# The Earth's Missin Ingredient

### The discovery of a novel high-density mineral means that the earth's mantle is a more restless place than scientists suspected—and offers new clues to the planet's history • By Kei Hirose

KEITH KASNOT

## KEY CONCEPTS

- At high pressures, the most common type of mineral in the earth's lower mantle undergoes a structural change and becomes denser.
- The existence of this denser phase implies that the mantle is more dynamic and carries heat more efficiently than previously thought.
- Faster heat transport helps to explain why continents grew as fast as they did and even how the earth's magnetic field evolved in a way that enabled life to move onto land.

*—The Editors*

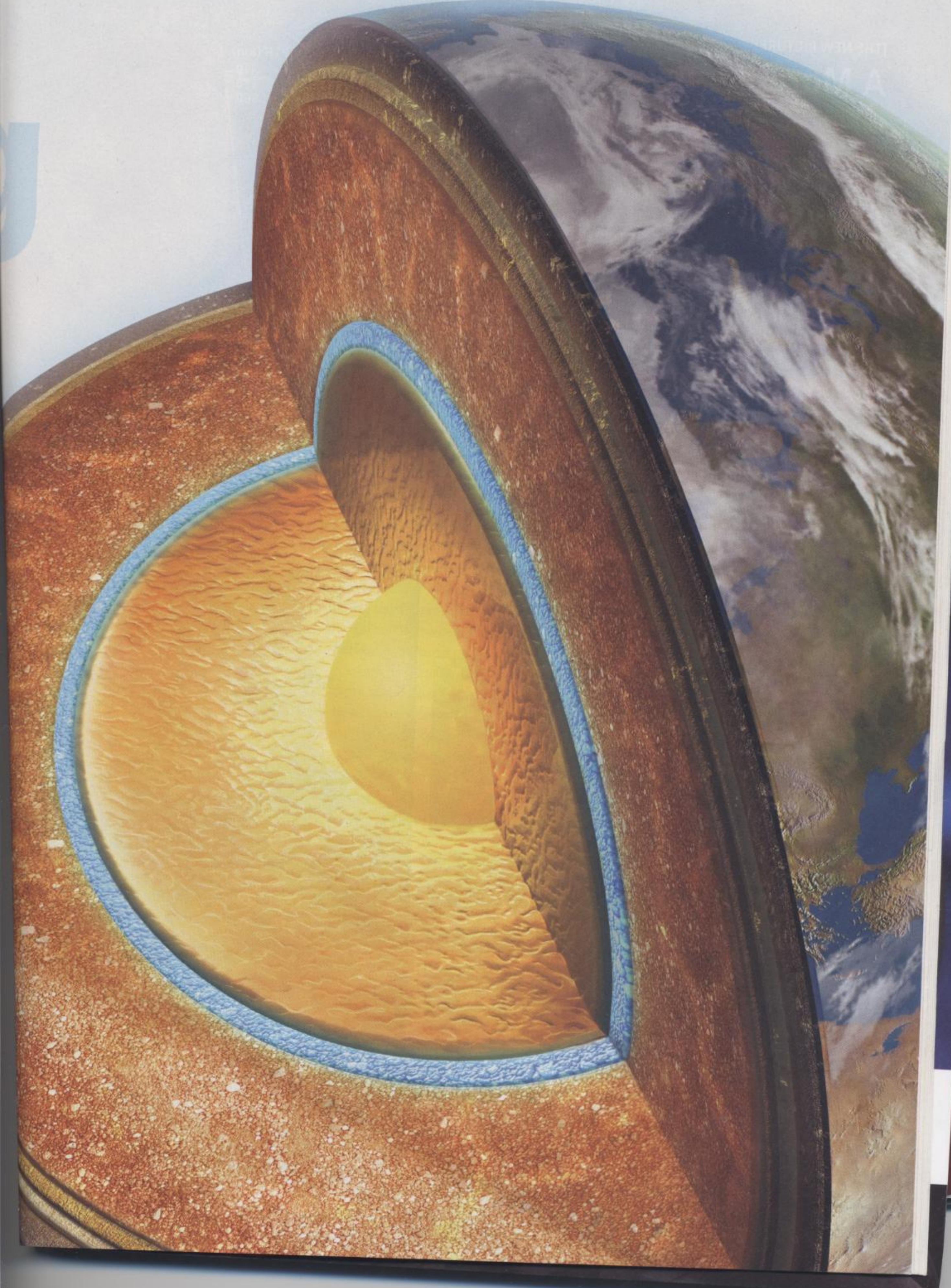
The deepest hole humans have ever dug reaches 12 kilometers below the ground of Russia's Kola Peninsula. Although we now have a spacecraft on its way to Pluto—about six billion kilometers away from the sun—we still cannot send a probe into the deep earth. For practical purposes, then, the center of the planet, which lies 6,380 kilometers below us, is farther away than the edge of our solar system. In fact, Pluto was discovered in 1930, and the existence of the earth's inner core was not established—using seismological data—until six years later.

