Application of synchrotron radiation and Kawai-type apparatus to various studies in high-pressure mineral physics

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ABSTRACT

A combination of Kawai-type multianvil apparatus and highly brilliant X-rays at the third generation synchrotron radiation facility (SPring-8) in Japan has been successfully applied to various studies in high-pressure mineral sciences such as determinations of phase transition boundaries, $P-V-T$ relations of high-pressure phases, kinetics of phase transitions, structure and viscosity of melts. These studies are now comfortably made at pressures of ~25 GPa and at temperatures to 2300°C, using the intense X-ray beam and the large capacity of the high-pressure apparatus at SPring-8. Moreover, efforts have been made to further extend the pressure limit using large sintered diamond anvils. Thus in situ X-ray observations are now possible at pressures to 50 GPa with the Kawai-type apparatus, which may be doubled in the near future when the potential of sintered diamond anvils is fully utilized. On the other hand, some problems, such as those related to pressure and temperature measurement, have been manifested in these studies. These should be overcome for further quantitative studies of the mineralogy of the Earth’s deep interior based on these techniques.

KEYWORDS: synchrotron radiation, high pressure, mineral physics, multianvil apparatus, phase transition.

Introduction

APPLICATIONS of synchrotron radiation to high-pressure mineral sciences have been made in the last two decades, where in situ X-ray observations under static pressure have been performed using various types of high-pressure apparatus. Among these high-pressure tools, the diamond anvil cell (e.g. Furnish and Bassett, 1983) and the single-stage multianvil apparatus (e.g. Shimomura et al., 1984) have been most commonly used for such in situ X-ray observations. The diamond anvil cell has advantages in producing higher pressures over the single-stage multianvil apparatus, as the pressures available for in situ X-ray observations in the latter apparatus are normally limited to ~15 GPa (Morishima et al., 1994; Utsumi et al., 1995; Zhang et al., 1996). Nevertheless, the latter is superior to the diamond anvil cell in terms of accurate determinations of phase boundaries, $P-V-T$ relations, physical parameters, etc., because far larger sample volumes of ~10 mm$^3$ (cf. 10$^{-3}$ mm$^3$ in the diamond anvil cell) and stable pressure/temperature conditions are available. A number of in situ X-ray studies on mantle minerals have been made with the single-stage multianvil apparatus at the second-generation synchrotron facilities at KEK in Tsukuba, NSLS in Brookhaven, and HASYLAB in Hamburg, although the pressures have generally been limited to those of the upper mantle (see Shimomura et al., 1992).

The pressure limit of the single-stage multianvil apparatus is overcome in the Kawai-type high-pressure apparatus, a general name for the double-stage (6-8) multianvil system after the late Prof. N. Kawai (Kawai and Endo, 1970), which has been widely used in studying the mineralogy of the mantle transition region and of the lower mantle on the basis of the quench method. Application of synchrotron radiation to Kawai-type apparatus has been made using sintered diamond for eight second-stage anvil cubes, and some in situ X-ray diffraction studies relevant to
mantle mineralogy have been successfully made, mostly at pressures of 25–30 GPa, using MAX–80 and MAX–90 at KEK (Ohtani et al., 1989; Kato et al., 1995; Funamori et al., 1996a,b). However, the smaller press capacities and less brilliant and less stable nature of the synchrotron radiation, as compared to those at third-generation synchrotron facilities, has hindered comprehensive experimental studies under these pressures, except for a few successful experiments on the stabilities and measurements of $P-V-T$ relations of high-pressure phases (Funamori et al., 1996a,b; Irifune et al., 1996a; Oguri et al., 1998).

The construction of SPring-8, a third-generation synchrotron source operated at 8 GeV, in Hyogo prefecture, Japan, and the High Pressure Earth Science beamline (HPES beamline at BL04B1) with a large Kawai-type apparatus (SPEED-1500, SPring-Eight Energy Dispersive system with a hydraulic ram of 1500 ton; Utsumi et al., 1998), has dramatically changed this situation. Irifune et al. (1998) successfully determined the spinel–postspinel phase transition boundary in Mg$_2$SiO$_4$ using an in situ diffraction technique soon after the beamline was opened to researchers. This was the very first experimental result obtained from all the beamlines at SPring-8. Since then, many studies have been conducted at this beamline, producing abundant experimental data relevant to the mineralogy of the Earth’s deep interior. Here, I review some research results from the HPES beamline since it was opened in late 1997, with special emphasis on those related to phase transitions in mantle minerals. I also discuss the advantages and problems of the SPEED-1500 system, and describe future perspectives and some technological developments currently being pursued at this beamline by Japanese mineral physicists.

**High-pressure Earth Science Beamline at SPring-8**

The HPES beamline was one of ten, of a planned total of ~60, opened at SPring-8. A white X-ray beam from the bending magnet light source is collimated with vertical and horizontal slits to form a thin beam possessing a cross-section typically of $50 \times 100 \mu m$, which is then directed to the sample via a gap between the first- and the second-stage anvils of SPEED-1500. SPEED-1500 can apply press loads up to 1500 tons and weighs about 20 tons itself. It is mounted on a three-dimensionally moving stage, which is fully operational from outside the hutch to micrometer precision (Fig. 1).

An energy dispersive X-ray diffraction system is attached to SPEED-1500. X-rays diffracted by samples of the order of a few mm$^3$ under high pressure and high temperature are detected with a 4096-channel analyser via a pure Ge detector (Fig. 2). Use of a receiving slit of ~50 micrometers at a fixed angle to the direct beam permits only the diffracted X-rays from the sample to be detected. The diffraction angle ($2\theta$) is variable with a precision of $\pm 0.001^\circ$, but is normally fixed at an angle of 4–8$^\circ$ because of geometrical constraints imposed by the high-pressure appa-

![Fig. 1. SPEED-1500 at the HPES beamline (BL04B1), SPring-8.](image)
ratus and also to avoid effects of the direct X-ray beam. Photon energies, generally between 10 and 150 keV, are assigned to the multiple channels of the above analyser. These are calibrated with known characteristic X-ray lines of some reference elements, so that the uncertainty of the measurements is about 30–40 eV, depending on the energy range used. Thus the lattice parameters of a crystalline sample can be determined within an uncertainty of 0.1% using this system. The X-ray acquisition time to obtain such a diffraction profile for refinements of lattice parameters is typically one to several minutes.

