Review Article

Earth Science in SPring-8

Among the activities of SPring-8, researches in the field of Earth science plays an important role. In particular, two beamlines, BL04B1 and BL10XU, are equipped with state-of-the-art high-pressure and high-temperature apparatus and have been used to carry out numerous high quality works that had led to advances in Earth science in the last decade. In this review, we introduce some studies focused on the Earth's deep Interior.

1. Laser-heated diamond anvils at BL10XU

High-pressure and high-temperature *in situ* X-ray diffraction provides the most direct and reliable information on the minerals expected to exist deep inside the Earth. Such experimental study has only been made possible by the use of strong X-ray sources and synchrotron radiation to greatly expand the pressure and temperature ranges of the experiments. The first trial experiment of this nature was performed at the Photon Factory in Tsukuba in the 1980's using a large-volume high-pressure apparatus named MAX-80 [1]. Following the success of this apparatus, a new system was developed to extend the pressure to beyond 100 GPa that employed a diamond anvil apparatus combined with a laser heating system. This system was reproduced at SPring-8 and then further improved to take full advantage of the quality of the third generation source at SPring-8 [2,3]. Laser heating combined with the diamond anvil can heat samples to beyond 5000 K, although the heating spot is very small (typically less than 20 μm in diameter) and a very large temperature gradient exists in the heated area. The X-ray optics at BL10XU was designed so that a very sharp and small monochromatic X-ray beam can be obtained. As a result, very high quality powder X-ray diffraction patterns can be obtained even under the extreme conditions corresponding to the deep part of the Earth.

1-1. *Discovery of the post-perovskite phase of $MgSiO_3$ in the deep mantle of the Earth*

It is well known that the upper part of the mantle of the Earth, the area down to about 400 km below the surface, mainly consists of three minerals: olivine (Mg_2SiO_4), pyroxene ($MgSiO_3$), and garnet ($Mg_3Al_2Si_3O_{12}$). It was discovered in the 1970's that pyroxene and garnet transform into much denser minerals with a perovskite structure, while olivine decomposes into a mixture of phases with perovskite and rock salt structures. Many studies have been carried out to clarify the stability limit of these silicate perovskites, and these studies suggested that the silicate perovskite is stable down to the bottom of the lower mantle, which extends a depth of 2900 km. Since the volume of the lower mantle is more than half the entire volume of the Earth, the silicate perovskite is the most abundant mineral of our planet, even though we cannot observe this high-density mineral at the surface of the Earth.

Hirose's group at Tokyo Institute of Technology has been working intensively to clarify the behavior of various rocks under the conditions of the deep lower mantle, and they found unidentified diffraction peaks using the system at BL10XU. Further studies clarified that even for the very simple mineral $MgSiO_3$ (bridgmanite), the perovskite structure transforms into a new phase above about 120 GPa, which is only 10 GPa below the pressure at the core-mantle boundary. They summarized this work and published it with the title "Post-perovskite phase transition in $MgSiO_3$" in Science (2004) [4]. This new phase of the silicate made it possible to solve various baffling problems arising from seismic studies of the core-mantle boundary region. Since then, numerous works have started to clarify the nature of this post-perovskite phase and the above-mentioned paper has been cited more

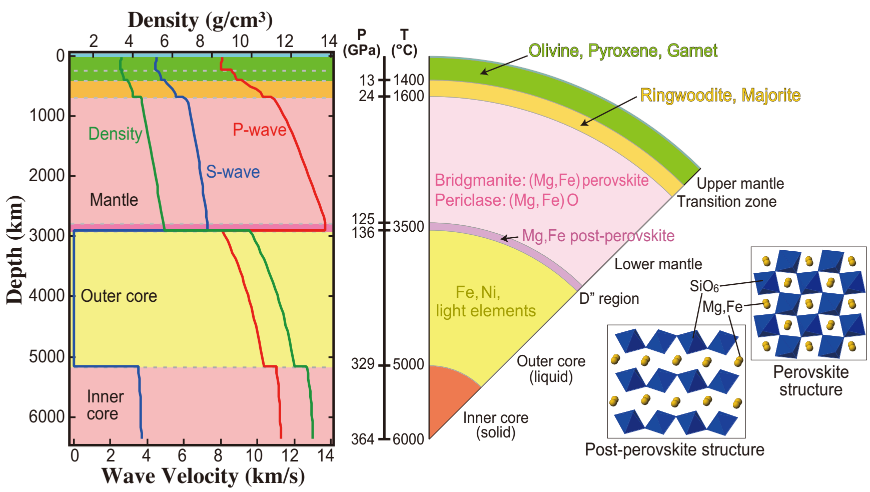

Fig. 1. Major minerals in the Earth.

than 800 times by researchers around the world. This clearly shows the huge impact of this work in the field of Earth science. Figure 1 shows the main minerals expected to exist inside the Earth. As is clear from this figure, the post-perovskite phase is the last and the most dense silicate mineral expected to exist in the Earth, and the research carried out at SPring-8 has played a key role in clarifying this new paradigm in Earth science.