Still, earth scientists have gained a surprising amount of insight about our planet. We know it is roughly structured like an onion, with the core, mantle and crust forming concentric layers. The mantle constitutes about 85 percent of the earth's volume, and its slow stirring drives the geologic cataclysms of the crust. This middle domain is mainly a mix of silicon, iron, oxygen, magnesium—each of which appears in roughly the same concentrations throughout the mantle—plus smaller amounts of other elements. But depending on the depth, these elements combine into different types of minerals. Thus, the mantle is itself divided into concentric layers, with different minerals predominating at different depths.

Although the nature and composition of most of those layers have been fairly well understood for decades, until recently the lowermost layer remained a bit of a puzzle. But in 2002 the synthesis in my laboratory of a novel, dense mineral that forms at the temperatures and pressures of the bottom 300 kilometers of the mantle solved the mystery. Since then, studies have revealed that the mineral, called postperovskite, dramatically af-

ALZHEIMER'S ADVANCES

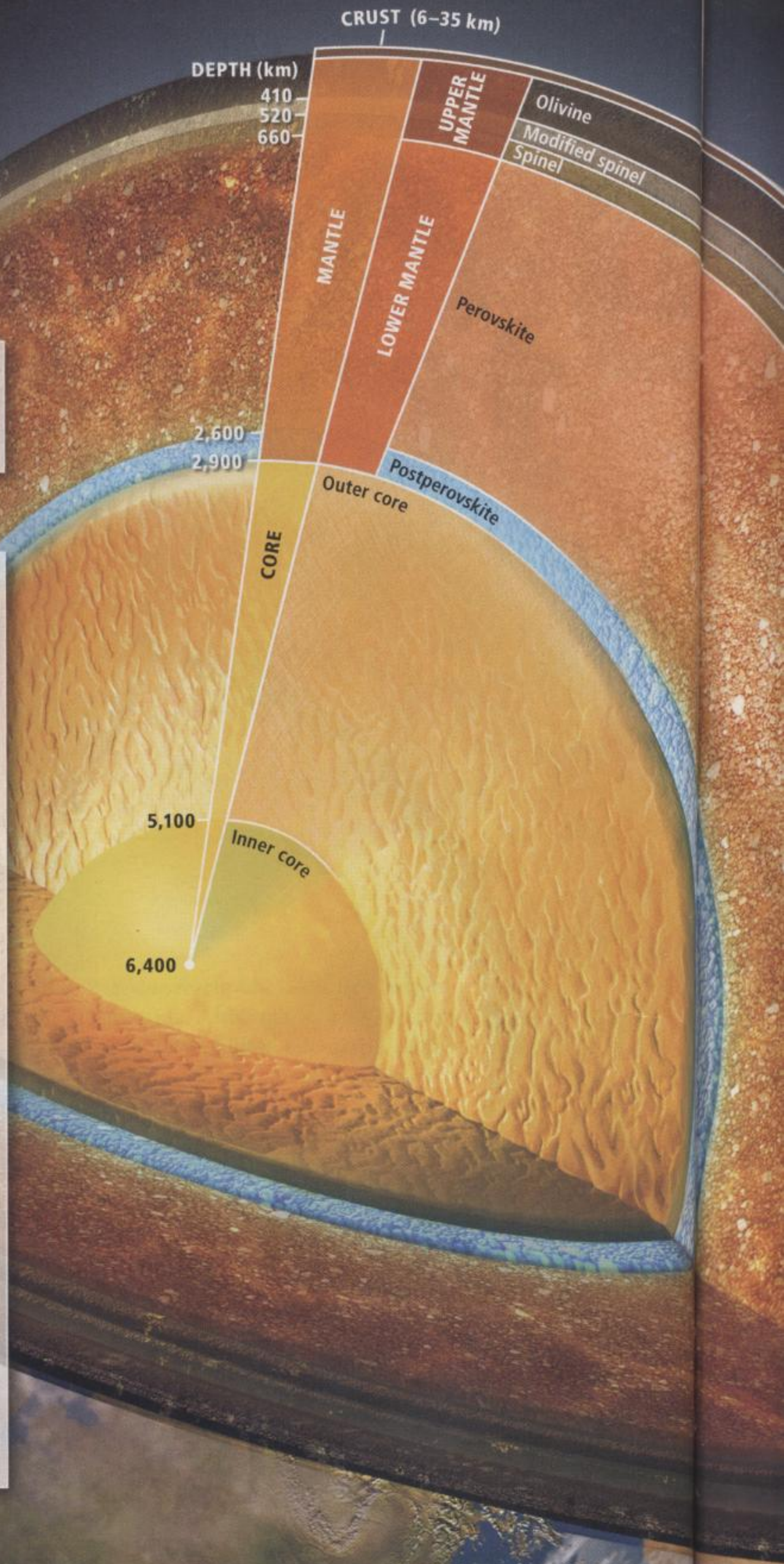
Dementia



[THE NEW PICTURE]