Figure 3a depicts a typical cell assembly used by our group for in situ X-ray observations with SPEED-1500 (Irifune et al., 1998). Twin sheet heaters made of cemented TiC + diamond powders can produce stable temperatures exceeding 2000°C, which are sufficiently high for measurements of phase transitions in silicate minerals. Temperature is measured with a W$_{97}$Re$_3$-W$_{75}$Re$_{25}$ thermocouple, whose hot junction is placed in the middle of the sample/pressure marker (Fig. 3b). Although there is a significant temperature gradient in the sample, diffracted X-rays from only the sample close to the thermocouple junction are acquired. Thus the uncertainty due to the temperature gradient may be within ±2% of the nominal value, as demonstrated in Fig. 4. However, the effects of
pressure on the thermocouple e.m.f. are usually ignored in these experiments, which may result in some errors in temperature measurements, as discussed later.

Pressure is usually measured from the unit-cell volume changes in reference materials, such as NaCl, gold, platinum, and MgO, whose equations of state are relatively well documented. However, it has been recognized that these equations of state may not be accurate enough for the determination of geophysically important phase boundaries. It has also been noted that grain growth of the reference materials, particularly NaCl, often hinders the accurate determination of lattice parameters and hence unit-cell volumes, especially at temperatures above 1000°C. Moreover, possible errors in temperature measurements may introduce uncertainty in the pressure measurements. This will also be revisited in a later section.

A high-resolution CCD camera is attached to SPEED-1500 so that we can see the macroscopic change of the sample shape under high pressure and temperature via the transmitted X-ray image of the sample, which is visualized via a fluorescent screen and is captured by the camera (Fig. 2). The use of the CCD camera not only makes it easy to direct the X-ray beam to the desired position within the sample, but has also led to the development of new techniques to observe dynamic processes under high pressure, such as sample deformation and melting.

Observation of phase transitions and determination of the phase boundaries

Irifune et al. (1998) were first to demonstrate that SPEED-1500 is a potential tool to investigate phase transitions under simultaneous high pressures and high temperatures corresponding to those of the lower mantle. Since then a number of studies have been directed at the precise determination of phase boundaries relevant to mantle mineralogy, as well as those related to materials science. Here, I summarize the results of in situ X-ray diffraction studies of the phase transitions in the major mantle minerals, i.e. olivine, pyroxene, garnet, and those in a representative mantle.

\( \text{Mg}_2\text{SiO}_4 \) olivine

As olivine is the most abundant mineral in the upper mantle, its phase transitions to high-pressure forms have been thought to be responsible for the seismic discontinuities at 410, 520 and 660 km. The 410 km discontinuity is generally attributed to the olivine—modified spinel transition in \((\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4\) olivine on the basis of both quench and in situ X-ray diffraction measurements (Katsura and Ito, 1989; Morishima et al., 1994). The largest seismic discontinuity in the whole mantle at 660 km was considered to be caused by the dissociation of spinel into the postspinel phase.
assemblage (i.e. MgSiO$_3$-rich orthorhombic perovskite + (Mg,Fe)O magnesiowustite), based on quench experiments (e.g. Ito and Takahashi, 1989). However, Irifune et al. (1998) demonstrated that this transition occurs at significantly lower pressure (~21 GPa) than that corresponding with 660 km depth (23.4 GPa), on the basis of an in situ X-ray diffraction study (Fig. 5). In this study, pressures were evaluated with a gold pressure marker using the equation of state of Anderson et al. (1989).

Two different groups have since made extensive studies using SPEED-1500 and different cell assemblages. The results of Fei et al. (Y. Fei, pers. comm., 2001) agree with those of Irifune et al. (1998), while the boundary at temperatures near 1600°C is shown at slightly higher pressures of ~0.5 GPa by Katsura et al. (2002). However, the results of this study and that of Irifune et al. (1998) agree well at lower temperatures, and the deviation of this magnitude at 1600°C may be attributed to the random errors of the pressure determination (~±0.2 GPa). Thus the results of three groups on the phase boundary between spinel and postspinel phases are in good agreement with one another when Anderson’s gold pressure scale is adopted.

$\text{MgSiO}_3$ and $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{SiO}_3$ pyroxenes

Pyroxenes [MgSiO$_3$ enstatite and $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{SiO}_3$ diopside] are the next abundant minerals after olivine in the upper mantle, and their phase relations have been studied extensively, mostly in quench experiments. The boundary of the ilmenite-perovskite transition in MgSiO$_3$ was investigated by Kato et al. (1995) using in situ X-ray diffraction measurements with sintered diamond anvils at KEK. However, the large uncertainties both in temperature and pressure in their experiments hindered precise determination of the phase boundary, and the transition pressures were constrained only within ±2 GPa.

Kuroda et al. (2000) and Ono et al. (2001) independently determined the ilmenite-perovskite phase boundary using SPEED-1500. The former study had difficulty in effectively constraining the phase boundary by changing the $P/T$ conditions in a single run because of grain growth of the ilmenite phase at high temperatures, which hindered unambiguous identification of the phases present in the X-ray diffraction patterns. Nevertheless, the boundary was fairly well determined by making use of additional quench experiments using pressure calibrations based on the results of in situ X-ray observations. The study demonstrated that the boundary is close to or slightly lower than that of the spinel-postspinel transition reported by Irifune et al. (1998). The result of Ono et al. (2001) was also consistent with Kuroda et al. (2000) within 0.5–1 GPa when Anderson’s pressure scale was used, showing that the boundary is located 2–3 GPa lower than determined by earlier quench experiments (Fig. 5).

