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A crystal cave from Jules Verne's *Journey to the Centre of the Earth* (1864), illustrated by Édouard Riou.

Crystallography's journey to the deep Earth

Improved methods for studying minerals at extreme pressures and temperatures promise a new era for exploring our planet's centre, says **Thomas Duffy**.

Jules Verne's travellers in his 1864 science fiction novel *Journey to the Centre of the Earth* encountered "crystals... like globes of light". One hundred and fifty years later, the study of crystals is poised to shine new light on the deep Earth.

The journey to our planet's centre began a century ago when William Henry Bragg and his son, William Lawrence, used X-ray diffraction to reveal the atomic configuration of common minerals such as halite, diamond, fluorite and calcite. Decades of challenging experimental work to unravel how the structures of such minerals are altered by the extreme pressures and temperatures found in the deep Earth culminated in 2004 when researchers discovered^{1,2} that the main mineral of the lower mantle, iron-bearing magnesium silicate ((Mg,Fe)SiO₃) perovskite, transforms to a compact configuration known as post-perovskite at conditions similar to those at the core-mantle boundary.

Post-perovskite's characteristics explain many of the unusual seismic properties of a distinct 200-kilometre-thick zone at the base of the mantle, a layer that might be a remnant of Earth's formation. This region plays a key but poorly understood part in the thermal structure of the planet.

Ten years on from its discovery, the post-perovskite story remains incomplete. The roles of crystal deformation, chemical variation and temperature in controlling the deep mantle's characteristics are yet to be fully understood. And work on the iron alloys that make up the core is only just beginning. New crystallographic techniques will usher in a deeper understanding of crystal structures and their connection to our planet's architecture, composition and evolution.

PHASE TRANSITIONS

Earth's rocky mantle extends 2,900 kilometres below the surface. About one-quarter of the way down (at about 660 kilometres) it divides into an upper and lower mantle, a discontinuity visible as a sharp change in the speed of seismic waves traversing the boundary. Since geophysicist Francis Birch

of Harvard University in Cambridge, Massachusetts, proposed the idea in 1952, this division and other more

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► complex seismic structures in the mantle have been attributed to phase transitions of the constituent minerals.

Birch's prediction has been verified experimentally over the decades as the technologies to examine minerals at ever higher pressures and temperatures have developed and matured. The requisite pressures are substantial, ranging from 24 gigapascals (GPa) at 660 kilometres to 135 GPa at the core–mantle boundary. Because 100 GPa corresponds to 1 million bars of pressure, the difficulty in simulating deep-mantle conditions is known as the megabar barrier. Temperatures of more than 2,000 kelvin, exceeding that of molten steel, must be achieved at the same time to reproduce the deep-Earth conditions in the laboratory.

UNDER PRESSURE

The diamond anvil cell is the primary tool for high-pressure and temperature mineral studies. Samples of minerals less than 50 micrometres across are compressed between the tips of gem-quality diamonds. Then researchers fire lasers or X-rays through the diamonds at the samples, to heat them and to investigate their structures using crystallographic methods.

The picture that has emerged is that the main minerals found in the upper mantle — olivine, pyroxene and garnet — undergo a series of phase transitions to denser forms with increasing depth. The lower mantle is composed of more dense minerals, which are stable over a wide range of thermodynamic conditions.

(Mg,Fe)SiO₃ perovskite is an array of SiO₆ octahedra with magnesium atoms sitting in spaces in between (iron atoms can sometimes replace magnesium ones). Materials with perovskite's structure are of great interest because they exhibit superconductivity and unusual magnetic behaviour and have applications in fuel cells and memory devices. The other major mineral of the lower mantle is ferropericlase, (Mg,Fe)O, which adopts the rock-salt crystal structure.

So it was a surprise in 2004 when a new deep-Earth mineral form was discovered. In laboratory experiments, perovskite transforms to a tightly layered arrangement called post-perovskite at the pressures and temperatures of the core–mantle boundary^{1,2}. Researchers quickly realized that the properties of this new phase could explain the puzzling presence of a seismically distinct layer in the deepest 200–300 kilometres of the mantle, known as D'' (see 'Inside Earth').

"The impressive improvements in pressure-generating technology must continue."

STEVE JACOBSEN/NORTHWESTERN UNIV.

Compressed between the tips of diamonds in an anvil cell (top), a crystal (bottom) is transformed into perovskite by laser heating, which simulates lower-mantle conditions.

Over the past decade, experimental geophysicists have studied post-perovskite intensely. There is widespread agreement that this mineral phase is influencing the structure and dynamics of the D'' region, and thus heat flow from the core and convection in the mantle³.

