billions of years, the water cycle includes exchanges into and out of the mantle, as illustrated in figure 1: Water is released, or degassed, from the mantle through midocean ridges and volcanoes; it's returned, or regassed, through the subduction of hydrated minerals in tectonic plates. Other volatile species—including compounds of carbon, nitrogen, and sulfur—engage in their own deep cycling.

With volatiles moving in and out of the mantle, the density and makeup of the atmosphere and hydrosphere could conceivably have changed significantly over geologic time. Yet life has existed continuously on Earth for most of the planet's history. Despite mass extinctions and dramatic transformations in the nature of living things, conditions on Earth—unlike those on, say, the Moon or Venus—have always been suitable for organisms of some form. Understanding the history of volatile recycling is an important part of understanding Earth's past and present habitability.

Now Rita Parai (Washington University in St Louis) and Sujoy Mukhopadhyay (University of California, Davis) have established the first quantitative constraints on how the mantle–surface volatile exchange evolved over time.<sup>1</sup>



They numerically modeled the degassing and regassing of xenon, a rare gas that nonetheless can be a powerful tracer of more abundant volatiles.

Water-bearing minerals, in particular, all carry some Xe. Because the Xe-to-water ratio varies, it's not usually possible to derive a detailed quantitative relationship between Xe fluxes and water fluxes. But if, for a particular time and place, the deep Xe flux is zero, then the deep water flux is likely to be as well. The researchers found from their model that for much of Earth's early history, Xe—and thus water—moved only out of the mantle, not back into it.

## Tracking isotopes

Xenon has nine stable isotopes; all are present on Earth, but their local relative abundances are not fixed. Atmospheric Xe has grown progressively heavier over time, probably due to the selective escape of the lighter isotopes into space, although the details of the mechanism remain unknown. As trapped samples of ancient air reveal, the change was smooth and steady from early in Earth's history until 2 billion years ago; since then, the isotopic composition of Xe in the atmosphere has been constant.<sup>2</sup>

Meanwhile, processes in the mantle have also driven isotopic change. Five of the nine Xe isotopes are radiogenic, produced in characteristic amounts by the

#### FIGURE 1. PATHWAYS FOR VOLATILES.

Water, xenon, and other volatile substances are degassed from the mantle through hot-spot volcanoes and mid-ocean ridges. They're returned through subducting slabs: Whatever isn't expelled from the slab and returned to the atmosphere through arc volcanoes is regassed into the deep mantle.

decay of iodine-129 and fission of plutonium-244 and uranium-238. Whereas <sup>129</sup>I and <sup>244</sup>Pu were present in early Earth but have long gone extinct, <sup>238</sup>U is still in the mantle and producing Xe.

The Xe in the mantle today—whose composition is known from analysis of erupted basalts—is a mixture of Xe from five sources: the primordial Xe that's been in the mantle since its formation (as inferred from chondritic meteorites, which largely preserve the initial composition of the solar system), the three Xe-producing radioisotopes, and atmospheric Xe regassed into the mantle. If the atmospheric isotopic composition had been constant over time, one could figure out how much each source contributed to the mantle by solving a system of nine linear equations (one for each isotope) in five variables (one for each source). In general, such an overdetermined system of equations doesn't always admit a solution-but if it's an accurate description of a physical phenomenon, it does.

Parai and Mukhopadhyay recognized

that they could solve the equations if they assumed that all the regassed Xe came from an atmosphere with a modern isotopic composition. (In practice, they left out several isotopes and the <sup>129</sup>I fission source, but they still had an overdetermined linear system.) If they assumed that an ancient atmosphere was the source of the regassed Xe, however, the equations had no solution.<sup>3</sup> That simple test was a first hint that regassing had grown stronger over time.

## **Testing histories**

To probe the idea more rigorously, the researchers developed a numerical model that could simulate the mantle's Xe dynamics over time. They started with a mantle of chondritic composition; at each time step, some Xe is degassed, some is regassed, and some is produced through radioactivity. The mantle was assumed to be well mixed, so the degassed Xe had the same isotopic composition as the mantle as a whole. For the regassed Xe, the researchers used the known time-dependent atmospheric composition.

The degassing and regassing rates

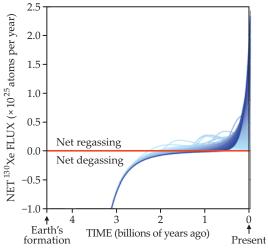


FIGURE 2. HISTORIES OF XENON REGASSING that successfully reproduced today's mantle Xe composition. Shown here is the net Xe flux into the mantle: the regassing rate minus the degassing rate. Although it's not evident from the figure, all of the successful histories show essentially no regassing at all prior to 2.5 billion years ago. (Adapted from ref. 1.)

were hypothesized. Parai ran the simulation many times, each with a different regassing history randomly chosen from a parameter space of functional forms. Histories that correctly reproduced the Xe concentration and composition in the present-day mantle were deemed successful; figure 2 shows the net Xe flux into the mantle for each successful history.