The nature of the phase transitions in diopside at pressures greater than 20 GPa has been a matter of debate in the last decade. Some have reported that it transforms to cubic perovskite at pressures above 24–25 GPa (Liu, 1987; Kim et al., 1994), while others have demonstrated that it decomposes into an assemblage of MgSiO$_3$ orthorhombic and CaSiO$_3$ cubic perovskites under similar pressures (Mao et al., 1978; Tamai and Yagi, 1989; Irifune et al., 1989; Kim et al., 1994). There had been no in situ X-ray diffraction studies on the phase transition in diopside under simultaneous high-pressure and high-temperature conditions, until Irifune et al. (2000) demonstrated using SPEED-1500 that diopside and the corresponding glass starting materials decomposed into two perovskites. Although the phase boundary was not tightly constrained, the results suggest that the boundary between the assemblages of MgSiO$_3$ ilmenite + CaSiO$_3$ perovskite and MgSiO$_3$ perovskite + CaSiO$_3$ perovskite is located at ~23 GPa at 1000°C, which is close to the ilmenite-perovskite transition determined by Kuroda et al. (2000) and Ono et al. (2001).

$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet and pyrolite

Pyroic garnet is the third most abundant mineral that constitutes the peridotite or pyrope upper mantle, and is the most important host for Al in the upper mantle. Irifune et al. (1996b) found that $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ pyrope decomposes into a mixture of aluminous perovskite plus corundum at ~27 GPa and 1500°C, based on quench experiments. Hirose et al. (2001a) further studied this reaction by in situ X-ray diffraction using SPEED-1500, and demonstrated that the boundary lies at 25.2–24.5 GPa, depending on the temperatures studied (1200–2000°C; Fig. 5).

Phase transitions in pyrolite, a representative mantle composition, have been studied extensively by Irifune (1994) using the quench method. Virtually no in situ X-ray diffraction studies for
such multi-component systems with complex chemical compositions have been performed because of technical difficulty in assigning the diffraction peaks to multi-phases, maintaining high temperatures for a sufficient period of time to achieve chemical equilibrium, finding an appropriate capsule material, etc. These problems have been overcome by using SPEED-1500 and a specially designed cell described by Nishiyama et al. (2002), where the spinel–postspinel transition pressure was determined precisely at a fixed temperature of 1600°C. The result showed that this transition occurs at 20.7 GPa, slightly lower than the pressure for the same transition in Mg2SiO4 (21.1 GPa, 1600°C; Irifune et al., 1998).

Hirose et al. (2001a) and Nishiyama et al. (2002) used a similar technique of fixing temperature and pressure (in reality, press load) and identifying the phases after a heating time of >1 h to reduce kinetic problems. However, phase identification was made for the quenched sample in the former study, while pressure measurement and phase identification were simultaneously made by in situ X-ray measurements in the latter study. It should be noted that the phase boundary pressures thus determined for pyrope and pyrolite are again lower than those determined by quench experiments by 2–3 GPa, consistent with those observed for the phase transitions to MgSiO3-perovskite bearing phases in olivine and pyroxenes using SPEED-1500.

Reliability of the pressure and temperature estimations

The pressure reference materials suitable for in situ X-ray observations should satisfy the following conditions: chemically inert, possessing a simple crystal system and a high X-ray scattering factor, stable over wide P/T ranges. NaCl is an ideal pressure marker and an equation of state by Decker (1971) has frequently been used for the pressure estimation in both multianvil apparatus and diamond anvil cell. However, the use of NaCl as pressure marker is limited to pressures below 25 GPa and temperatures below ~1000°C, because of its phase transition to the CsCl structure at high pressure and crystal growth at high temperatures. Thus, alternative pressure reference materials such as gold have been used for higher pressure and temperature conditions.

Funamori et al. (1996a) systematically tested various pressure reference materials and their equations of state for a wide temperature range to 1700°C at 25 GPa. They found that the equation of state of gold proposed by Anderson et al. (1989) produces pressures consistent with those determined by Decker’s NaCl scale at temperatures to ~1000°C, and used this equation of state of gold for the determination of thermoelastic properties of MgSiO3 perovskite at lower mantle conditions.

Hirose et al. (2001a,b) also made a comprehensive comparison of the existing pressure scales, such as NaCl, gold, Pt, Mo and W, and
concluded that the pressures obtained by these markers are generally consistent with each other.

It was also demonstrated that the pressures from the gold scale of Anderson et al. (1989) may be slightly (~0.5 GPa) higher than those derived from other scales (Fig. 6). Thus the pressures for the phase transition boundaries based on Anderson’s gold scale cited above should be consistent with those based on other scales or maybe even slightly overestimated. In other words, the pressure for the spinel–postspinel transition in Mg$_2$SiO$_4$ (21.1 GPa, at 1600°C) determined by Irifune et al. (1998) could have been further reduced if another pressure scale was adopted.

Recently, Shim et al. (2001a) reported that the phase boundary of the spinel–postspinel transition in Mg$_2$SiO$_4$ is located at 23.6 GPa at 1600°C, consistent with the results of the quench experiments by Ito and Takahashi (1989) but in contrast to those of Irifune et al. (1998). They used a combination of laser-heated DAC and synchrotron radiation, and estimated the pressures using an equation of state of Pt. As the comparison by Hirose et al. (2001a,b) clearly showed that the pressures obtained using Au and the Pt scales are almost identical or that the latter gives lower pressures, there must be something wrong with the experiments of Shim et al. (2001a) or with all of the studies on the phase transition boundaries using SPEED-1500.

One possible cause of the discrepancy is inaccurate estimation of temperatures in the multianvil apparatus and/or diamond anvil cell. The temperature fluctuation during high-temperature and high-pressure runs in multianvil apparatus is quite small, normally within ±5°C, and the uncertainty due to the temperature gradient in the sample is also not very significant, typically of the order of ±20°C or less, as discussed earlier. Thus the net uncertainty due to these factors should be less than ±30°C. However, the pressure effect on the e.m.f. of the thermocouple (usually W$_{97}$Re$_{3}$-W$_{75}$Re$_{25}$) in multianvil experiments is generally ignored, as this effect depends largely on the cell assembly and hence its evaluation is very difficult. This may lead to some additional uncertainty in the temperature measurements in these experiments.