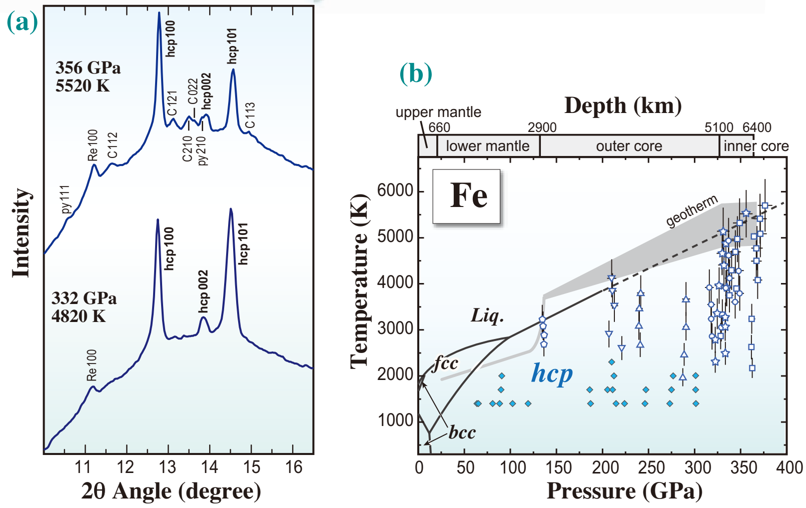

Fig. 2. (a) Diffraction spectra under the conditions at the center of the Earth and (b) phase diagram of iron.

1-2. *X-ray diffraction study under conditions corresponding to the center of the Earth*

Further efforts were made to extend the pressure and temperature ranges of powder X-ray diffraction studies to the deeper part of the Earth, the core, mainly by reducing the size of the sample. In 2010, Tateno *et al.* reported a stable phase of iron under the conditions at the center of the Earth [5]. At a pressure of about 360 GPa and a temperature of over 5000 K, they showed that the *hcp* phase is the stable phase of iron. Many groups worldwide have attempted to clarify the phase relation of iron, which is the main component of the core, and various results have been reported. Among them, the work of Tateno and his coworkers covered the highest pressure and temperature ranges and, as is clear from Fig. 2, the quality of the diffraction data was sufficiently high to convince many other scientists of the validity of their results. Therefore, so far as pressure and temperature conditions are concerned, it is now possible at SPring-8 to achieve conditions at any part of the Earth and to study in detail the stable phases of materials under these extreme conditions.

1-3. *Efforts to further extend the pressure range*

Efforts to extend the pressure range beyond that of the Earth are also being made using the double-stage diamond anvil technique. In the solar system and in the universe, there are many places subjected to much higher pressures than the center of the Earth, such as the inside of Jupiter and Saturn. The behavior of materials above 500 GPa is also a very interesting and fascinating target for research in physics and chemistry, and many groups worldwide are attempting to further extend the pressure range of experiments. We employed the double-stage diamond anvil technique, described as follows. A very tiny anvil with a culet (a top flat part to generate a very high pressure) diameter of only 3 μm was prepared using a focused ion beam (FIB) that was developed to process very small samples for electron microscopy. As shown in Fig. 3, a pair of these tiny anvils was placed in the sample chamber of a conventional diamond anvil and squeezed with a sample between them. In this way, a high confining pressure is applied to these second-stage anvils, which is expected to extend the pressure range further. Although many technical problems still remain and the achieved pressure has not exceeded that of the single-stage diamond anvil technique, the results have high reproducibility and very promising results have been obtained [6]. In this study, the size of the powder sample was only a few microns in diameter and the thickness was less than one micron. As a result, a very small and strong X-ray beam is required to obtain measurable diffraction from such a tiny sample. The quality of the X-ray optics of BL10XU is sufficiently high in terms of stability and brilliance to obtain good diffraction data from the small area of such a tiny sample.

1-4. *Multiple-property measurements under extreme conditions*

Although X-ray diffraction data to determine the crystal structure is the most basic information when investigating the properties of materials, information on many other physical properties is also desirable. The most basic and directly obtainable information about the deep interior of the Earth is provided by seismic

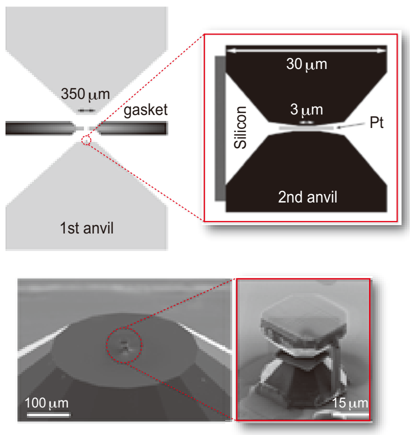

Fig. 3. Double stage diamond anvil.