But several of the layer's characteristics are still mysterious. The faster velocity of seismic shear waves when they are polarized parallel to the core–mantle boundary than when polarized perpendicular to this interface has yet to be conclusively ascribed to post-perovskite. We also do not understand the relative importance of chemical variations and temperature in determining how the sharp seismic discontinuity varies with depth.

Two main issues are limiting studies. First, diamond anvil cell experiments and structural studies at extreme pressures and temperatures are difficult. Crystallography under deep-Earth conditions has been limited to polycrystalline or powder samples,

which give less-accurate results than single crystals. Solving the complex structures of high-pressure phases is sometimes beyond the capabilities of powder X-ray methods.

Second, the perovskite and post-perovskite phases have complex compositions, as well as structures. They readily incorporate iron and aluminium, which change their seismic properties. Iron is particularly vexing because it can adopt different valences, occupy different sites in the crystal and occur in different electronic states. Even subtle structural and compositional details might have important geophysical implications.

SINGLE CRYSTALS

New techniques hold promise for disentangling these complexities. Single-crystal X-ray diffraction studies are becoming possible at high temperatures and pressures. Once practical only up to 15 GPa and room temperatures, single-crystal diffraction is now becoming feasible beyond the megabar barrier thanks to steady improvements

INSIDE EARTH

Minerals adopt denser forms as pressures rise with depth in the mantle. At conditions near the core–mantle boundary, perovskite transforms into post-perovskite, explaining many properties of the D'' layer, a distinct zone visible in seismic data.

in X-ray sources and detectors, pressure-generating capabilities, sample-preparation techniques and data-collection and analysis software⁴.

New ways of supporting the anvils in the diamond cell expand the angular access for X-rays to get good coverage of the mineral structure without sacrificing pressure. Intense synchrotron X-ray beams are essential for megabar crystallography, to target minute single crystals (of around 5 micrometres) between the diamond tips. Synchrotron beamlines have improved detecting and focusing capabilities.

The tiny single crystal must survive its journey to extreme pressures inside the diamond cell. Crystals can easily be degraded by stresses or can disintegrate after passing through a structural phase transition. One solution is to surround the sample with a soft buffer of solidified helium or neon, although the diffusion of the small noble-gas atoms into the sample must then be considered.

Samples are heated by infrared laser beams from both sides of the diamond cell. Experimenters must avoid thermal and

chemical gradients, which compromise measurements. Pioneering single-crystal diffraction experiments⁵ at conditions of the mid-mantle (84 GPa and 2,050 kelvin) on silicate perovskite samples demonstrate that such studies at deep-mantle conditions are possible. A further challenge in post-perovskite research is that single-crystal samples cannot yet be synthesized by heating at high pressures. So, a combination of polycrystalline and single-crystal methods is being tried: individual grains in a polycrystalline sample are isolated and then subjected to single-crystal X-ray techniques^{6,7}.

The structural information provided by crystallography is being complemented by techniques for studying the chemistry and texture of samples subjected to ultrahigh pressures. Focused ion beam milling extracts the tiny sample from the diamond anvil cell after it has been heated, so that it may be subjected to further probing, such as by electron microscopy, at ambient conditions. This was previously difficult owing to the small size and fragility of diamond-cell samples.

Imaging techniques using nano-sized X-ray beams are making it possible to study variations in mineral textures, morphology and chemistry across heterogeneous samples⁸. These probes open up studies of melting behaviour, chemical reactions, element distributions and textural changes, important for interpreting seismic and geodynamic observations of the deep Earth.

CORE PUZZLES

The next major challenge for crystallographic studies of the deep Earth is the solid inner core at pressures of 330–363 GPa and temperatures above 5,000 kelvin. Recent seismic studies have revealed that the inner core is complex and fascinating⁹. It exhibits layering, and the eastern and western hemispheres have differing behaviours. Seismic waves travel faster along the spin axis than in the equatorial plane. None of these properties is understood.

Pioneering powder X-ray diffraction experiments have now reached the extreme conditions of the inner core¹⁰. But much work remains to identify the exact composition of the iron alloy in the core and how its crystal structure and physical properties connect to the seismic observations.

To answer these questions, the impressive improvements in pressure-generating technology must continue. Crystallographic studies will need to be combined with new techniques for measuring sound velocities and other physical properties, including thermal and electrical behaviour of iron alloys at more than two-and-a-half times higher pressure than the core–mantle boundary. These are formidable challenges, but they must be met to complete our scientific journey to the centre of Earth — and beyond to the makings of the gas giants and extrasolar planets. ■

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