Development of the Kawai-type Multi-anvil Apparatus (KMA) and Its Application to High Pressure Earth Science

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Abstract. Since Birch’s prediction on the structure of the Earth’s interior high pressure Earth science has rapidly been grown by the Kawai-type multi-anvil apparatus (KMA) and the diamond anvil cell (DAC). An important advantage of the KMA is its large specimen volume which makes it possible to conduct experiments under precisely controlled P-T conditions. A typical application of the KMA to the Earth science might be determination of the post-spinel phase equilibria in the system Mg₂SiO₄-Fe₂SiO₄. By adopting sintered diamond (SD) as the anvil material accessible pressure of the KMA has substantially increased. Melting experiments of mantle materials up to 35 GPa opened a new paradigm on the mantle fractionation in early Earth. Combining the KMA equipped with SD anvils with the synchrotron radiation phase equilibria of Fe GaN and Fe₂O₃ were determined by means of in situ X-ray diffraction. Special attention was paid to define the phase boundaries between perovskite and post-perovskite in MgGeO₃ and MnGeO₃ as analogues of MgSiO₃. We also observed the spin transition of Fe²⁺ in (Mg₀.87Fe₀.17)O at 300 and 700 K. Recently the maximum attainable pressure is reaching 100 GPa and high P-T experiments up to 90 GPa are our ordinary jobs. In order to produce still higher pressure however innovation of SD such as NPD is indispensable.

1. Beginning of the high pressure Earth science
In the early 20th century the Earth’s interior became an object of scientific research due to the information provided by seismology [1] which made it possible to determine the density and thereby pressure as functions of depth from the surface to the center [2]. Following these pioneering works Birch [3] analyzed homogeneity of the subdivided layers of the Earth’s interior [2] using the equation of state based on finite strain theory and Bridgman’s compression data and concluded that minerals constituting the uppermost mantle such as olivine pyroxenes and garnet successively transform into closed-packed oxides similar to corundum rutile spinel or perovskite in structure. As his analyses were so concrete and convincing that the prediction had been the guiding principle for exploration of the Earth’s interior for long time and strongly stimulated the high pressure experiments.

Figure 1 shows a standard Earth’s model PREM [4]. The mantle is characterized by two sharp increases in seismic velocities at depths of 410 and 660 km which divides the mantle into three parts the upper mantle (B) the transition zone (C) and the lower mantle (D). Following Birch [3] high pressure phase equilibria of the system Mg₂SiO₄-Fe₂SiO₄ were extensively studied by many workers represented by Ringwood and Major [5] and Akimoto and Fujisawa [6] because olivine (Mg₀.9Fe₀.1)₂SiO₄ is the most dominant (> 60%) constituent of the upper mantle. And the 410 km discontinuity was reasonably assigned to the transformation of the olivine (α) into the modified spinel
(β) structure up to the early 1970s. As capability of the apparatuses employed in these studies were limited to ca. 15 GPa neither synthesis of the end member Mg$_2$SiO$_4$ spinel (γ) nor acquisition of insight into the post-spinel transformation were successful at that time.

![Figure 1](image.png)

**Figure 1.** A standard Earth’s model (PREM) by Dziewonski and Anderson (1981). Layers A-G are correspond to division by Bullen [2].

2. **Devices employed in the high pressure Earth sciences**

Beginning of the high pressure Earth science

Soon after however γ-Mg$_2$SiO$_4$ was synthesized by Suito [7] in the Kawai-type multi-anvil apparatus (KMA) and the decomposition of γ-Fe$_2$SiO$_4$ into an assemblage of FeO (wüstite) and SiO$_2$ (stishovite) was found by Mao and Bell [8] by adopting the diamond anvil cell (DAC). Hereafter the high pressure Earth science has been extensively developed by adopting both the devices. In the DAC it is possible to compress a small amount of sample to multi Mbar heat it to thousands of Kelvin and observe the state of the sample under these extreme conditions by means of X-ray optical and other measurements. A marked advantage of the KMA over the DAC on the other hand is the much larger sample volume which makes it possible to conduct experiments under precisely controlled P-T conditions. Therefore the KMA has been adopted in various researches determination of phase equilibria synthesis of high pressure phases and measurements of physical properties. Development of the KMA was carried out mainly during 1965-1973 at Osaka University under the direction of the late N. Kawai [9]. Photos of the KMA are shown in Figure 2. The cubic assemblage of eight cubes of tungsten carbide (WC) an octahedral pressure medium and gaskets so-called the Kawai-cell (left) is squeezed along the [111] direction in the split sphere guide blocks with the aid of a uniaxial press (right).
Figure 2. The Kawai-type multi anvil apparatus (KMA). The Kawai-cell composed of cubic WC anvils MgO octahedral pressure medium pyrophyllite pre-gaskets etc. (upper photo) is squeezed in the split sphere guide block with the aid of uniaxial press (lower photo).
The easiest way to convince the performance of the KMA may be to show “huge (over 1 mm)” as grown single crystals of MgSiO$_3$ perovskite [10] (see Figure 3) which is stable only at pressures higher than 23 GPa and could be the most abundant material in our planet. The single crystals of the deep mantle material thus synthesized have been used to measure various kinds of physical properties.