# A More Complex Planet

**The earth is structured like an onion, with different materials appearing in each concentric layer. The discovery of a new, high-density material, called postperovskite, implies the existence of a new layer of that onion and explains puzzling behavior by seismic waves traveling through the planet.**



## CRUST (UP TO 35 KILOMETERS OF DEPTH)

The continents, which are in part submerged by the oceans, are made of diverse rock that is up to several billion years old and relatively light. Thus, they float on the denser mantle underneath. The heavy basaltic rock that forms the bulk of the oceanic crust originates from mantle magma that erupts at underwater ridges and eventually sinks back into the mantle, typically within 100 million years.

## MANTLE

Mantle rock consists primarily of oxygen, silicon and magnesium. Despite being mostly solid, it does deform on geologic timescales. In fact, the rock slowly flows as convective currents stir the entire mantle. That flow dissipates the earth's inner heat and propels continental drift.

### UPPER MANTLE (35–660 KM)

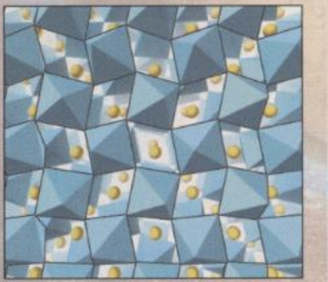
As greater depths bring higher pressures and temperatures, the mantle's elemental components arrange into different crystal structures (minerals), forming layers. Three minerals—olivine, modified spinel and spinel—give the layers of the upper mantle their respective names.

### LOWER MANTLE (660–2,900 KM)

The lower mantle was for decades thought to be relatively uniform in structure. But seismological data suggested that something different was happening at the bottom.

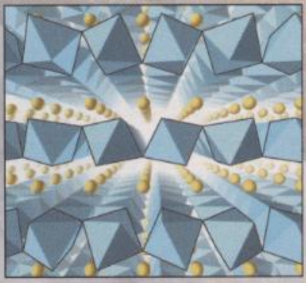
- **Perovskite layer**

The most prevalent mineral here (70 percent by weight) is a magnesium silicate ($MgSiO_3$) belonging to the family of crystal structures called perovskites. In this densely packed structure, magnesium ions (*yellow*) are surrounded by octahedral silicon-oxygen groups (*blue double-pyramid shapes*). Until recently, scientists thought that no denser crystal arrangement of these elements could exist.



- **Postperovskite layer**

At the pressures and temperatures of the bottom 300 km of the mantle, perovskite transforms into a new structure: the magnesium ions and the silicon-oxygen groups arrange themselves into separate layers. The transition releases heat and reduces volume by roughly 1.5 percent—a small difference, but one with dramatic effects on the entire planet [*see illustrations on pages 82–83*].



## CORE (2,900–6,400 KM)

The deepest part of the earth consists predominantly of iron, which is liquid in the outer core and solid in the inner core. Convection stirs the outer core just as it stirs the mantle, but because the core is much denser, little mixing occurs between the mantle and the core. Core convection is thought to produce the planet's magnetic field.

KEITH KASNOT (cutaway); KEN EWARD (minerals)

fects the planet's dynamics. Its apparent presence in the mantle, researchers have shown, implies that the mantle's convection currents (in which cooler rock sinks and hotter rock upwells, taking some of the earth's inner heat with it) are more dynamic and more efficient at carrying heat than was thought. Without postperovskite, continents would have grown slower and volcanoes would have been quieter. The formation of postperovskite may also have hastened the strengthening of the earth's magnetic field, which made life possible on land by shielding it from cosmic rays and solar wind. In other words, postperovskite was a key missing ingredient for understanding the evolution of our planet.

## Rock Bottom

Geophysicists map the structure of the earth by measuring seismic waves. After an earthquake, because waves travel through the entire planet, sensitive instruments can pick them up on the other side of the world. When waves cross the boundaries between different materials, they may be refracted or reflected. Global measurements of such behavior have shown that the mantle has five layers, with each boundary between the layers marked by a jump in the waves' velocity. Researchers have linked these jumps to changes in the structure of the rock—changes attributed to the pressures and temperatures that exist as one goes deeper down.

