

Research
Deep Matter & Energy—Review

Development of High-Pressure Multigrain X-Ray Diffraction for Exploring the Earth's Interior



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ARTICLE INFO

Article history:

Received 3 September 2018

Revised 16 January 2019

Accepted 1 February 2019

Available online 6 April 2019

Keywords:

High pressure

Synchrotron X-ray

Multigrain

Diamond anvil cell

Minerals

Petrology

Earth's interior

ABSTRACT

The lower mantle makes up more than a half of our planet's volume. Mineralogical and petrological experiments on realistic bulk compositions under high pressure–temperature (P – T) conditions are essential for understanding deep mantle processes. Such high P – T experiments are commonly conducted in a laser-heated diamond anvil cell, producing a multiphase assemblage consisting of 100 nm to submicron crystallite grains. The structures of these lower mantle phases often cannot be preserved upon pressure quenching; thus, *in situ* characterization is needed. The X-ray diffraction (XRD) pattern of such a multiphase assemblage usually displays a mixture of diffraction spots and rings as a result of the coarse grain size relative to the small X-ray beam size (3–5 μm) available at the synchrotron facilities. Severe peak overlapping from multiple phases renders the powder XRD method inadequate for indexing new phases and minor phases. Consequently, structure determination of new phases in a high P – T multiphase assemblage has been extremely difficult using conventional XRD techniques. Our recent development of multigrain XRD in high-pressure research has enabled the indexation of hundreds of individual crystallite grains simultaneously through the determination of crystallographic orientations for these individual grains. Once indexation is achieved, each grain can be treated as a single crystal. The combined crystallographic information from individual grains can be used to determine the crystal structures of new phases and minor phases simultaneously in a multiphase system. With this new development, we have opened up a new area of crystallography under the high P – T conditions of the deep lower mantle. This paper explains key challenges in studying multiphase systems and demonstrates the unique capabilities of high-pressure multigrain XRD through successful examples of its applications.

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1. Introduction

Various high pressure–temperature (P – T) experimental techniques have been developed in order to study mantle minerals existing in the Earth's interior. Under increasing P – T conditions that correspond to those of the deep Earth, the crystal structures of minerals that are stable under low P – T conditions are replaced by denser structures. The pyrolytic composition of the lower mantle has been tested using high P – T experiments [1,2]. At least five oxide components are required to describe the mantle system. Even in a single bulk composition (e.g., mid-ocean ridge basalt

(MORB) or pyrolite), phase changes are associated with element partitioning within the assemblage under high P – T conditions. Interactions of subducting slabs with the mantle system further complicate their phase relations [3,4]. For example, some amounts of water may be stored in nominally anhydrous lower mantle phases, but the presence of water components in subducting slabs may also stabilize hydrous phases under P – T conditions. Petrological experiments have been widely conducted in a multi-anvil apparatus up to the P – T range of the top of the lower mantle (< 30 GPa) [5], and the P – T range can be extended to the middle of the lower mantle (\sim 50 GPa) when sintered diamond anvils are used [2].

The ambition to explore the whole interior of the Earth has promoted extensive use of the laser-heated diamond anvil cell (DAC). Diamond is the hardest known material and is transparent to

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X-rays. Typically, a sample assembly less than 50 μm in diameter and about 10 μm in thickness is compressed between the tips of two diamond anvils and laser-heated from both sides of the sample [6]. Megabar pressure was first achieved 40 years ago, allowing the simulation of deep-Earth P - T conditions [7]. Through development of the DAC and laser-heating techniques, experiments have been conducted to study the structure of iron (Fe) under the inner-core P - T conditions of up to 377 GPa and 5700 K [8]. These experiments have mostly been limited to a single mineral phase or a simple system (e.g., MgO-SiO₂). However, interpretations of key enigmatic features in the deep lower mantle—namely, the sharp upper boundary of the D' layer [9], the seismic anisotropy [10], and the large low-shear-velocity provinces in the bottom third of the lower mantle [11]—require information from high P - T petrological experiments on a realistic lower mantle multicomponent system, which produces an assemblage consisting of multiple phases under high P - T conditions in a laser-heated DAC.

In a multiphase assemblage, most diffraction peaks overlap in a powder X-ray diffraction (XRD) pattern; even without overlap, powder XRD alone is inadequate for studying new structures. Single-crystal XRD is regarded as the ideal method for structural analysis, and has been widely developed for high-pressure research in a DAC [12–14]. However, single crystals of around 5 μm in size, as required for conventional single-crystal XRD experiments, are unachievable in a realistic mantle assemblage under the corresponding high P - T conditions. Instead, a polycrystalline multiphase sample is always obtained in phase equilibrium experiments corresponding to the deep mantle. In this paper, we review the applications of the multigrain XRD technique for studying multiphase systems under high P - T conditions, including *in situ* characterization of new phases in a multiphase assemblage, crystal structure determination of selected individual grains in a polycrystalline sample, and two-dimensional (2D) mapping through the precise determination of unit-cell parameters for individual phases at steps of a few microns.