It is known that the e.m.f. of the W-Re thermocouples mostly used in these studies has less pressure dependency than others such as Pt-
Rh (Getting and Kennedy, 1970; Mao and Bell, 1971), and it seems unlikely that such pressure effects lead to errors of >10% of the nominal temperature readings at 20 GPa. In fact, the possible underestimation of temperature if the pressure effect of e.m.f. is ignored is estimated to be ~15°C at 4 GPa for a temperature of 1500°C (Mao and Bell, 1971; Fig. 7), which yields an underestimation of temperature of only ~80°C when this relationship is extrapolated linearly to the pressure region of the spinel–postspinel transition. Moreover, Ohtani et al. (1982) demonstrated that a W-W$_{75}$Re$_{25}$ thermocouple gives a temperature of ~100°C higher than that determined by Pt-Pt$_{87}$Rh$_{13}$ at 1600°C and at a pressure of 7 GPa. Underestimation of temperature by ~250°C for the W$_{97}$Re$_{3}$-W$_{75}$Re$_{25}$ thermocouple is required to explain the difference between the spinel–postspinel transition pressure at 1600°C and that of the 660 km seismic discontinuity, which is probably unlikely, if not impossible.

The uncertainty in the temperature measurements in diamond anvil cells is generally even more significant, and some studies (e.g. Zerr and Boehler, 1993) actually use the melting temperatures of some minerals determined by multianvil experiments to warrant their results at higher pressures. In addition, there are a number of unresolved contradictory results using diamond anvil cells among different research groups, for instance, in the studies of melting temperatures of MgSiO$_3$-rich perovskite (e.g. Nittle and Jeanloz, 1989; Zerr and Boehler, 1993) and Fe (e.g. Williams et al., 1991; Boehler, 1993; Shen et al., 1993, 1998), and in the studies of high-pressure and high-temperature phase transitions, such as the ‘β’ phase of iron and its crystallographic structure (Saxena et al., 1995, 1996a; Yoo et al., 1995; Andrault et al., 1997; Shen et al., 1998), and dissociation of MgSiO$_3$-rich perovskite into an oxide mixture (Meade et al., 1995; Saxena et al., 1996b; Serghiou et al., 1998; Shen et al., 1998; Shim et al., 2001b). These are due, at least partly, to the unreliable estimations of temperature and/or pressure in this high-pressure apparatus at pressures greater than ~30 GPa. Such problems will certainly be solved when these pressure ranges are covered by SPEED-1500, which may be realized in the near future as suggested in the next section. It seems to be more or less by chance that the

![Figure 7](image-url)

**FIG. 7.** An estimation of the effect of pressure on the e.m.f. of the W$_{97}$Re$_{3}$-W$_{75}$Re$_{25}$ thermocouple used in most Kawai-type multianvil experiments, based on a linear extrapolation of the measurements by Mao et al. (1971) at 2 and 4 GPa. The actual temperature under pressure may be calculated as a sum of the nominal temperature and the ΔT value in this figure. For instance, a temperature of 1600°C at ~20 GPa may be underestimated by ~80°C. It should be noted, however, that such extrapolations using only a few experimental data in a limited pressure range may suffer significant uncertainties.
pressure for the spinel–postspinel transition of Shim et al. (2001a) using an in situ X-ray observation agrees with that of Chudinovskikh and Boehler (2001) based on a quench experiment, when the current state of the art for diamond anvil cell and the many unsolved inconsistent results, especially at high temperature, are taken into account.

In any case, it has become clear that both the multianvil apparatus and the diamond anvil cell may still have significant uncertainties in the determination of phase transition pressures at high temperature, and it is fair to say that the boundary between the spinel and the postspinel phases in Mg$_2$SiO$_4$ should be located at ~22.5±1.5 GPa, at 1600°C (corresponding to ~635±40 km depth in the mantle), considering the transition pressures reported thus far and the possible error sources. Further theoretical and experimental studies on the accurate measurements of temperature and pressure are certainly required to improve this determination.

**Other studies conducted at the HPES beamline**

In addition to the phase equilibria studies cited above, a number of other studies have been conducted using SPEED-1500 at the HPES beamline, using the unique characteristics of this high-pressure apparatus and the bright and stable light source of SPring-8. Here I review the results of some recent studies conducted at this beamline.

**P–V–T relations of high-pressure phases**

One advantage of SPEED-1500, as compared to the existing multianvil apparatus at the second-generation synchrotron sources, is that a larger sample volume is available, in addition to higher pressures and temperatures. With this advantage, we can realize homogeneous temperature/pressure gradients within the sample, by adopting thermally insulating materials, using larger heaters, etc., for the cell assembly. Thus, it is expected that P–V–T data of better quality and over extended pressure and temperature ranges will be obtained than by using the smaller apparatus, and we can therefore obtain thermo-elastic parameters to describe the volume (density) changes in high-pressure phases more accurately.

In order to avoid possible overlapping of the X-ray diffraction lines from a sample and the capsule for precise determination of lattice parameters, BN has frequently been used as the capsule material in high pressure in situ X-ray observations, because this material yields only very few diffraction lines that overlap those from the sample. BN is a relatively soft material, which also makes it also suitable as a capsule material because of reducing macroscopic deviatoric stress acting on the sample. Moreover, BN is often mixed with NaCl, which is used as the pressure marker, to suppress the grain growth of this material at high temperature.