Rock is made of different minerals. A mineral is an arrangement of atoms into a particular geometric pattern, or crystal, and thus has its own composition, physical properties and even color—think of the different types of grains in an ordinary granite kitchen counter. Below certain thresholds of depth down in the mantle, the enormous pressures and temperatures force the elements to rearrange into new crystal structures. As physicists say, the materials undergo a phase transition.

Lacking the ability to probe the depths of the earth, early geologists who wanted to study these structures had to look for mantle rocks to be brought up to the surface by magmas of deep origin. These rocks often enclose diamonds. Because diamonds form under the pressures and temperatures that exist at 150 kilometers of depth or more, their host rocks can be presumed to originate from a similar depth; they thus provide a wealth of information about the uppermost part of the mantle. But mantle rocks or minerals derived from depths greater than 200 kilometers reach the surface only rarely.

As researchers learned to generate high pressures and temperatures in the laboratory, they became able to synthesize the minerals believed to make up lower levels of the mantle. The predominant minerals in the rock give the mantle's layers their names: in the upper mantle, those are the olivine, modified spinel and spinel layers. Then, starting at a depth of 660 kilometers, a dense form of magnesium silicate ($MgSiO_3$) becomes the main component of the rock. It belongs to a vast family of crystals called perovskites, which are arrangements of negatively charged oxygen ions and two types of positively charged ions—in this case magnesium and silicon—held together by electrostatic attraction. Perovskites can have a wide variety of chemical compositions and include superconductors as well as materials widely used in electronics, for example, in piezoelectric actuators or in capacitors.

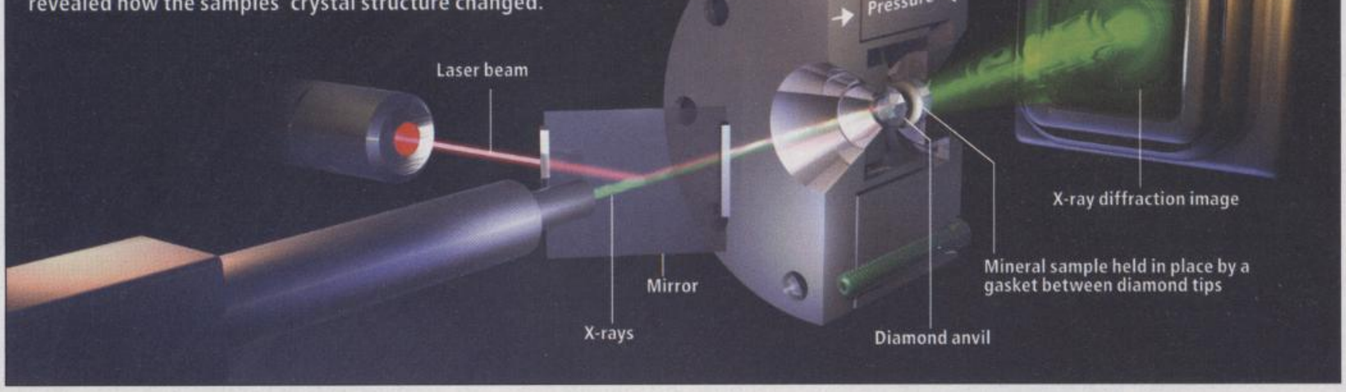
Magnesium silicate perovskite was first synthesized in 1974 under 30 gigapascals of pressure. (One gigapascal, or one billion pascals, is about equivalent to 10,000 times atmospheric pressure at sea level.) In the following 30 years the consensus among experts was that this mineral should be present all the way down to the bottom of the mantle, located at a depth of 2,890 kilometers, without undergoing another phase transition.

In the1960s, however, a new seismic anomaly was found, around 2,600 kilometers down. The lower mantle, which used to be called the D-layer, was now divided into two sublayers, D′ and D″ (D-prime and D-double-prime), with the D″ region occupying the bottom 300 kilometers or so of the shell. In 1983 the anomaly was found to be an actual discontinuity, but it was attributed to a change in the relative abundances of the elements, not to a phase-transition boundary. This assumption was made in part because perovskite is an "ideal" crystal structure—one in which the atoms are arranged in a tightly packed geometry that seems to maximize the mass per unit volume. Experts doubted that perovskite could be compressed into any structure with tighter packing than that. On the other hand, a change in the element abundances

[THE DISCOVERY]

## DEEP EARTH IN THE LAB

The author's team re-created the conditions of the lower mantle using a diamond-anvil cell. The cylindrical steel cell is designed so that tightening its screws—usually done by hand—concentrates pressure onto a surface just microns wide between the tips of two diamonds. The team placed samples between the tips and heated them with a laser. At the same time, an x-ray beam revealed how the samples' crystal structure changed.