![Figure 3. “Huge” (over 1mm) single crystals of MgSiO3 perovskite which is stable only at pressures higher than 23 GPa. After [10].](image)

3. The post-spinel transformation in the system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$: An application of the KMA to phase equilibrium study

Synthesis of MgSiO$_3$ perovskite (Pv) and confirmation of the dissociation of γ-Mg$_2$SiO$_4$ into an assemblage of MgSiO$_3$Pv and MgO-periclas were first carried out by Liu [11] using DAC coupled with the laser heating system. Later the post-spinel transformation was examined in detail all over the system Mg$_3$SiO$_4$-Fe$_2$SiO$_4$ by Ito and Takahashi [12] using the KMA. Pseudobinary diagrams at 1100 and 1600 °C determined by quenching method are reproduced in Figure 4. The diagrams indicate that the mantle spinel with composition (Mg$_{0.9}$Fe$_{0.1}$)$_2$SiO$_4$ dissociates into an assemblage of (Mg$_{0.9}$Fe$_{0.1}$)$_3$SiO$_3$ perovskite (Pv) and (Mg$_{0.83}$Fe$_{0.17}$)O magnesiowüstite (Mw) (or ferropericlase Fp) at pressures of 23.1-24.5 GPa and at 1100-1600 °C. As the dissociation brings about 10 % increases in density and seismic velocities [13] the dissociation must be responsible for the 660 km discontinuity. It is realized that the silicate Pv’s and Fp are by far dominant constituents of the lower mantle taking the high pressure transformations in pyroxenes and garnet into consideration as well.

The post-spinel dissociation possesses two important characteristics. First it completes within a quite narrow pressure interval less than 0.15 GPa (or 4 km in depth) for the mantle spinel. Therefore by making the dissociation boundary correspond to the depth of the 660 km discontinuity we have a temperature fixed point of 1600 ± 100 °C at the depth and can construct the temperature profile through the transition zone [14].

Secondly the phase boundary has a negative slope dP/dT~ -3 MPa/deg. Seismic tomography has revealed that some of descending slabs stagnate around the 660 km discontinuity before collapsing.
down into the lower mantle [15]. On the other hand, it is known that a phase boundary with a negative slope in the mantle suppresses material transport through the boundary [16]. Therefore, it is highly likely that the spinel dissociation substantially contributes to the stagnation of slabs.

![Figure 4. Pseudobinary diagrams of the post-spinel transformation in the system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ at 1200 and 1600°C. After [12].](image)

4. Adoption of sintered diamond (SD) for anvils of the KMA

Decisive disadvantage of the KMA in comparison with the DAC was that the maximum attainable pressure was limited to 28 GPa so far as WC was used as the anvil material. Fortunately, sintered diamond (SD) which was twice harder than WC [17] became available for anvils of the KMA in the late 1980s. Figure 5 shows SD cubes of Co-binder. We have employed cubes of an edge length 14 mm with truncated corners of 2 to 0.75 mm.

We first adopted the split-sphere system [9] to squeeze the Kawai-cell of SD cubes and compared the performances with those of WC cubes. Generated pressure was calibrated using several fixed points and plotted versus oil pressure for both the SD and WC cubes as Figure 6. Superiority of SD to WC is overwhelming suggesting high potential of SD in pressure generation. Following these
calibration runs we carried out high P-T quenching experiments. The followings are summaries of studies which had never been achieved by using WC anvils.

Figure 5. Sintered diamond cubes with Co binder.

Figure 6. Comparison of pressure generation using SD with WC anvils. Superiority of SD to WC anvils is overwhelming.