The room-temperature bulk moduli of some high-pressure phases have been successfully determined after reducing the deviatoric stress by annealing the sample at high temperature (e.g. Wang et al., 1996a). Initial attempts to determine the bulk moduli of high-pressure phases at room temperature, using a cell assembly similar to those used at the lower pressures and temperatures, have been unsuccessful, however, because BN transforms to very hard hexagonal or cubic forms at pressures above ~10 GPa, at high temperature. Inoue et al. (T. Inoue, pers. comm., 2001) tried to define thermo-elastic parameters of modified spinel and spinel forms of Mg$_2$SiO$_4$ using SPEED-1500 and following the methodology used in earlier studies at lower pressures, but found that the derived bulk moduli of these phases at room temperature were significantly (more than 10%) lower than those reported from diamond anvil cell experiments with a liquid pressure medium or ultrasonic measurements. As these values at temperatures above 1000°C are in good agreement with earlier results, Inoue et al. concluded that the apparent low values of bulk moduli at relatively low temperatures are due to underestimation of pressure at these temperatures. Inoue et al. used BN capsules, where the sample and the pressure marker (a mixture of MgO plus Au) were enclosed separately, and measured the unit-cell volumes of both sample and the pressure marker. The transition of BN to hard high-pressure forms is thought to hinder homogenization of deviatoric stress produced upon decreasing temperature within the capsule, and the pressures estimated from the pressure marker could have been quite different from those actually acting on the sample.

Recently, we (Suenda et al., in prep.) studied phase transitions in diopside to ~35 GPa using sintered diamond anvils and SPEED-1500, and also determined the P–V–T relations of MgSiO$_3$ and CaSiO$_3$ perovskites. In this study, a mixture of diopside and pressure marker (Au) was enclosed directly in the MgO pressure medium.
We recently demonstrated that diopside decomposes into an assemblage of essentially pure MgSiO$_3$ and CaSiO$_3$ perovskites at temperatures lower than 1200°C and at pressures of ~25 GPa based on quench experiments (Irifune et al., 2000). Thus $P-V-T$ data of both of these end-member perovskites, as well as of gold, can be obtained in the course of decreasing temperature after the dissociation took place at high temperature and pressure.

Analyses of the results of these experiments yielded a room-temperature bulk modulus ($K_0$) of 256 (2) GPa and 233 (2) GPa for MgSiO$_3$ and CaSiO$_3$ perovskites, respectively (Fig. 8). The former value is consistent with most of the earlier studies (Mao et al., 1991; Fiquet et al., 1998), and the latter is also consistent with the recent results using a multianvil apparatus at lower pressures (Wang et al., 1996a) and a diamond anvil cell under quasi-hydrostatic conditions (Shim et al., 2000), but disagrees with earlier results using diamond anvil cells (Tamai and Yagi, 1989; Yagi et al., 1989; Tarrida and Richet, 1989; Mao et al., 1989). Few unit-cell volume data have been available for these silicate perovskites at high temperature, at pressures above 20 GPa, and analyses of the present experimental data, which are currently being pursued, will provide important constraints on the density changes of these perovskites at lower mantle conditions.

In addition to these anhydrous phases, some attempts have been made to determine the $P-V-T$ relations of some DHMSs (dense hydrous magnesian silicates) at SPring-8. Inoue et al. (2001) used a Ag-Pd capsule to confine the DHMS sample, which has been proved to work at temperatures to ~1400°C, at pressures of ~20 GPa. X-ray diffraction data of sufficient intensity have been obtained using such a metal capsule because of the high brilliance of the synchrotron radiation at SPring-8, and the water released upon dehydration of the sample was retained in the capsule as a result of the significant increase of the melting temperature of the alloy with pressure. Corresponding studies containing other volatiles, such as CO$_2$, may be conducted readily using similar techniques and SPEED-1500.

**Kinetics of phase transitions and rheology of high-pressure phases**

The large volume available in SPEED-1500 and highly brilliant light source at SPring-8 have made it possible to obtain X-ray diffraction data of high quality in a relatively short period of acquisition time. Thus a time-resolved measurement of rapidly changing X-ray diffraction profiles under high pressure and high temperature is possible using the SPEED system. Some studies

![Fig. 8. Room-temperature compression curves of MgSiO$_3$ and CaSiO$_3$ perovskites determined by in situ X-ray diffraction after annealing under high temperature. MgSiO$_3$ perovskite is obviously more compressive than CaSiO$_3$ perovskite (Sueda et al., in prep.).](image_url)
relevant to the kinetics of phase transitions and dynamic processes of mantle materials have been conducted using this technique.

Kubo et al. (2000) studied reaction kinetics of some high-pressure phase transitions relevant to mantle and subducted slab lithologies, such as those in Mg$_2$SiO$_4$, and constrained the conditions of formation and persistence of metastable lower pressure phases across the phase transitions (Fig. 9). Such information is vital to address the behaviour of subducting slabs and the cause of deep-focus earthquakes, and is now accessible with SPEED-1500 at higher pressures than earlier studies, encompassing the mantle transition region to the uppermost lower mantle.

It has been demonstrated that the yield strength of a high-pressure phase at high pressure and high temperature can be evaluated via the analysis of the changes in the shapes of the diffraction peaks with heating duration: the peaks become sharper because of relaxation of microscopic stresses within the sample, and the changes of the FWHM of the diffraction peaks yield localized strains, which are converted to microscopic stresses using appropriate elastic constants (e.g. Weidner et al., 1994). The observation of the relaxation of the microscopic stresses then provides the yield strength of the sample, which is vital to understand deformation behaviour in the Earth's interior.

Such rheological properties of high-pressure phases may also be obtained via the observations of macroscopic changes of the sample shape under controlled strain (in reality, sample displacement) rate at high pressure and high temperature. Attempts in this direction have been made using SPEED-1500 with the CCD camera, and some preliminary results on the deformation of sintered polycrystalline samples have been reported (Ando et al., 2001). Strains of the order of 5% were found to be produced upon compression in SPEED-1500, which were estimated by the measurements of sample shortening with a precision of $\sim 8 \mu m$. Further developments of this technique to address the rheological properties of high-pressure phases are currently being conducted at the HPES beamline.

**Viscosities of melts and melting temperatures**

Viscosities of silicate melts under pressure were first studied by Kushiro (1976) using the ‘falling sphere’ technique. The terminal velocity of a small falling sphere in a melted sample was determined by measuring the distance from the original position in the quenched sample after the experiment using piston-cylinder apparatus. Then the viscosity of the silicate melt was calculated from the terminal velocity of the falling sphere using Stokes’s law.