2. Challenges in experimental petrology under high P - T conditions

Phase identification and structural analysis in a multiphase assemblage have long been recognized as a challenge in high-pressure research. Frost and Fei [15] pointed out difficulties in identifying the hydrous phases D, F and G, of dense hydrous magnesium silicates from powder XRD patterns of recovered samples when the synthesis pressure was as low as 22 GPa. However, if such a multiphase assemblage contains individual crystals with grain sizes greater than 5 μm and the structure can be preserved under ambient conditions, these grains can be picked out for single-crystal studies in the recovered sample.

Higher pressure is generated in an apparatus at the expense of sample volume. The sample volume decreases from a few millimeters in dimension in a multi-anvil apparatus to tens of micrometers at above 60 GPa in a DAC. Furthermore, most structures obtained at ultrahigh pressures, such as MgSiO₃ or (Mg,Fe)SiO₃ post-perovskite (pPv), cannot be preserved under ambient conditions [16–18]. Meanwhile, the grain size in a polycrystalline sample generally decreases with increasing pressure. For example, the grain size of a hydrous phase in a mantle assemblage could be as small as about 100 nm under the high P - T conditions of the deep lower mantle [4]. The grain size of the hydrous δ -phase decreases from about 2 μm at 68 GPa to about 200 nm at 128 GPa after heating treatment at a similar temperature [4], indicating that pressure has a dominant effect on grain size. Other factors may also influence grain size; for example, lower temperature tends to decrease grain size [19]. The recovery of tiny crystals (< 1 μm) for single-crystal

diffraction thus becomes practically infeasible. In conclusion, *in situ* characterization is needed in order to study phase changes and structural details in a multiphase system under the P - T conditions of the deep lower mantle.

High P - T conditions produce a wealth of new structures. In a high P - T experiment, a few new peaks often appear in a powder XRD pattern; however, a perfect match to a known structure is not easy to find. One type of new structure is due to atom rearrangement into a denser structure, such as the B1–B2 structural transition in NaCl. Another type involves new pressure-induced stoichiometry, such as NaCl₃ and Na₃Cl [20]. *In situ* structure determination of a high-pressure phase can be very challenging when the chemical composition is not known. In a petrological experiment, phase transitions are often associated with compositional changes under high P - T conditions. For example, in a high P - T experiment on a natural MORB composition, a four-phase assemblage of the MgSiO₃-rich pPv phase, α -PbO₂-type SiO₂, Ca-perovskite, and CaFe₂O₄-type Al-phase was identified by a combination of *in situ* powder XRD and *ex situ* transmission electron microscopy (TEM) under the P - T conditions of the deep lower mantle, in which the pPv phase has a high Na₂O content and a high ratio of Fe³⁺/total Fe [21]. Solving the complex structures of the pPv phase under realistic deep lower mantle conditions is beyond the capabilities of existing powder XRD methods. Furthermore, a minor phase will be overshadowed by the diffraction peaks of coexisting phases in a powder XRD pattern of a multiphase assemblage, making phase identification of a minor phase extremely difficult using the powder XRD technique.

In summary, conventional single-crystal or powder diffraction techniques are inadequate for studying multiphase systems under high P - T conditions. New methods are required in order to explore phase changes and their detailed structures occurring in the deep lower mantle.

3. *In situ* multigrain synchrotron XRD

Synchrotron radiation X-rays have been regarded as an ideal probe for *in situ* studies of materials under high P - T conditions in a laser-heated DAC [22–24]. Heat treatment often promotes crystal growth, and spotty powder XRD patterns of mantle phases are obtained under high P - T conditions. Fig. 1 shows a representative spotty powder XRD pattern of (Mg,Fe)SiO₃ pPv [25]. Such a spotty pattern is a combined result of the small X-ray beam size ($\sim 6 \times 8 \mu\text{m}^2$ full width at half maximum) and crystal growth upon heating at about 2400 K. The recent development of high-pressure beamlines has enabled reduction of the X-ray beam to the current 2–3 μm [22], which can help to reduce the level of overlapping spots in powder XRD patterns.

The recent achievement of multigrain XRD in high-pressure research has made it possible to index hundreds of individual crystallite grains simultaneously through the determination of crystallographic orientations for these individual grains [25,26]. Once indexation is achieved, a multiphase assemblage can then be treated as an aggregate of thousands of individual single crystals. An accurate and efficient indexing algorithm is required to process such datasets. We have found that GrainSpotter [27], which is part of the FABLE package [28], is an efficient algorithm that can be readily applied to a rotation-scan dataset for indexing grains in an assemblage contained in a DAC [25,29,30]. In some cases, experienced crystallographers can index a few grains manually in a high-pressure rotation dataset and solve their crystal structures [6,31]. However, only by applying the multigrain XRD method to search and index tens to hundreds of grains for each individual phase simultaneously, it is possible to systematically study crystal structures of each individual phase including a minor phase.