As the figure shows, Earth began in a state of net degassing, with more Xe leaving the mantle than entering it. Sometime between 2.5 billion years ago and several hundred million years ago, it switched to a regime of net regassing. Many of the successful histories show a sharp increase in the regassing rate over the past few hundred million

years, but that late rise doesn't necessarily represent a physical phenomenon. "The approach we took was to find everything that's possible," says Parai, "so we can't figure out relative probabilities among the workable scenarios." Any of the successful histories with earlier rise times and low present-day regassing rates are also possible.

But there was one stark result: None of the successful histories had any significant Xe regassing prior to 2.5 billion years ago. "We were surprised by how little early regassing could be tolerated," says





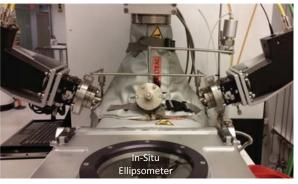


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Parai. "We suspected that the amount might be limited, but we had no idea how much until we did the computations."

If Xe regassing was limited until 2.5 billion years ago, then water regassing was as well. That's especially curious because of evidence that plate tectonics, and therefore subduction, has been going on for at least 3 billion years. If that's true, then for hundreds of millions of years, subducting slabs were being returned from the crust to the mantle, but they carried no water at all. Maybe their volatiles were efficiently expelled in the process of subduction—Parai and Mukhopadhyay's

model counts volatiles as being regassed only when they make it deep enough into the mantle to be well mixed. Or maybe the ancient crust wasn't hydrated to begin with.

Geologists consider 2.5 billion years ago to be the boundary between the Archean and Proterozoic eons, and a number of important changes happened at approximately that time. Most notable among them, perhaps, was the first accumulation of oxygen in Earth's atmosphere (see Physics Today, June 2018, page 16). The onset of regassing is another near-simultaneous event to add to the mix.

"But we don't know whether there are any cause-and-effect relationships or whether these are just temporal coincidences," says Parai. "That will need to get worked out in the future."

Johanna Miller

#### References

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## Ants know the secret to avoiding traffic jams

In a confined environment, ants divide labor to optimize nest excavation.

roups of interacting agents in a confined system, whether cars on a highway or insects in a tunnel, often generate clogs that can persist for long durations. For tasks that demand a steady flow of agents, with each performing a repetitive task, those clogs hinder the collective goal. When a traffic jam happens, it's not just detrimental to each driver; rather, the total number of cars traversing the road at any given time is reduced. Road engineers put a lot of thought into infrastructure design to keep traffic flowing as smoothly as possible. Insects have instinctive strategies for accomplishing the same goal.

With GPS and mobile communications technology, humans can see other cars on the roads and make informed decisions about avoiding congested areas or venturing out in the first place. But for agents operating in other confined systems, like ants working in a nest or micromachines carrying drugs in a patient's blood, it's impossible for an individual to know about the other participants and the conditions affecting the overall system.

Fire ants (*Solenopsis invicta*), like most ants, work together to dig complex tunnel networks. Now Daniel Goldman and colleagues at Georgia Tech have found that workers follow counterintuitive and seemingly counterproductive rules to optimally excavate the collective's early-stage tunnels. The team used tools from soft-matter physics² to analyze how clus-



**FIGURE 1. FIRE ANTS EXCAVATING A TUNNEL.** The ants, painted different colors for identification, dig along the wall of a transparent container filled with 0.25-mm-diameter glass particles. (Photo courtesy of Rob Felt, Georgia Tech.)

ters formed and dissolved in a collection of ants.

## When the ants go marching in

For his research, Goldman sought an organism that met a behavioral study's basic requirement of repeating a task over and over again. He settled on fire ants. "If the organism is local and easy to collect with a shovel and bucket, that's even better," he said. Fire ants arrived via infested shipping crates in the US 80 years ago and now thrive in the subtropical southeastern states.

To learn about ants' soil excavation, Goldman built a model environment whose transparent enclosure contained 0.25-mm-diameter glass particles mixed with water to mimic the damp soil that ants typically remove. The model ensured that moisture conditions stayed the same in each experiment. Goldman's earlier work showed that a fire ant contributed to digging complex nests by entering a tunnel, collecting a load of soil that was always the same size, and climbing back out. In the early stages of nest construction, ants built vertical tunnels one body