Preface. Some remarks on the evolution of mineral physics over the past 40 years

This preface to the thematic issue echoes the introductory talk by the author to the 9th High-Pressure Mineral Physics Seminar, held in Saint-Malo, France, from 24 to 28 September 2017.

Welcome to Saint-Malo and welcome to the 9th High-Pressure Mineral Physics Seminar!

The organizers of this meeting, the first to be held in France, have asked me to give an introductory talk. I have no doubt that this is due to the dubious privilege of age, as I am old enough to have witnessed the early stages of high-pressure mineral physics.

Three years ago, in *Physics of the Earth and Planetary Interiors*, Bob Liebermann provided a most interesting and entertaining review of all eight meetings before this one. I will not, therefore, repeat what he has said so well.

Instead, I will avail myself of this opportunity to cast a retrospective glance over the last forty years or so and highlight a few of the many significant advances in high-pressure mineral physics. Many of the actors of this adventure are present in this room, so I will be mostly addressing the younger part of the audience. I will also indulge in a few reminiscences.

Forty years ago, I saw the light and was born again from the physics of materials to mineral physics and geophysics.

In 1979, I believe the last year the AGU Spring meeting was held in Washington DC, I remember that Alvin van Valkenburg showed me high-pressure phases of ice through his diamond-anvil cell.

Some years before, Li-Chung Ming and Bill Bassett had developed a diamond-anvil cell heated by a YAG laser. And in Japan, under the influence of Prof. Akimoto, large-volume multi-anvil presses were already allowing the characterization of several high-pressure phases.

In my budding laboratory, Jean Peyronneau built a desktop laser-heated diamond-anvil cell and attained once a pressure of 1 Mbar. Nowadays, when I see James Badro's laboratory, I feel as somebody who used to fly one of the Wright brothers' airplanes would feel in the cockpit of a Boeing 777.

About ten years before, Binns and co-authors had identified the high-pressure phase of olivine, with spinel structure, in the Tenham meteorite, a shocked L6 chondrite, which they had named *ringwoodite*. Their identification had been done by traditional petrographic methods, and I decided to use transmission electron microscopy to investigate the dislocations in this phase. I had been Friedel's student and dislocations and transmission electron microscopy were my bread and butter. With my first student, Michel Madon, we obtained electron diffraction patterns and images of stacking faults. In England, Andrew Putnis and David Price had had the same idea and they published their results a couple of months before us… Nevertheless, we became friends.

Shocked L6 chondrites hold a special place in the history of mantle high-pressure minerals. They provide metastable samples of very high-pressure phases, of much larger size than those obtained in diamond-anvil cells and more easily amenable to electron microscopy and structural analysis. And, last but not least, it is only when high-pressure phases of the mantle are found in nature that they become proper minerals and get a name less unwieldy than, for instance, "magnesium silicate with perovskite structure". So, *ringwoodite* was found in Tenham, *majorite* in Coorara, *wadsleyite* in Peace River, *akimotoite* also in Tenham, and recently, in 2014, *bridgmanite* in Tenham again (Tschauner et al., 2014).

As far as I know today, the post-perovskite phase has still not been identified as a mineral, but I have no doubt that it will be someday, maybe in Tenham, and may I suggest it be named *Francisbirchite*, in honor of Francis Birch, the author of the 1952 article, which I believe to be the founding paper of mineral physics (Birch, 1952).

Forty years ago, high-pressure research in mineral physics was mostly a US–Japanese affair, and only a handful of foreigners were, so to speak, admitted to the club. I therefore was proud to be invited in 1981 to the second meeting at Hakone, Japan, together with one

Russian, one German and one Australian, out of 59 attendees. Ten years later, I was again invited to the 4th meeting, again in Japan, at Ise. The community had grown a bit: there were 87 attendees and still only 5 outsiders, again from the Soviet Union (which still existed until the end of that year), Germany, Australia, and France.

There I met the cream of the high-pressure community and made many good friends, some of whom I am happy to see here. I have a thought for those who passed away: Ted Ringwood, Tom Ahrens, Don Anderson, Syun-Iti Akimoto, Harry Green.

Since that time, there have been considerable advances, due to the improvement of the diamond-anvil cell and to the use of synchrotron radiation from sources with better and better brilliance: ESRF at Grenoble and NSLS at Brookhaven in 1994, APS at Argonne in1995, SPring-8 in Japan in 1997 and, this year, PETRA III at DESY, Hamburg and NSLS-II at Brookhaven.