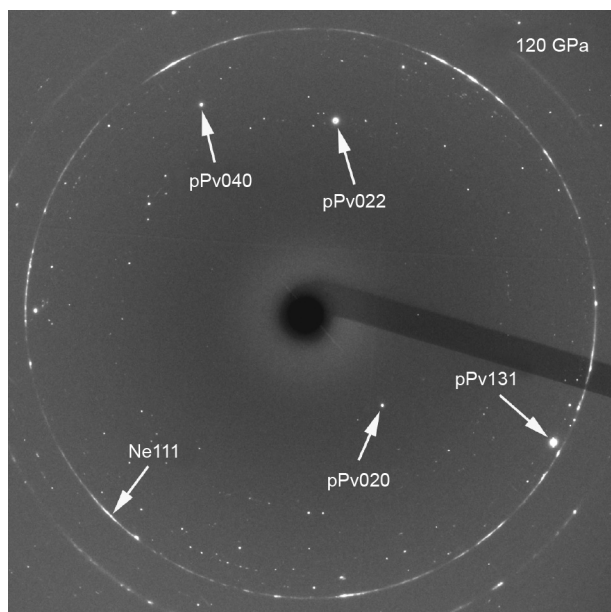


Fig. 1. A representative spotty powder XRD pattern of (Mg,Fe)SiO₃ pPv. The diffraction pattern was collected at a fixed ω angle at 120 GPa after temperature quenching from 2400 K, showing the spottiness of the XRD pattern. Ne: neon. Reproduced from Ref. [25] with permission of PNAS, © 2013.

Fig. 2 shows the setup for high-pressure multigrain XRD data collection. Similar to the “rotation method” used in conventional single-crystal crystallography, diffraction patterns in step-scans are collected on a rotation stage up to the maximum angular access allowed by the DAC design. We have achieved a good balance between an angular access of 50°–60° for X-rays and the maintenance of stable high pressures up to the core-mantle boundary (CMB) at 136 GPa. We used angular steps as small as 0.2° to improve the signal-to-noise ratio in XRD patterns. We used an exposure duration ranging from 1 to 10 s per frame in our experiments, and tested the exposure before each collection until the strongest diffraction spots were near intensity saturation. Software packages, including CrysAlis [32], XDS [33], and GSE_ADA/RSV [34], were used to calculate the intensities of the reflections in a high-pressure dataset. The structure solution and refinement steps were performed by conventional single-crystal programs, such as, the SHELX package [35].

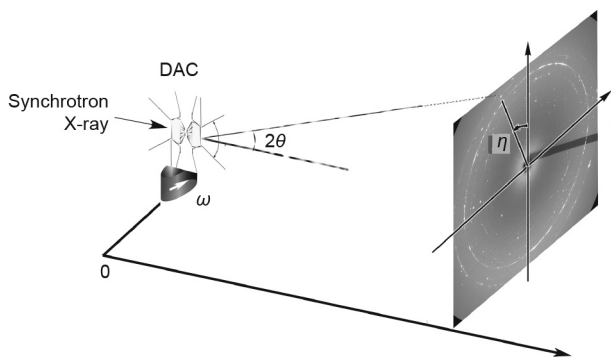


Fig. 2. Experimental setup for high-pressure multigrain XRD data collection in a DAC. The sample is aligned to the rotation center, and a set of 2D XRD patterns are collected at small incremental steps, e.g., 0.2°, to the angular access of a DAC, typically 50°–60°, where ω , η , and θ represent the rotation, azimuth, and Bragg angles of each reflection, respectively.

The synthesis of high-quality individual crystallites within the assemblage is the prerequisite for applying the high-pressure multigrain XRD technique. It has been found that a quasi-hydrostatic sample environment and stable heating significantly promote crystal growth under high P – T conditions in a laser-heated DAC [29]. In mantle petrological experiments, phase chemistry is frozen after temperature quenching; most structures are temperature-quenchable but often not pressure-quenchable, so a multigrain sample is often indexed *in situ* at high pressure and after temperature quenching.

Spotty diffraction patterns enable multigrain indexing, but such spottiness can result in unreliable intensity measurements in an integrated powder XRD pattern, leading to unreliable estimation of phase proportions in an assemblage. Spottiness implies crystal growth in the assemblage, in contrast to the smooth rings that are displayed in an XRD pattern of a fine-grained sample. In a sample synthesis, the high-temperature conditions required for crystal growth should facilitate thermodynamic equilibrium. On the other hand, the kinetics in phase transitions in a coarse-grained starting sample can be much slower than that occurring in a fine-grained sample under similar P – T conditions, because the higher surface area in a fine-grained sample can facilitate the nucleation for a phase transformation. Spotty XRD patterns are commonly observed in high P – T experiments conducted in a laser-heated DAC, and more attention should be paid to the kinetics issues in phase transitions occurring in coarse-grained samples.

4. Applications of multigrain XRD in high-pressure experiments

Multigrain XRD enables the phase identification and structural analysis of tiny individual grains in a multiphase assemblage contained in a DAC. Here, we summarize the applications of *in situ* multigrain synchrotron XRD for the phase identification of unknown phases and minor phases, the determination of high-pressure crystal structures, and the refinement of unit-cell parameters by merging reflections from multiple grains for each individual phase.

4.1. Phase identification in a multiphase assemblage

The unique capability of multigrain XRD has been demonstrated for the phase identification of an unknown phase in a mixture. When Fe-bearing bridgmanite (Bdg) decomposes to a nearly Fe-free MgSiO₃ Bdg and a Fe-rich phase with a hexagonal structure (H-phase), only three peaks above 2.4 Å were specific to the H-phase, with many peaks of the Bdg phase overlapping with other peaks of the H-phase [29]. By searching for the orientation matrices of individual grains, 154 grains of the H-phase were indexed from one rotation XRD dataset. A grain is indexed when tens to hundreds of reflections are shown to satisfy the stringent geometrical angles determined by its particular orientation matrix. Each reflection has three variables (ω , η , and 2θ) to constrain the orientation matrix, where ω , η , and θ represent the rotation, azimuth, and Bragg angles (Fig. 2), respectively. Furthermore, 154 individual crystallites, each with its particular orientation matrix, redundantly confirmed the same lattice.