[THE AUTHOR]

**Kei Hirose** is professor of high-pressure earth sciences at the Tokyo Institute of Technology. He chose to major in geology at the University of Tokyo in the hope that the line of work would take him to Antarctica or allow him to explore the deep sea in a submersible. His research focuses on the generation of ultrahigh pressures and temperatures in laboratory experiments—with a special interest in deep-earth and planetary materials—but he has not yet given up his travel dreams.

was also problematic, because convection should stir up the lower mantle and mix its contents with those of the overlying layers, leading to uniformity in the kinds and ratios of elements.

To clarify the situation, experiments would need to push above 120 gigapascals and 2,500 kelvins. I got interested in this problem in the mid-1990s and later started laboratory experiments using a diamond-anvil cell, in which samples of mantlelike materials are squeezed to high pressure between a couple of gem-quality natural diamonds (about two tenths of a carat in size) and then heated with a laser. Above 80 gigapascals, even diamond—the hardest known material—starts to deform dramatically. To push pressure even higher, one needs to optimize the shape of the diamond anvil's tips so that the diamond will not break. My colleagues and I suffered numerous diamond failures, which cost not only research funds but sometimes our enthusiasm as well. Finally, by using beveled anvils, we broke the 120-gigapascal ceiling in 2001. We were one of the first labs in the world to do so and the first to study the effects of such pressures on perovskite.

### Crystal Clear

To understand what went on inside our samples, we set up our experiment at SPring-8, the world's largest synchrotron x-ray facility, located in the mountains of western Japan. For nearly a century scientists have decoded the structure of crystals by looking at how x-rays diffract through them (based on the fact that interatomic distances are in the same range of lengths as the wavelengths of x-rays). SPring-8's hair-thin, intense beams of x-rays enabled us to take high-quality shots at intervals of just one second, which is quite useful for monitoring the change in crystal structure in such extreme conditions.

In the winter of 2002 at SPring-8, my student Motohiko Murakami came to me saying that the diffraction pattern of magnesium silicate perovskite had drastically changed when it was heated at 125 gigapascals. Such an observation usually points to a change in crystal structure—precisely what I had been looking for. If true, this discovery was going to be the most important in high-pressure mineralogy—and possibly in all of deep-earth science—since 1974, when silicate perovskite itself was first synthesized.

Nevertheless, at first I did not take these data too seriously, because diffraction patterns can change for any number of reasons. For example, samples can react chemically with the materials that hold them in the anvil—typically clay—resulting in a radical change in the diffraction data. When I told my close colleagues about this new observation several days later, their first reaction was rather negative. "You must be doing something wrong," a crystallographer told me: perovskite is an ideal, tightly packed structure, he noted, and no phase transformation from perovskite into a denser structure had ever been seen before.

We repeated the experiments many times. Encouragingly, we observed the new diffraction pattern each time. We also found that when we

ALFRED T. KAMAJIAN (*top illustration*); COURTESY OF KEI HIROSE (*Hirose*)

reheated the sample at low pressure the new pattern changed back to that of perovskite. Thus, the transition was reversible, which ruled out a change in the sample's chemical composition. At that point, I became convinced that we had transformed magnesium silicate perovskite into a new structure.

Next, we found that at a temperature of 2,500 kelvins, the transition happens at 120 (rather than 125) gigapascals—precisely the pressure corresponding to 2,600 kilometers of depth, where the mysterious discontinuity jump in seismic-wave velocity was found. I realized that the long-standing enigma had now been settled: we had discovered a new phase transition and a new material which must be predominant in the D″ layer. Furthermore, I speculated that the properties of the new phase might have important consequences for the dynamics of the mantle.

But before continuing our work, we first needed to determine the crystal structure of the new phase, which was challenging because at the time no perovskite-type crystals were known to transform into other crystals under pressure. For almost a year we scoured crystallography catalogues trying to fit our diffraction data to known patterns—a needle-in-a-haystack search, given that there are tens of thousands of such crystal structures. Then, at the end of 2003, during the New Year's holidays, my colleague Katsuyuki Kawamura, a chemist, ran a computer simulation of magnesium, silicon and oxygen atoms at high pressure. He started out with randomly distributed atoms at a very high temperature, and as he cooled his virtual sample, the mix began to rystallize. He then calculated the diffraction atterns such a crystal structure would produce, nd the result perfectly matched the pattern we ad observed experimentally.

We decided to name the new phase postpervskite. (Strictly speaking, it is not a mineral, beuse it has yet to be found in nature.) As it turns t, its structure is essentially identical to that of o known crystals, uranium ferrous sulfate ($FeS_3$) and calcium iridiate ($CaIrO_3$), which e stable under ambient conditions. And our dit measurements have shown that the density postperovskite is indeed higher than that of ovskite, by 1 to 1.5 percent.

