Mineralogy at the extremes

Thomas S. Duffy

The discovery of a new silicate structure at conditions corresponding to a depth of 2,700 kilometres below Earth's surface has fundamentally changed our understanding of the boundary between the core and mantle.

Connections between scientific disciplines can emerge in unexpected ways. In 2004, mineralogists rushed to their libraries to locate a somewhat obscure 40-year-old paper[1] that described an unusual crystal structure found in a compound of calcium iridium oxide ($CaIrO_3$). The reason for the sudden geological interest in the iridate family was the discovery that (Mg,Fe)SiO_3 perovskite — the major mineral in Earth's vast lower mantle — adopted this same structure when subjected to pressures of more than 125 GPa (1.25 million bars) and temperatures above 2,000 K in the laboratory[2,3]. Under these crushing pressures and searing temperatures, Earth's mantle finally divulged one of its deepest secrets. The new structure, commonly referred to as post-perovskite, is composed of layers of SiO_6 octahedra sharing edges and corners to form sheets interleaved with layers of larger Mg and Fe cations (Fig. 1). Although mineralogists had speculated over the years that perovskite might undergo some kind of transformation at high pressures, the formation of this $CaIrO_3$-type structure had been wholly unanticipated by theory and experiment.

New view of the deep Earth

Earth's lower mantle, which extends from a depth of 660 km to 2,890 km, is the largest region of Earth, with a mass that is roughly 100 times that of the crust. Understanding the mineralogical constituents of this region is vital to unravelling Earth's origin, evolution and dynamic behaviour (see page 261). Without any way to sample it directly, our fuzzy picture of the lower mantle comes mainly from seismic studies, and most of the region seems to be fairly homogeneous. However, a puzzling aspect has been a thin layer extending about 200 km above the boundary between the core and the mantle (known for historical reasons as D′′) that has several anomalous properties[4]. The D′′ region is separated from the rest of the mantle by a discontinuity in seismic velocity. Compared with the rest of the lower mantle, the D′′ region is very heterogeneous and has increased anisotropy of seismic waves (see page 266). Complexity in the deepest mantle should not be surprising. The hot but solid silicate minerals of the mantle are juxtaposed against the churning liquid iron core. The region is a likely source for the hot plumes that reach all the way to Earth's surface, as well as perhaps the final repository for subducting slabs from Earth's surface.

So what has been learned about the connection between D′′ and post-perovskite in the three years since its discovery? On balance, many of post-perovskite's characteristics match those predicted by seismic observations of D′′ (ref. 5). Although it is difficult to measure pressure accurately under such extreme conditions in the laboratory, the transformation seems to occur at pressures corresponding to those found at the top of the D′′ region. More importantly, the strongly positive pressure–temperature, or Clapeyron, slope of the transition means that the transformation occurs deeper in locally hotter regions and shallower in cooler regions, which is consistent with seismic observations. But it can be much more complex than this. Earth has a steep thermal gradient near the core–mantle boundary, and temperatures at the base of the mantle might become hot enough for perovskite to re-emerge just above the core[6]. In this case, complex structures such as localized lenses of post-perovskite could be expected (Fig. 2). Attempts to image the structures in this region seismically have already yielded some tantalizing results[7,8].

Going beyond the core–mantle boundary

Are there more discoveries of the magnitude of post-perovskite awaiting us in the deep Earth? The answer to this question is almost certainly yes. Several trends are fuelling a vibrant and vigorous research enterprise in the exploration of deep planetary interiors and the wider high-pressure realm. In the laboratory, sustained pressures in excess of 1 Mbar (relevant to Earth's deep mantle and core) can be achieved with a diamond anvil cell. However, mineralogists are now finding that they can carry out increasingly reliable studies under extreme conditions without experimental input, by using computer calculations based on quantum-mechanical principles, such as density-functional theory[9]. The major advantage of such methods is that they can simulate pressure conditions of 1 Mbar nearly as easily as they can simulate 1 bar. The disadvantage is that the theory's inherent approximations mean that the results have to be compared with experiments. Theoretical studies have provided tremendous insights into post-perovskite — confirming its thermodynamic stability and providing predictions of the Clapeyron slopes, seismic anisotropies and other key properties, some of which have yet to be confirmed experimentally. Rapid improvements in theoretical methods and their applications to increasingly complex systems will certainly be a major driving force for the field in the coming years.

In laboratory studies carried out at high pressures, the megabar era has now been entered. Pressures above 1 Mbar (100 GPa), which until recently were the domain of a determined few, are now just the starting point for much forefront science. Pressures in Earth's interior range up to 360 GPa, and temperatures are perhaps 5,500–6,000 K near Earth's centre. Much of the deep mantle and core thus remain *terra incognita* from

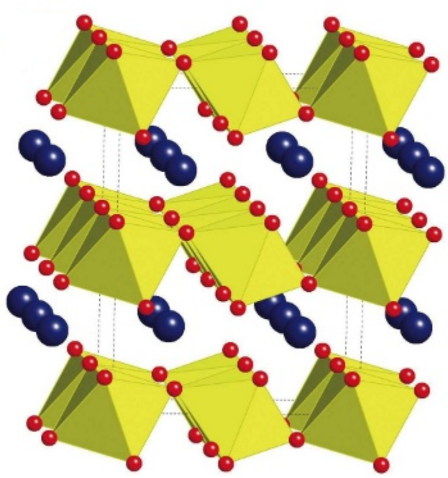

Figure 1 | Crystal structure of the post-perovskite phase of Mg,Fe)SiO_3. The structure consists of layers of linked silicon octahedra (yellow). Red spheres at vertices of SiO_6 octahedra are oxygen ions, and blue spheres are magnesium and iron ions.