Powder XRD patterns only contain d -spacing information, and successful indexing of several obvious peaks for a new phase can sometimes lead to an incorrect unit cell. For example, the recently discovered hexagonal hydrous phase (HH-phase) in (Fe,Al)OOH was examined using the multigrain XRD, and its lattice parameters of $a = 10.5803(6)$ Å and $c = 2.5897(3)$ Å were obtained at 110 GPa [36]. However, if the weak peaks of (211) and (311) in the powder XRD pattern were not selected for indexing, a small orthorhombic lattice was obtained instead, with the lattice parameters of

$a = 4.03(2) \text{ \AA}$, $b = 3.699(5) \text{ \AA}$, and $c = 2.78(1) \text{ \AA}$. However, this orthorhombic lattice did not pass the three-dimensional (3D) multigrain XRD test because most of the reflections predicted from a specific orientation matrix were not found in the measured rotation dataset. It was only when the hexagonal lattice was input for searching that 104 reflections were observed at the predicted angles for one of the crystallites and 27 individual crystallites were found, each with its particular orientation matrix, confirming the correct lattice of the HH-phase [36].

The unique power of multigrain XRD has been further demonstrated by its capability to identify a minor phase in an assemblage. Most peaks of a minor phase are overshadowed by the diffraction of major phases in a powder XRD pattern. In a previous experiment, seifertite (SiO_2) was found to exist as a minor phase in a lower mantle assemblage; only peak (110) was visible without overlapping with the peaks from the major phase pPv [30], as shown in Fig. 3(a). Still, over 100 grains of seifertite were confirmed by applying multigrain XRD, although most grains showed

weak diffraction due to their tiny grain sizes. The proportion of a minor phase to a major phase can be roughly estimated by the relative intensities in the integrated powder diffraction peaks (Fig. 3(a)). In a multigrain XRD dataset, sometimes only a small number of grains can be indexed for a minor phase. Nevertheless, a tiny grain from a minor phase can still be identified and treated as a single crystal, which is otherwise impossible using conventional XRD techniques (Fig. 3(b)). Thus, the development of high-pressure multigrain XRD enables these previously impossible tasks and drives forward laboratory exploration of the Earth's entire interior.

4.2. Crystal structure determination

The $(\text{Mg,Fe})\text{SiO}_3\text{-pPv}$ phase has been a focus of study since its discovery in 2004 as a dominant mineral in the bottom of the lower mantle [16–18]. Compositional variations in pPv can induce changes in its density and structure; thus, even subtle structural changes have significant implications for interpretations of the seismic and dynamic features observed near the CMB. For example, the pPv phase synthesized in a MORB composition was enriched in Na_2O and had a high ferric content [21]. On the other hand, the pPv phase may have become very Fe-enriched at the CMB in contact with the liquid iron core [18]. Chemical composition in individual phases can be measured by *ex situ* TEM on a recovered sample; however, determination of structure changes induced by chemical impurities in the pPv phase is beyond the existing capabilities of powder XRD and theoretical methods. In addition, the pPv structure cannot be preserved after recovery under ambient conditions. Thus, *in situ* crystal structure determination is required. A high-quality multigrain sample of $(\text{Mg,Fe})\text{SiO}_3\text{-pPv}$ was synthesized in a quasi-hydrostatic neon (Ne) environment (Fig. 1), and *in situ* crystal structure determination was performed on an individual grain of pPv selected by the multigrain method [25]. The structure of this Fe-depleted pPv shows a nearly identical structure to that of the MgSiO_3 predicted by theory [16]. To the best of our knowledge, this is the first single-crystal structure determination of the pPv phase; it demonstrates the feasibility of *in situ* crystal structure determination of submicron crystallites above megabar pressures. This technique can then be applied to investigate the structure changes induced by compositional variations in high-pressure minerals in the future.

A DAC has a limited angular access; in a multigrain sample, several grains with different orientations can be scaled and merged to increase the coverage of a structure for the structure determination [30]. Clearly, reflection conditions combined from multiple grains can provide a more definite determination of the space group of a high-pressure phase. The intensities of the reflections from each selected grain were calculated using the XDS software, and compatibility between the data sets was checked by merging them using the XSCALE software in the XDS package [33]. For example, a total of 613 reflections were combined from the merged datasets of six grains to provide a redundancy of 6.6 and data completeness of 92% in the d -spacing range down to 0.72 \AA , which allowed high-quality structure refinement for seifertite at 129 GPa [30]. Note that CrysAlis and other softwares may also be used for integration and scaling purpose. *In situ* crystal structure determination enabled by high-pressure multigrain synchrotron XRD opens up a new area of megabar crystallography by providing crystallographic solutions that are otherwise extremely difficult to achieve using conventional XRD techniques [25,30].