The diamond-anvil cell is almost sixty years old. Bill Bassett (2009) and Bob Hazen (1993) have recounted the history of this wonderful instrument, and I will not dwell on the many improvements that have led to important results. Let me only recall that thirty years ago, Dave Mao and Peter Bell, at the Geophysical Lab, had already reached a pressure of 5.5 Mbar. A couple of years ago, Leonid Dubrovinsky, using a double-stage diamond-anvil cell, reported attaining 7.7 Mbar, more than twice the pressure at the center of the Earth (Dubrovinsky et al., 2015).

Even though it is now possible to obtain the pressure at the center of the Earth in diamond-anvil cells, there remain considerable difficulties in measuring the physical properties and equation of state of the deep-earth materials in the relevant domain of temperature and pressure.

In recent years, progress in computer capabilities and in computation methods have allowed parameter-free, ab-initio calculations of the physical properties of specific minerals, using molecular dynamics and quantum mechanics.

In the last fifteen years, a number of crucial problems bearing on the constitution and structure of the lower mantle and core of the Earth have been, if not entirely solved, at least for a large part unraveled, thanks both to high-pressure experimentation and ab-initio calculations and computer simulation. Let me briefly quote a few, among the most important, some of which will be reported here.

1. Convection in the lower mantle is controlled by its viscosity, which depends on the creep mechanism by which the mantle material deforms. Is it by diffusion-controlled dislocation glide, or by diffusion creep, which depends on the unknown grain-size?

Small samples of bridgmanite, admittedly the major phase of the lower mantle, can be prepared in diamond-anvil cell, but they are not (should I say not yet?) amenable to high-temperature, high-pressure creep experimentation. And even if they were, the experimentally accessible strain-rates are not smaller than 10^{-5} s^{-1}, and the creep mechanisms at mantle strain-rates are probably different. Strain-rates in the mantle are of the order of 10^{-12} s^{-1}, which means that, in a creep experiment, a strain of 1% could be obtained after about 300 years, assuming that temperature, pressure and stress are kept constant during that time... as well as funding, of course.

This is one case where computer simulation is the only solution. The technique known as "dislocation dynamics" simulates the dynamic collective behavior of dislocations and their interactions. Dislocations are represented by line segments that move under driving forces, which can be calculated: dislocation line tension, dislocation interaction forces and external loading. Now, in recent years, dislocation dynamics simulation has made considerable progress. Using it, Cordier and co-workers (Boioli et al., 2017) have very recently shown that, for bridgmanite at low stresses, the dislocation glide velocity is much slower than climb velocity. Hence, the efficiency of dislocation glide as a strain-producing mechanism becomes negligible compared to climb, and strain is produced by pure climb of dislocations, a hitherto little investigated mechanism in minerals. Pure climb creep is independent of grain-size, which is nice because we do not know the grain size in the lower mantle. Also, it does not produce crystal preferred orientation, which is compatible with the weak seismic anisotropy in the lower mantle.

2. For a long time, one of the most tantalizing questions in deep-Earth geophysics has consisted in finding the nature of the seismically complex D" layer at the core–mantle boundary and of the mysterious ultra-low velocity zones.

The orthorhombic "post-perovskite phase", as it is known, was discovered in 2004. In May of that year, a paper from a Japanese team, with the title "Post-perovskite phase transition in MgSiO$_3$" (Murakami et al., 2004) appeared in Science, and in July, Nature published "Theoretical and experimental evidence for a post-perovskite phase of MgSiO$_3$ in Earth's D" layer" by a European author and a Japanese one (Oganov and Ono, 2004).

The authors of the first paper reported the in-situ characterization of the post-perovskite phase, by X-ray diffraction, in a laser-heated diamond-anvil cell, at 2600 K and 1.34 Mbar, a temperature and pressure expected in the D" layer. They used the SPring-8 synchrotron X-radiation facility. The authors concluded that "the post-perovskite phase transition occurs at depths matching those of the D" discontinuity."

At the same time, Oganov and Ono, by ab-initio calculations, had found that a post-perovskite phase with the layered structure of calcium iridate CaIrO$_3$ would be stable at high pressure and temperature. They experimentally confirmed their prediction, finding a stability domain in agreement with the theoretical prediction and with the results of Murakami et al. Both teams (Iitaka et al., 2004) calculated ab-initio the elastic constants of the new phase (they agreed) and concluded that many of the seismic features of the D" layer could be explained.