4.1. Synthesis of perovskite with pyrope (Mg$_3$Al$_2$Si$_3$O$_{12}$)
As the system MgSiO$_3$-Al$_2$O$_3$ represents the compositions of pyroxene and garnet in the mantle high pressure phase equilibria of the system are also indispensable to understand mineralogy of the lower
mantle. Systematic study by Irifune et al. [18] had shown that pyrope (Mg$_3$Al$_2$Si$_3$O$_{12}$) broke-down into solid solutions of the MgSiO$_3$-rich perovskite and Al$_2$O$_3$-rich corundum structures at ca. 27 GPa and that the binary loop between the two phases would persist to higher pressures. We examined the stability of pyrope composition using SD anvils and confirmed formation of the orthorhombic perovskite phase at 37 GPa and 1600 °C [19]. The result indicates closing of the binary loop and the silicate perovskite can accommodate certain amount of Al$_2$O$_3$. Ubiquitous coexistence of tiny amount of SiO2 stishovite suggested slight nonstoichiometry of Al$_2$O$_3$-bearing perovskite.

4.2 Melting experiments of the primordial mantle materials

In order to simulate possible material fractionation in a deep magma ocean formed on the early Earth melting phase relations of the Earth material and element portioning between liquidus phases and melt are indispensable. Therefore melting experiments of fertile peridotite [20] and CI chondritic mantle material (CMM) [21] had been carried out up to 25 GPa. Nevertheless a clear model for the mantle fractionation had been postponed.

![Figure 7. Back scattered electron images of quenched charges of peridotite at 29, 31 and 33 GPa.](image)

We extended melting experiment on both the materials to 35 GPa [22]. In peridotite the first liquidus phase changed from ferropericlase (Fp) to Mg-perovskite (Mg-Pv) at 31 GPa and at 33 GPa
liquidus Mg-Pv was successively followed down temperature by Fp and Ca-perovskite (Ca-Pv) within a small temperature range. The change of liquidus phase with pressure is clearly demonstrated in a series of pictures shown in Figure 7. In the CMM Mg-Pv was the liquidus phase which was followed down temperature by Ca-Pv at pressures higher than 28 GPa and Fp was absent in super solidus conditions. Differentiation in a deep magma ocean was examined by crystal fractionation of Mg-Pv Fp and Ca-Pv for CMM and peridotitic bulk silicate Earth models. Mass balance calculation indicated that subtraction of about 40% Mg-Pv and 2% Ca-Pv from CMM yielded a residual melt with characteristics of fertile upper mantle composition. The fractionated Mg-Pv and Ca-Pv would pile up to a depth ca. 1400 km from bottom of the mantle and might be characterized as an enriched and possibly heat producing reservoir by the higher capability of Ca-Pv to accommodate large cations such as rare earth elements and alkaline elements than melt. The observed effect of pressure on element partitioning suggested that better mass balance solutions might be obtained for higher pressure liquidus composition.

5. In situ X-ray observation using the KMA
In situ X-ray observation using synchrotron radiation has rapidly pushed the high pressure Earth science towards the exact sciences because the pressure value is determined continuously and uniquely from volume of a pressure marker via its equation of state. The pressure marker is usually mixed with the sample or put next to the sample. By being interfaced with synchrotron radiation versatility of the KMA has been expanded in various research fields such as phase equilibria, reaction kinetics, equation of state, radiographic measurements, etc. At the synchrotron facility SPring-8 two DIA-type presses [23] were installed on beam line BL04B1 to squeeze the Kawai-cell. One of them SPEED mkII [24] has exclusively been used to squeeze the Kawai-cell of SD cubes. Experimental methodology of in situ X-ray observation using the Kawai-cell were described to some extent elsewhere [25].

5.1. In situ X-ray diffraction studies on Fe, GaN, and Fe₂O₃
We have first studied high pressure polymorphism of iron by means of in situ X-ray diffraction. Our aim of the study was to clarify the stability of β-phase, the 5th polymorph of iron [26]. Our experiments up to 44 GPa and 2100 K confirmed progression of the ε → γ and the reverse transitions on increasing and decreasing temperature, respectively. The presence of β-phase was thus excluded.

We successively examined phase relations in GaN [28] and Fe₂O₃ [29]. In GaN onset of the wurtzite → rocksalt transformation was observed at conditions of 54 GPa/300 K and 51.5 GPa/750 K, suggesting a negative dP/dT slope. However, it was observed that the rocksalt phase persisted for 90 min at 48.9 GPa/850 K. Therefore, the reverse transformation is rather sluggish, and more examination is needed to decide the equilibrium phase boundary. Electrical resistance of GaN was tens of mega ohms up to ca. 62 GPa at 300 K and no remarkable change in resistance was observed on the wurtzite – rocksalt transformation.