4.3. Determination of unit-cell parameters in a multiphase assemblage

The determination of unit-cell parameters for individual phases in an assemblage is a common task in mineralogical and petrological studies. To ensure a high-quality sample and reliable pressure

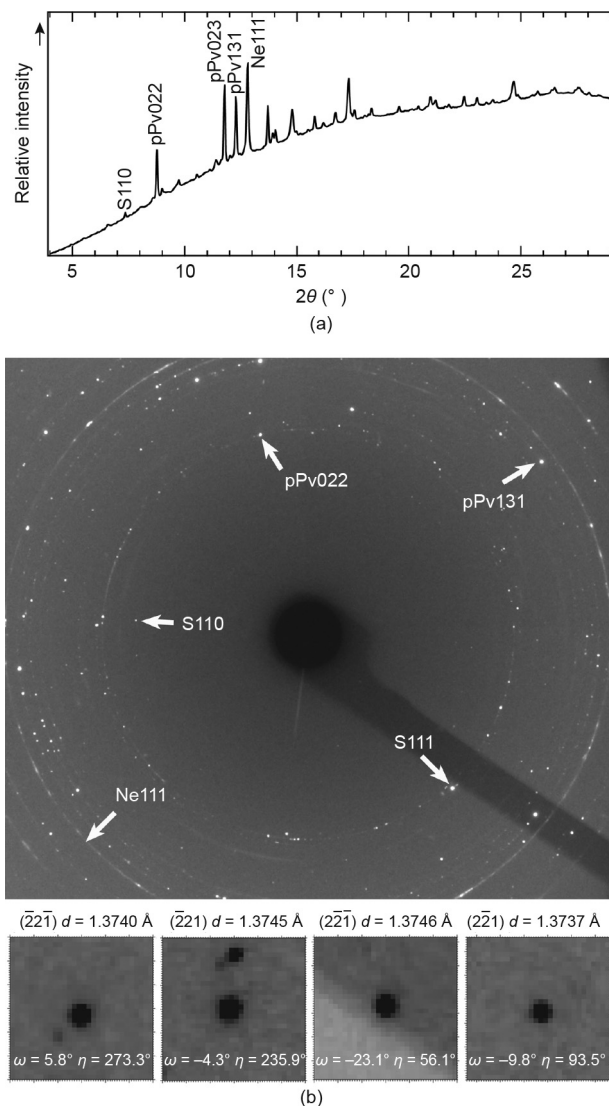


Fig. 3. XRD data of a phase assemblage including a dominant pPv phase and a minor phase of seifertite (SiO_2). (a) An integrated powder XRD pattern showing the weak proportion of SiO_2 at 129 GPa and after temperature quenching; (b) the multigrain XRD pattern including two Friedel pairs of {221} from one selected grain of seifertite. S: silica. Reproduced from Ref. [30] with permission of GeoScienceWorld, © 2016.

determination, a pressure medium and/or thermal insulator, a pressure calibrator, and sometimes a laser absorber are loaded together with the sample into a DAC chamber of only tens of micrometers in diameter. During high P - T treatment or after temperature quenching, most peaks from these materials overlap in a powder XRD pattern. Only a few peaks can be selected for the unit-cell determination of the sample or the pressure scale, which leads to large uncertainties. Fortunately, multigrain XRD makes it possible to constrain the unit-cell parameters from many reflections belonging to an individual grain. The 3D orientation and geometrical relationships in the multigrain dataset allow the separation of reflections with close d -spacing. Using seifertite as an example, the uncertainties in the unit-cell parameters were gradually reduced by increasing the number of reflections merged from multiple grains in the refinement [30]. For this reason, uncertainties of the unit-cell parameters from the multigrain dataset are mainly defined by the resolution of the monochromator within 0.1%.

Conversely, precise unit-cell parameters can be used to evaluate subtle compositional effects on the mineral phases. Iron enters the crystal structures of all dominant lower mantle phases—silicate Bdg, pPv, and ferroperricite [37,38]. Multigrain XRD was applied to calculate the unit-cell parameters of the coexisting pPv and H-phase in (Mg,Fe)SiO₃ at 119 GPa [39]. Because the uncertainties of the unit-cell parameters were reduced by increasing the number of reflections in the refinement (> 150 reflections), the refined unit-cell parameters were able to resolve small differences of the Fe content across the center area (20–30 μm) of a laser-heated area, while the sample pressure remained unchanged in the Ne quasi-hydrostatic environment. The unit-cell volumes of the pPv phase decreased by only 0.16% over a 10 μm distance from the heating center to a colder region, while the unit-cell volume of the H-phase decreased by 0.54% over the same distance, indicating that both phases were more Fe-enriched in the slightly hotter center [39]. In contrast to the Soret effect that drives heavy elements, such as Fe, from hot to cold regions, we conclude that the observed Fe distribution was caused by a temperature effect on the element partitioning. Thus, high-pressure multigrain XRD can be applied to calculate the unit-cell parameters of each individual phase precisely that allows 2D mapping of element partitioning or phase distributions.