## king the Heat

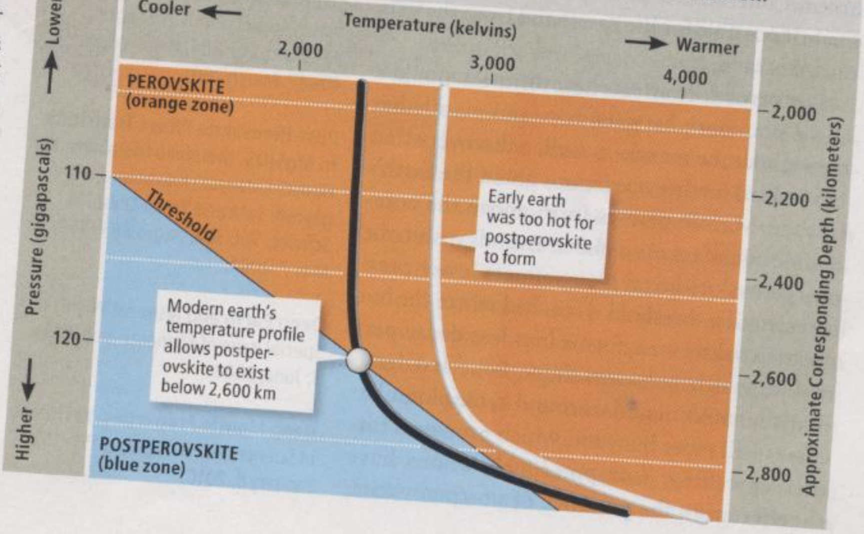
ce we announced our results in 2004, archers in various fields have built on them to t an exciting new picture of the many differ- processes within the earth. To begin with, our discovery cast light on the amount of heat flowing from the core to the mantle. The core is mostly iron, making it twice as dense as the mantle. As a consequence, virtually no mixing occurs at the boundary between the two, and heat is exchanged predominantly by conduction. Whereas the mantle is rich in radioactive uranium, thorium and potassium, the core is probably poor in radioactive isotopes, which implies that its current temperature of perhaps 4,000 to 5,000 kelvins derives mostly from heat left over from the formation of the earth. Since then, the core has cooled with time as heat has transferred into the mantle at the core-mantle boundary.

By making plausible assumptions about the heat conductivities of the materials in the lower mantle, my collaborators and I were able to estimate that the rate at which heat flows from the core into the mantle may be five to 10 terawatts, comparable to the average output of all the world's power stations combined. It is a larger flow of energy, and hence a faster rate of core cooling, than previously thought. To be at its current temperature, then, the core must have started out at a higher temperature than had been assumed.

That flow of heat has determined how the core evolved since the earth formed. Inside the young earth, the core was entirely liquid, but at some point in the planet's history the inner core started to crystallize, so that it now has two layers: an inner, solid core and an outer, liquid core. The faster rate of cooling suggests that the solid

Experts doubted that a mantle mineral could be compressed into a crystal structure with any tighter packing.

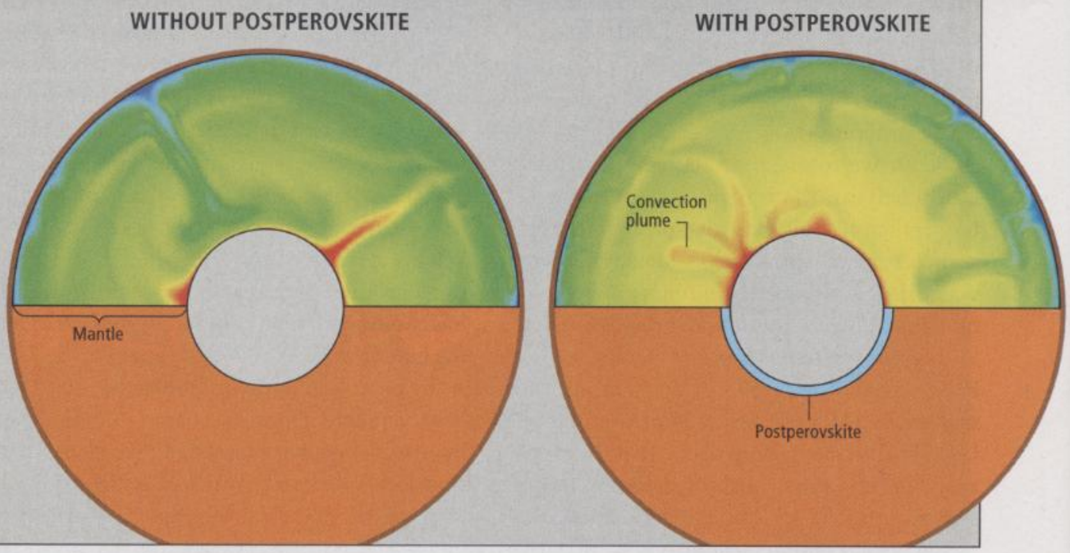
**EXPERIMENTAL DATA revealing the temperatures and pressures at which perovskite converts to postperovskite (*threshold line*) indicate that the earth's current range of temperatures (*black curve*) is just right for postperovskite to exist in the lowermost mantle, between about 2,600 and 2900 km of depth. In contrast, the early earth (*white curve*) was too hot to allow postperovskite's formation.**