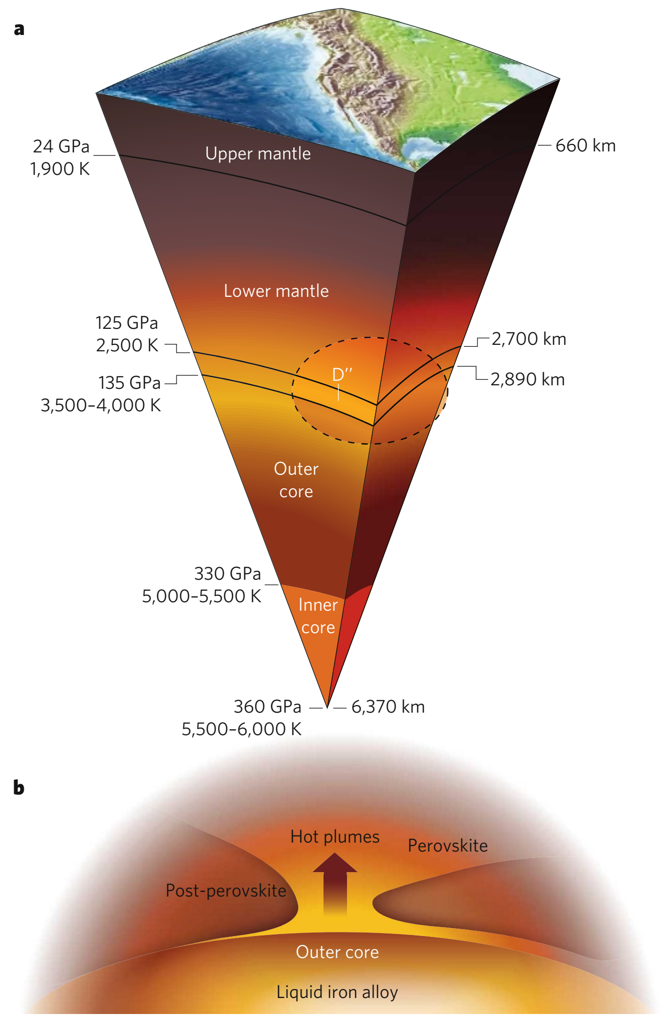

Figure 2 | Cross-section through Earth's interior showing the expected range of pressures and temperatures. a, The lower mantle extends from a depth of 660 km to a depth of 2,890 km, with the D″ region extending about 200 km above the core. **b**, A simplified diagram of possible structures of the D″ region near the core–mantle boundary (the region indicated by dashed lines in **a**)[6].

an experimental perspective. To progress, a coupled effort is required to achieve and sustain a well-characterized pressure–temperature state while making sophisticated measurements of a range of key physical variables on both solid and liquid phases, including structure, elasticity, bonding, transport properties, lattice dynamics, electrical and magnetic properties and chemical interactions among increasingly complex geological assemblages.

Key questions about Earth's core (which has a pressure range of 135–360 GPa) include the identity of its main light elements, the nature of melting and iron-rich liquids at core conditions, core–mantle interactions and the origin of the solid inner core's seismic anisotropy. Moreover, Earth cannot be studied in isolation. The interior structures of the giant planets present a myriad of fascinating questions, and their study requires even higher pressures and temperatures. For giant planets, the materials of main interest are the fundamental ices and gases (for example, hydrogen, water and methane) of the Solar System. Complexity abounds in these constituents, and new bonding configurations, structural changes and metallization are all expected[10]. Such studies can provide the answers to basic questions about the mechanisms of planetary formation and the origin of magnetic fields. Even further, new possibilities can be envisaged for the structures of hot 'Jupiters' and possible super 'Earths' and super 'Ganymedes' in solar systems beyond that of Earth, offering combinations of composition, pressures and temperatures that hold the promise of further surprises.

Scaling up

Aside from the scientific opportunities, a key driving force for mineral physics has been the union of high-pressure experiments with synchrotron X-ray facilities[11]. High-pressure studies are especially well positioned to benefit from the combination of high-energy and high-intensity radiation that synchrotrons specialize in delivering. X-ray spectroscopy techniques that have matured at synchrotrons have found important applications in the Earth sciences. The discovery that iron in mantle minerals transforms from a high-spin (or unpaired) state to a low-spin (or paired) state is another finding of great importance[12]. The change in spin state is accompanied by changes in partitioning behaviour, compressibility and optical properties, all of which can strongly affect the behaviour of the lower mantle. This is a reminder that mineral properties can change markedly under extreme conditions even without any accompanying changes in crystal structure.

Synchrotrons are now focal points around which communities of high-pressure scientists nucleate. The result has been a flowering of interdisciplinary interactions. This trend towards community facilities promises to grow as new opportunities abound to bring high-pressure mineral physics to neutron facilities such as the Spallation Neutron Source at Oak Ridge, Tennessee, and laser facilities such as the National Ignition Facility in Livermore, California. It is worth emphasizing that static techniques are only one method of achieving ultra-high pressure–temperature conditions. Historically, high pressures were first reached by shock-wave methods that sustain extreme conditions for no longer than a microsecond. Dynamic methods are also undergoing a renaissance driven by new capabilities in high-powered lasers. These techniques are achieving multi-megabar conditions, and there is potential to reach much greater pressures by using these methods alone or together with diamond anvil technologies[13].

The discovery of post-perovskite is likely to be remembered as a turning point in understanding the structure and dynamics of the deep Earth. But the elucidation of the connections between the geophysics of the deep Earth and its mineralogical constituents has only just begun. Given the fundamental questions that remain to be addressed, the unexplored territory of pressure–temperature–composition space and newly emerging scientific capabilities, post-perovskite promises to be just the first of many scientific highlights that will characterize the megabar realm of deep planetary interiors. ■

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