5. Combination of *in situ* XRD and *ex situ* TEM techniques: An example

In high P - T petrological experiments, *ex situ* chemical analysis on recovered samples is required to connect compositional changes associated with structural transformations determined by *in situ* XRD. The focus ion beam (FIB) has been widely used to cut and lift out a thin cross-section in a laser-heated sample in a DAC [40]. The thin section can then be analyzed in a TEM. *Ex situ* TEM analysis combining electron diffraction and energy dispersive spectrometer (EDS) chemical analysis can be used to verify the phases under ambient conditions. The consistency between *in situ* multigrain XRD and *ex situ* TEM analysis should be carefully checked. To ensure consistency, we always prepared a TEM specimen from the heating center where *in situ* XRD data were measured under high P - T . Meanwhile, 2D XRD scans were performed to record the phase distribution under high P - T as well as after recovery to ambient conditions. Note that most high-pressure structures are unquenchable to ambient conditions, and the recovered sample can sometimes be contaminated in the sample preparation for a TEM thin section.

Here, we provide an example to demonstrate the identification of hydrous phases in a multiphase assemblage through the combination of *in situ* synchrotron XRD and *ex situ* TEM. The identifica-

tion of hydrous phases in realistic lower mantle compositions is essential in order to understand the deep-water storage. We used a hydrous gel as our starting material with a composition of 30 mol% Al₂O₃–10 mol% Fe₂O₃–60 mol% MgSiO₃ containing about 7 wt% H₂O. As shown in Fig. 4, the XRD pattern contains a dominant pPv phase and a hydrous δ -phase, with only one weak peak indicating the presence of the cubic pyrite-type phase (py-phase). After multigrain indexing, we unambiguously confirmed the py-phase by sorting out 42 grains with 13–18 reflections consistent with the Pa -3 space group. Fig. 4(b) shows a composition-mapping image of a thin cross-section from the recovered sample prepared by FIB, showing several grains belonging to a very Fe-rich phase. EDS analysis verified only the elements Fe and oxygen (O) in the grains, while hydrogen (H) is undetectable if present. The grains range from 50 to 200 nm in size. From the 2D element mapping, the volume proportion of the py-phase is estimated to be less than 3 vol% in the assemblage. The chemical composition of these Fe-rich grains and their volume proportion in the assemblage are consistent with the *in situ* XRD observation of the py-phase under the high P - T conditions.

In this experiment, we used a higher Al₂O₃ content than realistic compositions in order to enhance the diffraction peaks of the δ -phase in the XRD patterns. In general, volatile-bearing phases exist as minor phases in a mantle assemblage. Regardless, this example demonstrated that high-pressure multigrain XRD is capable of identifying individual tiny grains of a minor hydrous phase with less than 3 vol% in an assemblage through a combination of *in situ* phase identification and *ex situ* chemical analysis.

6. Conclusions

This paper provides an overview of the high-pressure multigrain XRD technique, along with examples of its successful applications in studying multiphase systems under the P - T conditions of Earth's deep lower mantle. The crystal size in a multiphase assemblage can be as small as about 100 nm when the sample is synthesized under megabar pressures, making it infeasible to recover individual grains; thus, *in situ* characterization is needed. Meanwhile, peak overlapping renders the powder XRD method inadequate for investigating unknown phases and minor phases.

In situ multigrain XRD relies on an intense synchrotron X-ray beam, DAC rotation, and a fast indexing algorithm to identify tens to hundreds of crystallites belonging to each individual phase in a multiphase assemblage; in this way, it enables robust phase identification and structure determination in a multiphase assemblage. Examples were presented to illustrate the unique capabilities of the high-pressure multigrain XRD technique, including detecting the breakdown of iron-bearing Bdg into an iron-rich H-phase and Fe-free Bdg, identifying the HH-phase (Fe,Al)OOH, determining the crystal structures of (Mg,Fe)SiO₃-pPv and seifertite (SiO₂) under megabar pressures, measuring the unit-cell parameters of seifertite to a precision level of 0.1%, and examining subtle variations of Fe content in the coexisting pPv and H-phase over a temperature gradient. In some cases, the *in situ* high-pressure multigrain XRD technique can be combined with *ex situ* TEM analysis in order to connect structural transformation with compositional changes, which was demonstrated by the discovery of the py-phase FeOOH coexisting with the pPv phase in a model composition of subducted slabs under high P - T conditions. Through these effective illustrations, we have explained key challenges in studying multiphase systems and showed the important role of high-pressure multigrain XRD in exploring the Earth's deep interior.