Almost simultaneously, another team (Tsuchiya et al., 2004) had predicted the structure of the post-perovskite phase, by first-principles ab-initio calculation... a very powerful method indeed.

But the existence of the ultra-low velocity zones was still not explained.

Wendy Mao et al. (2004) experimentally found that, contrary to expectations, iron-rich post-perovskite phase containing up to 80% Fe was stable at pressures of the D" layer, a result in agreement with ab-initio calculations which also showed that the density of iron-rich post-perovskite phase was about up to 20% higher than that of any other known silicate at the core–mantle boundary (Mao et al., 2005). Using "synchrotron high-pressure nuclear resonant inelastic X-ray scattering spectroscopy", the authors determined the phonon density of state of the iron-rich phase and demonstrated that it has a low seismic velocity, high Poisson ratio signature of the ULVZ (Mao et al., 2006). The iron-rich phase that could be formed by infiltration of the outer core iron would be too dense to rise in the mantle and could pile up under the upwelling areas, forming seismically observable ultra-low velocity patches.

For a long time, it was not known whether the ULVZ was due to a phase transition or to a change in chemical composition. Now, we know that it may be due to both.

3. The geotherm is anchored at the temperature of the inner core-boundary, the crystallization temperature of the outer core alloy, somewhat lower than the melting temperature of pure iron. Some of you may remember the heated controversy, in the late 1980s and early 1990s about the melting curve of iron at high pressures.

An American team had combined shockwave experiments and melting experiments in a laser-heated diamond-anvil cell up to 1 Mbar. They had found a very steep melting curve and extrapolated it to 3.3 Mbar, the pressure at the inner core boundary, finding a melting point of about 7600 K.

A German team, also from experiments in a laser-heated diamond cell, had found that the melting point of Fe at 1.2 Mbar was 3000 K, more than 1000 K lower than the American value, and the extrapolation to 3.3 Mbar yielded a melting temperature of about 4800 K.

The quality of the experiments was undisputed in both cases, but there remained the problems of the extrapolation and above all, the fact that the determination of melting in a diamond-anvil cell is very difficult and that part of the discrepancy probably came from the different melting criteria used.

Some years later, with Tom Shankland (Poirier and Shankland, 1993), I calculated, not a melting curve, but the melting point of iron at the pressure and temperature conditions of the inner core boundary by a dislocation-melting theory, resting on the assumption that a liquid is a solid saturated with dislocation cores. The calculated melting temperature depends on the shear modulus and the bulk modulus at the temperature and pressure of melting, which can be provided at the inner core boundary by seismological data. We found a melting temperature at 3.3 Mbar of about 6100 K, which was right in the middle of the controverted experimental values. *In medio stat virtus*!

At about the same time, a British team (Alfé et al., 1999) calculated ab-initio the temperature at which the free enthalpies of the solid and liquid phase are equal for the pressure of the inner core boundary. They found a value of about 6700 K.

Four years ago, a French team (Anzellini et al., 2013), again made experiments up to 2 Mbar in a laser-heated diamond-anvil cell and, using fast X-ray diffraction; they could identify the appearance of a diffuse diffraction peak of the liquid as an unambiguous signature of melting. The extrapolation to 3.3 Mbar yields a temperature of about 6200 K.

So, it is probably not unreasonable to believe that the melting temperature of iron at the pressure of the inner core boundary is close to 6000 K and that the temperature at the inner core boundary is close to 5500 K, despite a large uncertainty due in part to the unknown melting point depression caused by light elements in the outer core.

4. It is agreed that the inner core is mostly iron and that at very high pressures the stable phase has the hexagonal closed packed structure. But, as the determination was done at room temperature, what about at core temperatures? What is the stable phase of iron at pressures higher than 3.3 Mbar and temperatures higher than 5000 K? Is it hcp or bcc or fcc, or even double hcp or orthorhombic, as it had sometimes been proposed?

By experiments in a laser-heated diamond-anvil cell, using synchrotron X-ray diffraction, a Japanese team (Tateno et al., 2010) determined the structure of iron up to 3.77 Mbar and 5700 K. They found that, in the temperature and pressure range of the inner core, iron is hexagonal closed packed with a c/a ratio of about 1.6, in agreement with previous ab-initio calculations, and this conclusion is now generally accepted. Now it has been proposed that the observed seismic anisotropy of the inner core might due to the preferred orientation of iron crystals due to deformation by glide on the primary slip system, basal or prismatic. Which of these systems is active depends on the stacking fault energies on basal and prism planes, which were calculated from first principles by David Price. We found that hexagonal iron slips primarily on the basal plane, unlike other metals with the same c/a ratio, like Ti, which slip on the prism plane (Poirier and Price, 1999).