![Graph showing the time-resolved measurements of X-ray diffraction profiles across the olivine-modified phase transition in Mg$_2$SiO$_4$ (Kubo et al., unpublished; see also, Kubo et al., 1998).](image)

**Fig. 9.** An example of the time-resolved measurements of X-ray diffraction profiles across the olivine-modified phase transition in Mg$_2$SiO$_4$ (Kubo et al., unpublished; see also, Kubo et al., 1998).
Synchrotron radiation was applied to this technique by Kanzaki (1987), who observed the falling metal sphere in situ using a CCD camera, and measured the velocity by analysing a series of the recorded radiography images. Thus the viscosity of albite melt was determined to 5 GPa at ~1100°C using this method.

With SPEED-1500, the pressure and temperature ranges of such measurements have been extended to pressures above 10 GPa and temperatures beyond 2000°C (Fig. 10). The viscosities of various silicate and other melts, including diopside, basalt, harzburgite, iron, and FeS have accordingly been determined using the advantages of the large Kawai-type apparatus and the bright light source (e.g. Funakoshi et al., 2001; Terasaki et al., 2001).

Melting of a crystalline solid can be defined by the sudden loss of X-ray diffraction peaks. However, it is generally difficult to determine precisely the onset of melting as there is a temperature gradient in the sample charge, and the loss of diffraction peaks and the complementary appearance of an amorphous halo occur rather gradually with increasing temperature. Moreover, some of the powder diffraction peaks may also be lost when crystals grow to the size comparable to the incident X-ray beam (~50 μm) at high temperature. In contrast, melting can be easily recognized from the changes of the sample shape using the X-ray radiography technique.

We recently tried to determine the melting temperature of gold at pressures to 20 GPa by observing the changes in various shapes of the sample, such as sheets, blocks, powders and wires (Irifune et al., 2001). We realized that the presence of temperature gradients within the furnace makes it difficult to unequivocally define the onset of melting in some of these samples, and found that use of a wire sample placed normal to the X-ray beam is most feasible for such measurements (Fig. 11). The nature of the pressure medium surrounding the sample also affects the precise determination of the melting temperature by this method, and we found that NaCl is one of the best media as it is soft and has relatively low melting temperatures, which yields instantaneous change of the sample shape upon melting because of the surface tension of the molten gold. The melting of the gold wire was monitored independently using changes in its electrical resistance, as was done in earlier experiments (Mitra et al., 1967). Melting temperatures agreed well with those determined by the radiographic measurements.

Fig. 10. Snap shots of a falling platinum sphere in an albite melt at 1700°C and 4.2 GPa: (a) initial position; (b) 10 s; (c) 20 s; and (d) 30 s after starting to drop.
High-pressure generation with sintered diamond anvils

The pressures produced in Kawai-type apparatus had been generally limited to ~25 GPa because of the plastic deformation of the tungsten carbide (WC) anvils used for the second stage anvils. Sintered diamond (SD) anvils, which are much harder than these conventional anvils, were then introduced to overcome this limit, and pressures greater than 30 GPa were successfully produced in Kawai-type apparatus (e.g. Kondo et al., 1993; Kato et al., 1995; Funamori et al., 1996a,b). However, only small SD anvil cubes of up to ~10 mm edge length (cf. normally 25–30 mm for WC anvils) were available at that time, as the sizes of the commercially available SD products were limited. Moreover, it was recognized that careful adjustment of alignment of the first stage WC anvils is essential to operate a high-pressure cell with such small second-stage SD anvils. Such adjustments were possible only in a DIA-type apparatus, such as MAX-80 and -90 at KEK (Shimomura, 1984; Shimomura et al., 1992) and SAM-85 at NSLS (Weidner et al., 1992; Wang et al., 1996b) or a split-sphere type apparatus operated in an oil chamber (Kawai and Endo, 1970). A DIA type apparatus, originally invented by Kobe Steel Co. Ltd., is one of the variations of multianvil apparatus, where the horizontally-placed four first-stage anvils move synchronously with the movement of upper and lower anvils so that the second-stage anvil assembly can be equally pressurized in three dimensions. However, the press capacity of existing DIA-type apparatus was limited to 500 tons until SPEED-1500 was constructed at SPring-8.

Ito et al. (1998) first adopted larger SD cubes (14 mm edge length) as the second stage anvils, and succeeded in extending the pressures up to 40 GPa using a split-sphere apparatus operated in a specially designed oil chamber. Since then, Ito’s group and our group have been working extensively to apply such technology with the large SD anvils to SPEED-1500 so that we can conduct in situ X-ray observations under these pressures. The use of larger second-stage SD anvils has a great advantage, as higher press loads can be applied to the cell assembly. The maximum load applicable to the second-stage anvils is limited by the strength of the first-stage WC anvils, which is ~400–500 tons when SD anvils of 10 mm edge length are used, while the limitation becomes twice as high when we adopt the larger anvils of 14 mm edge length.

With a combination of SPEED-1500 using the large SD anvils and synchrotron radiation, pressure generation of up to 50 GPa has been confirmed at a press load of 800 tons (Ito et al., 2001; Fig. 12). Higher pressures may be produced when the size and the design of the gasket-pressure medium system of the high-pressure cell are fully optimized. Moreover, if larger SD anvils are used, further higher pressures could be achieved within the press capacity of SPEED-1500 (1500 tons). Temperatures as high as 1800°C are produced comfortably under pressure with SD anvils, and in situ X-ray diffraction...
studies of some phase transitions have been successfully made, although the practicable pressures generally decrease at such high temperatures and to date are limited to ~45 GPa. Various studies on the phase transitions and the $P-V-T$ relations of high-pressure phases under these pressures have just started, and some preliminary results have been obtained as follows.

Ito et al. (2001) studied the phase relations of iron to 45 GPa and at temperatures up to ~1800°C to explore the presence of the $\beta$-phase, which has been a matter of debate between several research groups using diamond anvil cells, as mentioned earlier. They demonstrated unequivocally that some of the phase identifications in those studies were incorrect and that no such high-pressure form of iron existed at these pressure and temperature conditions. This shows that the quality of in situ X-ray diffraction data provided by a combination of Kawai-type apparatus and synchrotron radiation is far superior to that obtained from the very small amount of sample available in a diamond anvil cell. This is often critical if one wishes to address the details of crystal structures from X-ray diffraction data.