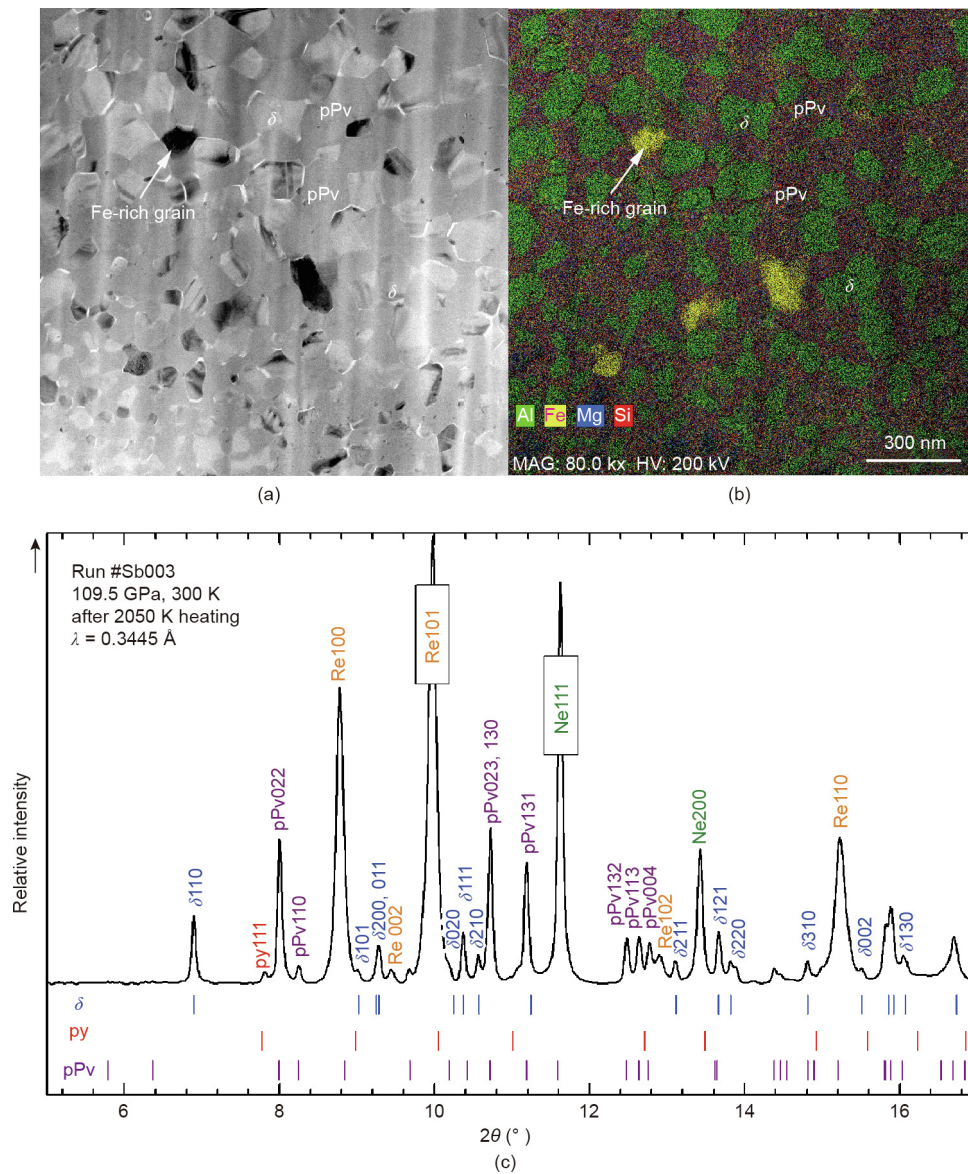


Fig. 4. A multiphase assemblage contains a dominant pPv phase, a hydrous δ -phase, and a minor pyrite-type phase (py-phase) FeOOH. (a, b) TEM mapping shows a few Fe-rich grains, which is consistent with the existence of a minor py-phase suggested by (c) *in situ* XRD.

Acknowledgements

The authors thank the anonymous reviewers for their constructive comments. This work was supported by the National Natural Science Foundation of China (41574080 and U1530402). Portions of this work were performed at High Pressure Collaborative Access Team (HPCAT) (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT operations are supported by the Department of Energy (DOE)/National Nuclear Security Administration (NNSA)'s Office of Experimental Sciences. The APS is a US DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory (DE-AC02-06CH11357). Portions of this work were performed at 15U1, Shanghai Synchrotron Radiation Facility (SSRF).

Compliance with ethics guidelines

Li Zhang, Hongsheng Yuan, Yue Meng, and Ho-Kwang Mao declare that they have no conflict of interest or financial conflicts to disclose.

References

- [1] Ricolleau A, Fei Y, Cottrell E, Watson H, Deng L, Zhang L, et al. Density profile of pyrolite under the lower mantle conditions. *Geophys Res Lett* 2009;36(6):36.
- [2] Irifune T, Shinmei T, McCammon CA, Miyajima N, Rubie DC, Frost DJ. Iron partitioning and density changes of pyrolite in Earth's lower mantle. *Science* 2010;327(5962):193–5.
- [3] Hirose K, Fei Y, Ma Y, Mao HK. The fate of subducted basaltic crust in the Earth's lower mantle. *Nature* 1999;397(6714):53–6.
- [4] Ohira I, Ohtani E, Sakai T, Miyahara M, Hiraon N, Ohishi Y, et al. Stability of a hydrous δ -phase, $\text{AlOOH-MgSiO}_3(\text{OH})_2$, and a mechanism for water transport into the base of lower mantle. *Earth Planet Sci Lett* 2014;401:12–7.
- [5] Bertka CM, Fei Y. Mineralogy of the Martian interior up to core-mantle boundary pressures. *J Geophys Res Solid Earth* 1997;102(B3):5251–64.
- [6] Lavina B, Meng Y. Unraveling the complexity of iron oxides at high pressure and temperature: Synthesis of Fe_3O_6 . *Sci Adv* 2015;1(5):e1400260.
- [7] Mao HK, Bell PM. High-pressure physics: sustained static generation of 1.36 to 1.72 megabars. *Science* 1978;200:1145–7.
- [8] Tateno S, Hirose K, Ohishi Y, Tatsumi Y. The structure of iron in Earth's inner core. *Science* 2010;330(6002):359–61.
- [9] Lay T. Sharpness of the D'' discontinuity beneath the Cocos Plate: implications for the perovskite to post-perovskite phase transition. *Geophys Res Lett* 2008;35(3):35.
- [10] Panning M, Romanowicz B. Inferences on flow at the base of Earth's mantle based on seismic anisotropy. *Science* 2004;303(5656):351–3.