Phase equilibria of Fe₂O₃ were examined up to 58 GPa and 1400 K. Hematite (phase I) transformed successively into the Rh₂O₃ II type structure (II) and an orthorhombic phase (III) with increasing pressure. The phase boundaries for I - II and II - III were defined to be P(GPa) = -0.015 T(K) + 44.2 and P(GPa) = -0.005 T(K) + 48.7, respectively, by observing both the forward and backward reactions in situ. It should be noted that the transformations were observed only at temperatures higher than 500 K and hematite persisted metastably at least up to 58 GPa at 300 K. The electrical resistance of hematite on the other hand decreased monotonically from tens of mega ohms at 10 GPa to a few ohms with increasing pressure and then plateaus at ca. 60 GPa as shown in Figure 8. The isostuctural electrical resistance reduction strongly suggests the occurrence of a Mott transition. The plateau point of electric resistance 60 GPa is usable as a pressure fixed point at room temperature.
5.2. Post-perovskite transformation in meta-germanates

The lowermost 200-300 km region of the mantle called the D” layer is characterized by various aseismic anomalies such as velocity jumps [30] anisotropy [31] anti-correlation between shear velocity VS and bulk sound velocity VC [32] and presence of ultra-low velocity zone at the base [33]. These enigmatic features would be reflected as the presence of active exchange of energy and material between the mantle and the core. Therefore understanding of the D” layer should be of essential importance to clarify dynamics and evolution of the Earth.

In 2004 Murakami et al. [34] and Oganov and Ono [35] discovered the transformation of MgSiO₃ perovskite (Pv) into the CaIrO₃ structure (the post-perovskite (PPv) transformation) at ca. 120 GPa and 2200 K using the laser-heated DAC. The post-perovskite transformation should play an important role in formation and structure of the D” layer. Therefore detailed knowledge on the transformation is of urgent need. Especially the slope of the phase boundary dP/dT would give some insight to the thermal structure through the D” layer and to estimate of thermal flux from the core [36].

As the P-T conditions for the PPv transformation in MgSiO₃ are out of the ability of the KMA at present we examined the PPv transformation in MgGeO₃ [37] and MnGeO₃ [38] which are regarded as the best analogs of MgSiO₃.

Cross section of a sample assembly adopted in MgGeO₃ experiments is shown in Figure 9. Fine mixture of MgGeO₃-ilmenite + 0.1 Au (in weight) was put in a cylindrical TiB₂ heater which is set at the center of octahedron of MgO + 5% Cr₂O₃. Temperature was measured by a thin W3%Re/W25%Re thermocouple whose junction was at the center of the sample. By adopting the TiB₂ heater we could see through the sample and the thermocouple by the CCD camera. Pressure value was determined from the volume of gold based on the Anderson et al.’s [39] Au scale.

The transformation from Pv to PPv was first confirmed at 63.2 GPa and 1325 K as shown by the diffraction profiles in Figure 10(A). Then we tried to observe the reverse transformation by decreasing pressure by reducing the applied load and keeping temperature constant at 1323 K. Growth of Pv was not recognized until pressure went down to 60.5 GPa as clarified by the successive profiles in Figure 10 (B). We carried out more runs to recognize growth either PPv or Pv from the counter phases over the conditions up to 74 GPa and 2200 K. Figure 11 shows P-T plots of the X-ray observations relevant to define the phase boundary between Pv and PPv. The phase boundary between Pv and PPv was defined by passing through the Pv-growth PPv-growth and the coexistence points and expressed by T(K) = 177P(GPa) – 9677 with dP/dT = 5.6 MPa/K.
Figure 9. A schematic drawing of the sample assembly for experiments for the post-perovskite transformation in MgGeO$_3$.

Figure 10. Diffraction profiles of run M511. Profiles in (A) demonstrate the growth of post-perovskite phase from the perovskite at 63.2 GPa and 1325 K and a series of profiles from the bottom to top in (B) do the reverse transformation at 60.5 GPa and 1323 K.
The dP/dT value is slightly smaller than those estimated for MgSiO₃ [36]. The smaller value sets the D'' discontinuity deeper and so called PPv lens formed by the double-crossing of the phase boundary and the geotherm [40] would be present only in relatively cold region such as beneath mantle downwellings. The slope of 5.6 MPa/K suggests a large heat flux of 16 TW across the D'' layer assuming thermal conductivity of 10 Wm⁻¹K⁻¹ [41]. Nevertheless if we adopt other Au pressure scale such as Tsuchiya [42] instead of Anderson et al.’s [38] our phase boundary shifts towards higher pressure by 3.5 GPa and the dP/dT increases to 8.7 MPa/K. Therefore establishment of reliable pressure scale is fatally important.