There are still a number of unresolved problems, but I have no doubt that, in her introductory talk to the 2057 seminar, one of you will be able to reflect on the many advances in high pressure mineral physics achieved since 2017.

Bon courage!
Thank you.

References

Alfé, D., Gillan, M.J., Price, G.D., 1999. The melting curve of iron at the pressure of the Earth's core from ab-initio calculations. Nature 401, 462–464.

Anzellini, S., Dewaele, A., Mezouar, M., Loubeyre, P., Morard, G., 2013. Melting of iron at the Earth's inner core boundary based on fast X-ray diffraction. Science 340, 464–468.

Bassett, W., 2009. Diamond-anvil cell, 50th birthday. High Press. Res. 29 (2), 163–186.

Birch, F., 1952. Elasticity and constitution of the Earth's interior. J. Geophys. Res. 57, 227.

Boioli, F., Carrez, P., Cordier, P., Devincre, B., Gouriet, K., Hirel, P., Kraych, A., Ritterbex, S., 2017. Pure climb creep mechanism drives flow in Earth's lower mantle. Sci. Adv. 3 (3), e1601958.

Dubrovinsky, L., Dubrovinskaya, N., Bykova, E., Prakapenka, V.B., 2015. The most incompressible metal osmium at static pressures above 750 Gigapascals. Nature 525, 226.

Hazen, R., 1993. The new Alchemists. Times Books, New York.

Iitaka, T., Hirose, K., Kawamura, K., Murakami, M., 2004. The elasticity of the $MgSiO_3$ post-perovskite phase in the Earth's lowermost mantle. Nature 430, 442–445.

Mao, W.L., Shen, G., Prakapenka, V.B., Meng, Y., Campbell, A.J., Heinz, D.L., Shu, J., Hemley, R.J., Mao, H.K., 2004. Ferromagnesian post-perovskite silicates in the D" layer of the Earth. Proc. Natl. Acad. Sci. USA 101, 15867–15869.

Mao, W.L., Shen, G., Prakapenka, V.B., Campbell, A.J., Heinz, D.L., Shu, J., Caracas, R., Cohen, R.E., Fei, Y., Hemley, R.J., Mao, H.K., 2005. Iron-rich silicates in the Earth's D" layer. Proc. Natl. Acad. Sci. USA 102, 9751–9753.

Mao, W.L., Mao, H.K., Surhahn, W., Zhao, J., Prakapenka, V.B., Meng, Y., Shu, J., Fei, Y., Hemley, R.J., 2006. Iron-rich post-perovskite and the origin of the Ultra Low Velocity Zones. Science 312, 564–565.

Murakami, M., Hirose, K., Kawamura, K., Sata, N., Ohishi, Y., 2004. Post-perovskite phase transition in $MgSiO_3$. Science 304, 855–868.

Oganov, A.R., Ono, S., 2004. Theoretical and experimental evidence for a post-perovskite phase $MgSiO_3$ in Earth's D" layer. Nature 430, 442–445.

Poirier, J.-P., Price, G.D., 1999. Primary slip system of epsilon-iron and anisotropy of the inner core. Phys. Earth Planet. Inter. 110, 147–156.

Poirier, J.-P., Shankland, T.J., 1993. Dislocation melting of iron and the temperature of the inner core, revisited. Geophys. J. Int. 115, 147–151.

Tateno, S., Hirose, K., Ohishi, Y., Tatsumi, Y., 2010. The structure of iron in the Earth's inner core. Science 330, 359–361.

Tschauner, O., Ma, C., Beckett, J.R., Prescher, C., Prakapenka, V.B., Rossman, G.R., 2014. Mineralogy. Discovery of bridgmanite, the most abundant mineral in Earth, in a shocked meteorite. Science 346, 1100–1102.

Tsuchiya, T., Tsuchiya, J., Umemoto, K., Wentzcovith, R., 2004. Phase transition in $MgSiO_3$ perovskite in the earth's lower mantle. Earth Planet. Sci. Lett. 224, 241–248.

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