[COMPUTER SIMULATIONS]

## CONVECTION ON STEROIDS

Simulations have shown that in the presence of postperovskite, convection is faster and more chaotic (*right*) than if the mantle contained only perovskite (*left*), as it did in the early earth. Convection plumes rise over the hot core, just like plumes of air form over hot ground. As a plume ascends, the postperovskite in it encounters lower pressures, causing it to transform into perovskite, which is less dense. The resulting expansion adds buoyancy to the plume, causing it to rise up faster and more chaotically than if the mantle contained only perovskite.



FROM "EFFECTS OF A PEROVSKITE-POST PEROVSKITE PHASE CHANGE NEAR CORE-MANTLE BOUNDARY IN COMPRESSIBLE MANTLE CONVECTION," BY T. NAKAGAWA AND P. J. TACKLEY, IN *GEOPHYSICAL RESEARCH LETTERS*, VOL. 31; 2004

JEN CHRISTIANSEN

inner core may be less than a billion years old, which is young compared with the earth's age of 4.6 billion years: otherwise the inner core would be much larger than we observe at present.

The formation of the inner core has implications for geomagnetism, which, in turn, has implications for life. Earth scientists believe that convection of liquid metal in the molten outer core is what generates the planet's magnetic field, by a dynamo action. The presence of a solid inner core makes the convection more regular and less chaotic, resulting in a stronger magnetic field than would exist if the core were entirely liquid. The geomagnetic field shields the earth from solar wind and cosmic rays, which can cause genetic mutations and would be especially dangerous for life on land. The change in the intensity of the geomagnetic field possibly around one billion years ago may thus have made it possible for life to expand from the seas onto dry land.

Postperovskite affects heat diffusion not just at the boundary between core and mantle but throughout the mantle as well, a discovery that has yielded further revelations about the earth's history. Mantle plumes form above the core-mantle boundary. As a plume ascends within the postperovskite layer, it encounters lower pressures, until a threshold is reached where the hot postperovskite transforms into less dense perovskite, which increases volume. Being less dense than the cooler material around it, the plume becomes still more buoyant, which promotes further upwelling. Computer simulations have shown that in the presence of postperovskite, plumes form more often and meander more than if all of the lower mantle were simply made of perovskite [*see box above*]. The simulations have shown that, in this way, the advent of postperovskite probably sped up heat flow through the mantle by 20 percent.

### Causing a Stir

By speeding up mantle convection, the presence of postperovskite increases the temperature of the upper mantle by hundreds of degrees. One of the consequences is that volcanoes are more active than they would otherwise be. In the early earth, when the core was hotter, the lowermost part of the mantle was also hotter and outside the range of temperatures at which postperovskite can form. Paradoxically, though, without postperovskite to speed up heat flows, the upper mantle would have been cooler than it is now. As the planet slowly cooled, some perovskite started to turn into postperovskite, probably some 2.3 billion years ago, boosting the heat flow from the core and raising temperatures in the entire mantle. As a consequence, researchers have estimated, faster plate motion and increased volcanism may have led the continents to grow twice as fast during the past 2.3 billion years than they did during most of the previous time—although this conclusion is still being vigorously debated.

The physical properties of the D″ layer may be remarkably different from those of the overlying mantle. Recent measurements have revealed that postperovskite has much higher electrical conductivity than perovskite, making the lowermost mantle more conductive by several

### ➡ MORE TO EXPLORE

**Perovskites.** Robert M. Hazen in *Scientific American,* Vol. 258, No. 6, pages 74–81; June 1988.

**Sculpting the Earth from Inside Out.** Michael Gurnis in *Scientific American,* Vol. 284, No. 3, pages 40–47; March 2001.

**Post-Perovskite Phase Transition in MgSiO3.** Motohiko Murakami, Kei Hirose, Katsuyuki Kawamura, Nagayoshi Sata and Yasuo Ohishi in *Science,* Vol. 304, pages 855–858; May 7, 2004.