In situ observations of phase transitions in some minerals related to the deep lower mantle have also been conducted using SD anvils and SPEED-1500. For instance, Irifune et al. (2002) studied phase transitions in MgAl$_2$O$_4$ spinel at pressures up to 40 GPa and at temperatures to 1600°C, and concluded that only the calcium ferrite-type phase is stable under these conditions. This result is inconsistent with those of earlier diamond anvil cell studies, which suggested that either an unknown form (Liu, 1978) or a CaMn$_2$O$_4$-type structure of MgAl$_2$O$_4$ (Funamori et al., 1998) are stable under these conditions. The room temperature bulk modulus ($K_0$) of the calcium-ferrite type MgAl$_2$O$_4$ was evaluated in this study, and the result ($K_0 = 213$ GPa) agrees with the recent estimate of Funamori et al. (1998), whereas it is significantly lower than the value reported earlier by Yutani et al. (1997).

Future perspectives

The SPEED-1500 system has been proved as a potential tool to investigate the mineralogy of the Earth’s deep interior, as shown in the above, but at the same time some limitations and problems in this system have become evident after use for more than four years since SPring-8 was opened. I explore these technical problems here and discuss

![Fig. 12. A comparison of pressure generation in SPEED-1500 using sintered diamond (SD) and tungsten carbide (WD) anvils as the second-stage anvils. Truncation edge length (TEL) of the anvil was 1.5 mm (SD, Ito et al.; WD, Irifune et al.; both unpublished data).]
the future developments and perspectives of high-pressure mineral physics studies with the Kawai-type apparatus at SPring-8, some of which are already being realized at the present HPES beamline.

In situ X-ray measurements under even higher pressures

The hardness of the anvil materials imposes constraints on the attainable pressures in high-pressure apparatus. The Knoop hardness of tungsten carbide is generally in the range of 10–15 GPa, while that of diamond of gem quality is ∼100 GPa. Thus the pressures available in a Bridgmann-type apparatus were limited to ∼20 GPa, while pressures at least one order of magnitude greater (100–200 GPa) are produced in a diamond anvil cell, in which the mechanism of the pressure generation is virtually the same as that of the former apparatus. As a sintered diamond anvil has a Knoop hardness of ∼50 GPa, roughly half of that of gem-quality diamond, pressures of 50–100 GPa should be produced when this material is used in the Bridgmann-type apparatus. It has been demonstrated that a multianvil apparatus can yield pressures much higher than those in Bridgmann-type apparatus when WC anvils of the same strength and hardness are used, because the former effectively utilizes the ‘lateral support’ principle to increase the strength of the anvils. Thus pressures higher than 100 GPa could be produced in Kawai-type multianvil apparatus with sintered diamond anvils, if the gasket and the pressure medium are fully optimized for such purposes.

The pressures routinely available in Kawai-type apparatus with sintered diamond anvil cubes of 14 mm edge length, however, have been limited up to now to ∼50 GPa as mentioned earlier (Ito et al., 2001; Irifune et al., 2002). One of the main reasons for the limit is the occurrence of frequent blow-outs at press loads >700–800 tons in SPEED-1500, which causes some damage to the first-stage WC anvils, which possess a square anvil top of 27 × 27 mm. It is thus risky to apply higher press loads although estimations based on the compressional strength of WC anvils indicate that press loads of ∼1000 tons may be safely applied. The occurrence of blow-outs in SPEED-1500 has been almost inevitable in the process of releasing pressure, when the maximum load applied exceeds ∼500 tons.

We investigated the reason for such frequent occurrences of blow-out under these high press loads, and concluded that the most likely cause is uneven compression (or de-compression) of the second-stage anvil assembly due to the deformation of the guide blocks. Although a DIA-type guide block is designed to drive the six first-stage anvils synchronously, elastic bending of the upper and lower guide blocks tends to produce larger vertical normal force (σ₁) than those applied horizontally (σ₂ = σ₃) with increasing press load. This effect would be serious at press loads >700–800 ton in SPEED-1500, and it becomes difficult to pressurize the small second-stage anvil assembly evenly under these press loads. This may also lead to uneven stress distributions within the gaskets between the second-stage anvils, and thus would cause blow-outs under these circumstances.

A new design has been introduced for a pair of guide blocks to overcome this problem, and we have just constructed a revised version of SPEED-1500, named SPEED-MkII, which will soon be installed at the HPES beamline in tandem with the existing SPEED-1500 (Fig. 13a). A new oil-pressure control system will be adopted for SPEED-MkII, which will mean smoother increase and decrease of pressure than that used in SPEED-1500. It is thus most likely that we can safely apply and reduce press loads >1000 tons using second-stage sintered diamond anvils, so that further expansion of the pressure range may be achieved using SPEED-MkII. In addition, the use of larger sintered diamond cubes with an optimized gasket-pressure medium system may further expand the pressure limit to the maximum value (∼100 GPa or higher), which is expected to be achieved within the strength of the sintered-diamond anvils when applied to Kawai-type apparatus as discussed above.

Technical problems and possible solutions

One of the difficulties encountered in X-ray diffraction measurements using SPEED-1500 is identification of phases under high temperature and high pressure, because we use an X-ray beam of typically ∼50 × 100 μm for these measurements and grain growth of the high-pressure phases to these sizes at high temperature hinders the production of characteristic powder diffraction patterns of these phases. The determination of unit-cell parameters of sample and pressure markers at high pressure and at temperatures above ∼1500°C is often quite difficult for the same reason.
In order to reduce this problem, oscillation of the sample would be helpful, as has been adopted in some diamond anvil cell experiments (e.g. Shim et al., 2001a,b). We have designed and constructed a new multianvil apparatus stage that can oscillate through \( \pm 20^\circ \) during the *in situ* X-ray diffraction measurements, in addition to the three-dimensional movements for adjusting the sample position (Fig. 13b). This stage has been adopted for the new Kawai-type apparatus (SPEED-MkII), which will soon be operational at the HPES beamline.