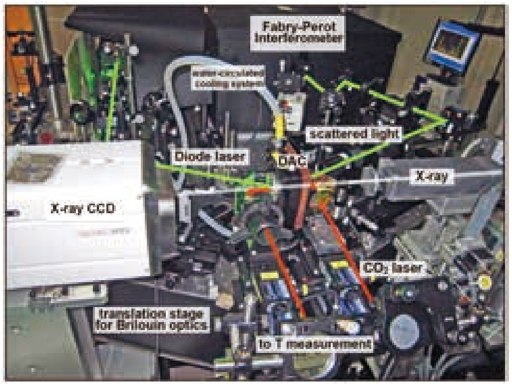

Fig. 4. Brillouin scattering setup.

observations. The propagation velocities of longitudinal and transverse waves through the whole of the Earth have been well studied. Using X-ray diffraction, however, we can obtain the crystal structure and density of minerals. By measuring pressure derivatives of the density, we can obtain elastic parameters related to longitudinal waves but no information can be obtained for transverse waves. Brillouin scattering is a powerful technique for directly measuring the elastic wave velocities of a tiny sample. At BL10XU, a new system for performing simultaneous measurements of X-ray and Brillouin scattering was constructed by Murakami *et al*. [7]. As shown in Fig. 4, the system is complicated because four probes, the X-ray beam for diffraction, the laser beam for Brillouin scattering, the laser beam for heating the sample, and visible light for sample observation have to be focused precisely at a tiny sample subjected to high pressures.

This system has made it possible to measure the elastic wave velocities of various materials over very wide pressure and temperature ranges and to obtain powder X-ray diffraction data simultaneously. Various studies have been carried out on $MgSiO_3$ perovskite [8], post-perovskite [9], and SiO_2 [10], and on the basis of these studies, important issues have been raised regarding the deep interior of the Earth.

2. Large volume high-pressure apparatuses at BL04B1

Two large-volume high-pressure apparatus, SPEED-1500 and SPEED-1500 Mark.II (Fig. 5), are installed at BL04B1 of SPring-8. They are driven by large hydraulic rams with a capability of 1500 tons and can compress a cubic or octahedral pressure-transmitting medium to a size of about 1 cm. Compared with the laser heated diamond anvil apparatus, the pressure and temperature range attainable using these apparatuses are rather limited, and routine studies have so far been carried out below 50 GPa. However, a much more well controlled and stable sample temperature can be achieved and the sample size can be on the order of a few mm, which is two orders of magnitude larger than that when using diamond anvils. These characteristic features are particularly important for studying multicomponent systems and mixtures of various minerals, i.e., rocks, which are the main component of the Earth. Efforts to increase the pressure beyond 50 GPa have been made and the successful generation of a pressure over 100 GPa was recently achieved using a Kawai-type multi-anvil high-pressure apparatus with large sintered diamond anvils [11]. At present, multi-anvil experiments at such high pressures are only possible at SPring-8. This technical breakthrough has contributed to the understanding of the Earth's entire mantle and is playing a major role in the growth of high-pressure research.

Since a sample under pressure is surrounded by many materials such as the capsule, heater, pressure-transmitting medium, and gasket, the X-ray beam has to travel through all these materials to reach the sample and the length of the propagation exceeds several centimeters. As a result, a very high energy X-ray beam, typically more than 50 keV, is required for such experiments. Fortunately, SPring-8 can produce a high-energy white X-ray beam whose maximum energy exceeds 100 keV. Combined with a solid-state detector (SSD), high-quality X-ray diffraction data can be obtained in a short time, typically on the order of 100 s.

Another characteristic feature of this beamline is the use of X-ray radiography. By combining brilliant and parallel X-ray beam with a CCD camera, we can obtain a precise image of a sample under a high pressure and high temperature with a resolution of a few micrometers. Radiography observation can provide a variety of information difficult to obtain by other measurements. For example, by measuring the sinking velocity of a small platinum ball in a molten silicate, the viscosity of the molten silicate has been studied as a function of pressure. Another example is the simultaneous measurement of stress and strain under pressure.