**Deep Earth and Mineral Physics.** Special issue of *Elements,* Vol. 4, No. 3; June, 2008.

**Deep Mantle Properties.** Kei Hirose in *Science,* Vol. 327, pages 151–152; January 8, 2010.

orders of magnitude. A highly conductive postperovskite layer would enhance the exchange of angular momentum between the liquid core and solid mantle whenever the core's flow-pattern changes. (The exchange results from what is called the Lorentz force.) According to simulations done by other researchers, this exchange would alter the earth's rotational speed in a way that closely agrees with millisecond variations that are actually observed in the length of the day on decadal time scales. The electric conductance of postperovskite and the resulting large exchange of angular momentum could also help explain the periodic precession of the earth's axis of rotation (nutation).

Although postperovskite is present only in the bottom few hundred kilometers of the earth's mantle, it could make up larger portions of other planets. Theory predicts that $MgSiO_3$ postperovskite is stable at up to 1,000 gigapascals and 10,000 kelvins, before dissociating into a mixture of silicon dioxide and magnesium oxide. Postperovskite should therefore be a main component of the rocky cores of Uranus and Neptune. In contrast, the rocky cores of both Jupiter and Saturn are enveloped in thick hydrogen layers, which would make pressures and temperatures too high to stabilize postperovskite.

What about planets in other solar systems? All the exoplanets observed so far are bigger than Earth. Those smaller than 10 Earth masses are presumed to be Earth-like rocky planets and are called super-Earths. Astronomers have inferred the composition of exoplanets by observing their host tars. The atmosphere of our sun is imilar in chemical composition to he planets of our solar system, as can e deduced from absorption lines in the un's optical spectrum. Astronomers have imilarly deduced from the optical spectra of ther stars that many super-Earths are likely to ave compositions similar to our own Earth's. nd postperovskite may be the most abundant onstituent of many of those planets, given the nges of pressures and temperatures that would ist in their innards.

## Be Continued

uestions remain about the structure of our anet's postperovskite-rich D″ layer. Large omalies in seismic-wave velocities have long en observed at those depths, as if the D″ layer re not uniform but had two conspicuous features, one located roughly under Africa and other one under the Pacific Ocean. Could there be two masses, denser than the surrounding rock but still light enough to float on the outer core, just like the continents float on the outer mantle? These "hidden continents" could affect the flows at the bottom of the mantle and indirectly the convection patterns in the entire mantle—and thus even plate tectonics at the surface. How did these masses form, and are they growing? Could it be that the one under the Pacific Ocean had something to do with the mantle plume that produced the archipelago of Hawaii? These and other questions may be answered in the near future.

The earth's lowermost mantle has long been enigmatic, but many of its characteristics are now well explained thanks to the discovery of postperovskite. In contrast, a number of questions remain about the iron-rich metallic core. The core has been much harder to study than the mantle because until recently diamond-anvil techniques were unable to re-create the pressures and temperatures that exist in the core. Researchers could produce higher pressures by the brute-force method of shock-wave compression, but the temperatures produced by that method would then be too high.

It has been known since 1952, however, that the liquid outer core is about 10 percent less dense than pure iron or iron-nickel alloy. One or more lighter elements, such as sulfur, silicon, oxygen, carbon and hydrogen, must therefore be present, but the identification of these light elements remains highly controversial. The temperature of the core is best estimated from the melting temperature of iron alloys at a pressure corresponding to the solid-liquid boundary in the core. But the current estimates include an uncertainty of more than 2,000 kelvins, because the melting temperature depends strongly on the exact composition, which is unknown. The crystal structure of iron at inner-core conditions is also still unknown, which makes it difficult to interpret seismological observations. Very recently, however, we have produced diamond anvils that can reach the full range of pressures and temperatures that exist in the earth's core, opening the door to addressing these unsolved mysteries about the deepest part of our planet.

It will be a bit like traveling all the way to the center of the earth, if only in our imagination. ■

## MANTLE AND CORE EVOLUTION

**When the earth formed, the mantle contained no postperovskite, and the hot, iron-rich core was entirely liquid. Because the mantle was inefficient at dissipating heat, the inner earth cooled slowly (*baby earth*). Some 2.3 billion years ago, the formation of postperovskite at the bottom of the mantle speeded up convection. This change in dynamics may have increased volcanism and, with it, the growth of continents (*teenage earth*). The consequent accelerated heat transport also cooled the core enough that, around one billion years ago, a solid inner core began to form (*mature earth*). Convection patterns in the liquid-core layer became more regular and began to produce a strong geomagnetic field, which shields the earth's surface from the dangers of solar wind and cosmic rays. This may have enabled life to move onto land.**