It is now recognized that estimated pressures based on equations of state of some reference
materials may not be accurate enough to quantitatively discuss the cause of the seismic discontinuities in the deep mantle, as discussed earlier. In principle, an absolute pressure scale may be established via simultaneous measurements of elastic velocities and X-ray diffraction of a reference material, such as MgO, at high pressure and high temperature. However, it has been difficult in practice to measure precisely the elastic velocities at pressures above 10 GPa, because such measurements using ultrasonic methods require samples with dimensions as large as ~2–3 mm in diameter and ~1–2 mm long and also need homogeneous temperature and pressure distributions within the sample charge (e.g. Li et al., 1996). To meet such requirements, use of a larger cell assembly with a relatively large heater and soft pressure-medium such as NaCl is essential, and accordingly an apparatus possessing a larger sample volume and press capacity than those used so far (<500 ton) is needed. The use of SPEED-1500 will thus expand the pressure range of such measurements and allow simultaneous in situ X-ray diffraction measurements of the sample. Attempts in this direction have just been started as a collaborative work between our group and that at SUNY Stony Brook.

Another important issue which has been recognized from the results of Irifune et al. (1998) and subsequent studies is that the effect of pressure on thermocouple e.m.f. may become significant at high pressures of ~20 GPa. The effect depends critically on the stress distribution within the colder parts of the thermocouple wire, which vary according to the high-pressure cell assemblies used and are difficult to generalize (e.g. Getting and Kennedy, 1970). Practically, a comparison of the melting temperatures of some reference materials, such as Au, determined using multianvil apparatus and diamond anvil cell may help to eliminate the mutual inconsistency of the temperature measurements between these two apparatus. Nevertheless, further theoretical and experimental approaches to this issue should be explored for accurate documentation of temperatures of in situ X-ray observations under high pressure, in order to apply the results of these measurements to more quantitative studies of the seismic structure and physical properties of the Earth’s deep interior.

Construction of a new beamline with brighter light source

Although the initial results obtained at the HPES beamline are highly encouraging, this beamline uses synchrotron radiation from a bending magnet and therefore does not fully utilize the advantage of the third-generation light source, where brighter (by ~two orders of magnitude) X-rays are available using insertion devices, such as wigglers or undulators. A new Earth and Planetary Science (EPS) beamline with a combination of a multipole wiggler light source and a 3000 ton Kawai-type press (SPEED-III) has been proposed by the authors, which is expected to expand the fields of Earth and related sciences and also to solve some of the technical issues mentioned above.

Use of the larger-volume Kawai-type apparatus at the proposed EPS beamline would have the advantage over SPEED-1500 and SPEED-MkII in precise measurements of some mineral physics parameters such as thermal conductivity, thermal expansivity and electrical conductivity, in addition to the elastic properties of the sample under high pressure and high temperature, because the larger sample volume in this apparatus would realize more homogeneous pressure and temperature distributions within the sample. The larger
sample volume and brighter light source available should also have great merits in introducing various capsules and pressure-transmitting materials to control fugacities of oxygen and other volatile components within the sample charge. Thus the effects of these volatiles on the phase transitions, melting relations, physical properties, etc., which have been recognized to have important implications for mantle mineralogy, can be investigated over wide temperature and pressure ranges corresponding to the Earth’s lower mantle. In situ X-ray observations for multi-component systems, representative of the actual mantle, subducting slabs, rising plumes, and core materials, can also be conducted under these conditions.

The brighter wiggler light source at the proposed EPS beamline should also reduce the X-ray acquisition time necessary for identification and characterization of the phases under high pressure and high temperature. This is important for such time-resolved measurements as those needed in studying kinetics of phase transitions and rheological properties of high-pressure phases. Other rapid processes such as melting, crystal growth, deformation and fracture may also be monitored using in situ X-ray radiographic observations of the sample using a combination of the large apparatus and the brighter light source. Thus the observations of rather ‘static’ properties, such as phase boundaries, \(P-V-T\) relations and physical properties, at the current HPES beamline are expected to shift toward those of ‘dynamic’ properties at the new EPS beamline. These studies are unlikely to be conducted with diamond anvil cells, where the available sample volumes are very limited.

Concluding remarks

The pressures in a Kawai-type multianvil apparatus have long been estimated based on a load (oil pressure)-pressure relationship, using the phase-transition pressures of some reference materials. However, such estimations inevitably have large uncertainties because of the limited reproducibility of each experimental run, difficulty in performing such pressure calibrations under various temperatures, and uncertainties in the transition pressures of the reference materials themselves. Thus the pressures of quench experiments have sometimes been quite different from those determined at other laboratories (e.g. Jeanloz and Thompson, 1983).

The combination of synchrotron radiation and the multianvil apparatus has made it possible to make inter-laboratory comparison of pressures using the same equipment and the same equations of state of the reference materials. It has indeed been demonstrated that the pressures of the phase transitions in major mantle minerals can be determined precisely and agree quite well with those studied by other groups at the HPES beamline. However, it is true to say that pressures thus determined may still suffer uncertainties of the order of \(\pm 5-10\%\), especially at pressures greater than 20 GPa and at temperatures \(>1000^\circ\text{C}\). This is because of the lack of an adequate equation of state and is also due to our limited knowledge of the pressure effect on thermostouple e.m.f., which should be borne in mind when applying experimental results to studies of the Earth’s deep interior.

Nevertheless, the large sample volume available in the Kawai-type multianvil apparatus leads to great advantages in simulating the physical and chemical behaviour of realistic Earth materials under high pressure and high temperature using in situ X-ray observations. Furthermore, pressures attainable in this apparatus will increase dramatically without sacrificing these advantages when large sintered diamond anvils are used. Thus the combination of this apparatus with synchrotron radiation provides an important window to the materials and dynamics in the Earth’s deep interior, which should certainly be one of the key technologies in mineral sciences in the 21st century.

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