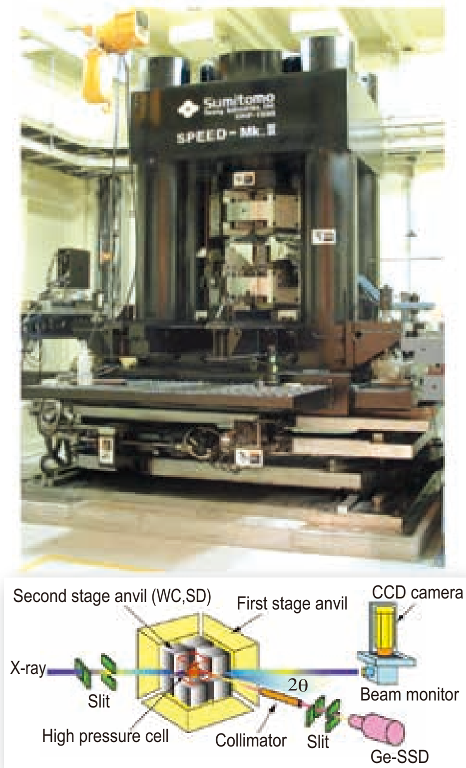

Fig. 5. Large-volume press and schematic illustration of the experimental setup.

Stress can be measured from the change in the unit cell volume using the powder X-ray pattern, while bulk strain can be measured by directly observing the bulk size of the sample by radiography.

Another characteristic feature of BL04B1 is the simultaneous measurement of X-ray and ultrasonic velocities of a sample. This allows us to precisely compare laboratory data and seismic observations of the Earth and we can make detailed argument about the composition and structure of the Earth's deep interior. Some examples of works performed using the above-mentioned features are introduced.

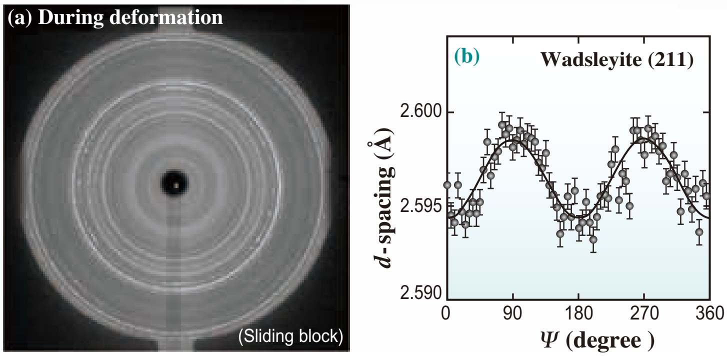

Fig. 7. (a) Typical X-ray diffraction pattern of wadsleyite and (b) variation of *d*-spacing with azimuth angle.

2-1. *Detailed study on the transition zone (from 400 to 700 km depth) of the Earth*

The transition zone is the area where various pressure-induced transitions occur in the minerals constituting the Earth, and both the sound velocity and density increase very rapidly in this area. Irifune's group performed simultaneous *in situ* velocity and X-ray measurements on garnets under the conditions of the transition zone using the systems at BL04B1 [12]. Using these data, they succeeded in clarifying that the chemical composition called the pyrolite model more convincingly explains the seismic velocity profile in this area than another competing model called the piclogite model (Fig. 6). Direct observation of the chemical composition at this depth is impossible and the systems at SPring-8 are becoming very powerful for such study.

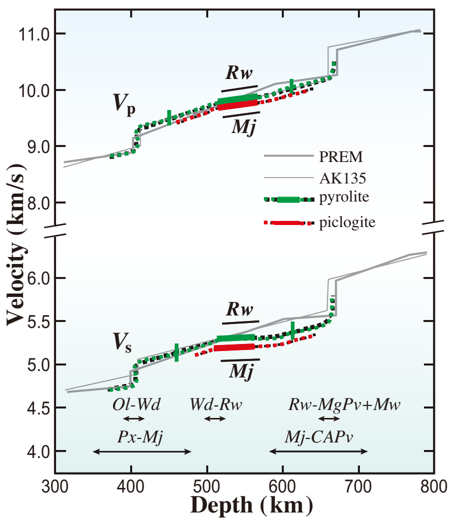

Fig. 6. Comparison of the sound velocities for pyrolite and piclogite compositions with representative seismological models.

2-2. *Rheological study of rocks and minerals in the deep mantle*

Not only the stable structures but also the dynamics is becoming increasingly important for obtaining a correct understanding of our planet. The most basic information for such studies is the rheological properties of the constituent materials, which are extremely difficult to obtain under very high pressures. Therefore, experimental studies have so far limited to the conditions of the shallow upper mantle. However, the systems developed by Kawazoe's group at BL04B1 have made it possible to extend such studies to the conditions of the transition zone [13]. By combining the capabilities of D-DIA high-pressure apparatus, X-ray radiography, and X-ray diffraction, they have succeeded in measuring the stress-strain relations of various materials under the conditions corresponding to the transition zone (Fig. 7). Such studies will greatly affect our understanding of the dynamics in the deep interior of the Earth.

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