![Figure 11. P-T plots of the X-ray observations relevant to define the phase boundary between Pv and PPv (see text). Circles squares and diamonds denote the different runs. Growing phases and phases present are indicated by the arrows and color markers. After [37].](image)

The Pv-PPv phase equilibria in MnGeO₃ [38] were also examined by in situ X-ray diffraction method as in MgGeO₃. The phase boundary was determined to be P(GPa) = 39.2 + 0.013T(K) based on Tsuchiya’s Au scale [42] which is located around ca. 10 GPa lower pressures than that of MgGeO₃ with a larger dP/dT value [38].

5.3 High spin-low spin transition in ferropericlase (Mg₀.₈₃Fe₀.₁₇)O

High spin-low spin transition of Fe²⁺ in (MgₓFeₓ)OFP occurring under lower mantle conditions has been attracted special attention because the transition is considered to substantially affect geophysical and geochemical processes [43]. The transition can be detected by observing an anomaly in the compression curve due to a drastic reduction of effective ionic radius of Fe²⁺ accompanied with the transition [44]. We selected FP with a composition (Mg₀.₈₃Fe₀.₁₇)O because the composition is a counter part of magnesian perovskite in the assemblage produced by dissociation of (Mg₀.₈₃Fe₀.₁₇)₂SiO₄ spinel [12].

We acquired pressure (P)-volume (V) data at 300 and 700 K and up to 90 GPa employing the sample assembly shown Figure 9. Pressure was determined from volume of Au mixed with the (Mg₀.₈₃Fe₀.₁₇)OFP powder based on Anderson et al.’s scale [39]. The acquired P-V data are shown in
Figure 12. Errors in pressure determination caused those of Au volume and temperature fluctuation were within ± 0.4 GPa and those in volume determination were typically within ± 0.05 %.

We tried to fit the 3rd order Birch-Murnaghan equation of state (B-M EoS) with $K_0' = 4$ to the data up to 40 GPa which were successfully performed as shown by the solid curves. And the resultant zero pressure values of volume $V_0$ and bulk modulus $K_0$ were in good agreement with the literature values [45] which are noted as HS values in the insertions of the figures. However volume data higher than 50 GPa at 300 K and those higher than 55 GPa at 700 K show gradual downward deviation from the solid curves with increasing pressure indicating onset of the spin transition. Assuming that the transition completes at 70 GPa at 300 K and 80 GPa at 700 K we tried to fit the B-M EoS with $K_0' = 4$ for the data higher than these pressures. The resultant $V_0$’s and $K_0$’s are noted in the insertions as LS values in the figures and the corresponding EoS’s are shown by broken curves. The $V_0$ and $K_0$ at 300 K for the low spin regime are larger and smaller than those of Lin et al. [46] respectively in the same composition. Our data suggest that the mixed spin region shifts toward higher pressure and expands with increasing temperature in accord with theoretical prediction [47]. Nevertheless it is evident that acquisition of LS data up to higher pressure is required to specify the LS state in more detail.

6. Recent pressure generation and future perspectives

By adopting SD anvils the attainable pressure of the KMA has increased year by year since 1998 [19]. Figure 13 shows our recent performance of pressure generation carried out by means of in situ X-ray observation at SPring-8 using anvils with 1.0 mm truncation. The maximum attainable pressure is reaching 100 GPa and high pressure and temperature experiments up to 90 GPa have become our ordinary jobs.

One of our urgent objects is to clarify the PPV transformation in detail just like done in the post-spinel transformation. In order to accomplish the object we have to extend the accessible pressure at
least by 20 GPa. The systematics between the hardness of anvil materials and the maximum attainable pressures for WC SD and single crystal diamond and the trends shown in Figure 13 suggest possibility to produce pressures higher than 100 GPa. However innovation of SD is of essential importance to produce still higher pressures. In this context binder-free nano-polycrystalline diamond (NPD) recently developed by Irifune et al. [48] expands our dream because its Knoop hardness reaches 140 GPa.

Figure 13. Plots of generated pressure vs. applied load. Truncation was 1.0 mm and pressure values are based on Tsuchiya’s Au scale [42].

Acknowledgements
I am very grateful to all those who have been in contact with me on the high-pressure research for their guidance help and collaboration. I would like to dedicate this article to the late professors N. Kawai S. Akimoto and T. Matsumoto and also to the late super technician K. Tanaka.

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