- [11] Su W, Woodward RL, Dziewonski AM. Degree 12 model of shear velocity heterogeneity in the mantle. *J Geophys Res* 1994;99(B4):6945–80.
- [12] Miletich R, Allan DR, Kuhs WF. High-pressure single-crystal techniques. *Rev Mineral Geochem* 2000;41(1):445–519.
- [13] Dera P, Zhuravlev K, Prakapenka V, Rivers ML, Finkelstein GJ, Grubor-Urosevic O, et al. High pressure single-crystal micro X-ray diffraction analysis with GSE_ADA/RSV software. *High Press Res* 2013;33(3):466–84.
- [14] Dubrovinsky L, Boffa-Ballaran T, Glazyrin K, Kurnosov A, Frost D, Merlini M, et al. Single-crystal X-ray diffraction at megabar pressures and temperatures of thousands of degrees. *High Press Res* 2010;30(4):620–33.
- [15] Frost DJ, Fei Y. Stability of phase D at high pressure and high temperature. *J Geophys Res Solid Earth* 1998;103(B4):7463–74.
- [16] Murakami M, Hirose K, Kawamura K, Sata N, Ohishi Y. Post-perovskite phase transition in MgSiO₃. *Science* 2004;304(5672):855–8.
- [17] Oganov AR, Ono S. Theoretical and experimental evidence for a post-perovskite phase of MgSiO₃ in Earth's D'' layer. *Nature* 2004;430(6998):445–8.
- [18] Mao WL, Meng Y, Shen G, Prakapenka VB, Campbell AJ, Heinz DL, et al. Iron-rich silicates in the Earth's D'' layer. *Proc Natl Acad Sci USA* 2005;102(28):9751–3.
- [19] Nishi M, Irifune T, Tsuchiya J, Tange Y, Nishihara Y, Fujino K, et al. Stability of hydrous silicate at high pressures and water transport to the deep lower mantle. *Nat Geosci* 2014;7(3):224–7.
- [20] Zhang W, Oganov AR, Goncharov AF, Zhu Q, Boulfelfel SE, Lyakhov AO, et al. Unexpected stable stoichiometries of sodium chlorides. *Science* 2013;342(6165):1502–5.
- [21] Hirose K, Takafuji N, Sata N, Ohishi Y. Phase transition and density of subducted MORB crust in the lower mantle. *Earth Planet Sci Lett* 2005;237(1–2):239–51.
- [22] Shen G, Mao HK. High-pressure studies with x-rays using diamond anvil cells, reports on progress in physics. *Physical Society* 2017;80:016101.
- [23] Duffy TS. Synchrotron facilities and the study of the Earth's deep interior. *Rep Prog Phys* 2005;68(8):1811–59.
- [24] Mao HK, Chen B, Chen J, Li K, Lin JF, Yang W, et al. Recent advances in high-pressure science and technology. *Matter Radiat Extremes* 2016;1(1):59–75.
- [25] Zhang L, Meng Y, Dera P, Yang W, Mao WL, Mao HK. Single-crystal structure determination of (Mg,Fe)SiO₃ postperovskite. *Proc Natl Acad Sci USA* 2013;110(16):6292–5.
- [26] Nisr C, Ribárik G, Ungár T, Vaughan GBM, Cordier P, Merkel S. High resolution three-dimensional X-ray diffraction study of dislocations in grains of MgGeO₃ post-perovskite at 90 GPa. *J Geophys Res* 2012;117(B3):B03201.
- [27] Schmidt S. GrainSpotter: a fast and robust polycrystalline indexing algorithm. *J Appl Cryst* 2014;47(1):276–84.
- [28] Sørensen HO, Schmidt S, Wright JP, Vaughan GBM, Techert S, Garman EF, et al. Multigrain crystallography. *Z Kristallogr* 2012;227(1):63–78.
- [29] Zhang L, Meng Y, Yang W, Wang L, Mao WL, Zeng QS, et al. Disproportionation of (Mg,Fe)SiO₃ perovskite in Earth's deep lower mantle. *Science* 2014;344(6186):877–82.
- [30] Zhang L, Popov D, Meng Y, Wang J, Ji C, Li B, et al. *In-situ* crystal structure determination of seifertite SiO₂ at 129 GPa: studying a minor phase near Earth's core-mantle boundary. *Am Mineral* 2016;101(1):231–4.
- [31] Merlini M, Hanfland M, Salamat A, Petitgirard S, Müller H. The crystal structures of Mg₂Fe₂C₄O₁₃, with tetrahedrally coordinated carbon, and Fe₁₃O₁₉, synthesized at deep mantle conditions. *Am Mineral* 2015;100(8–9):2001–4.
- [32] Oxford Diffraction Ltd. CrysAlis Red. Version p171.29.2 [software]; 2006.
- [33] Kabsch W. XDS. *Acta Crystallogr D Biol Crystallogr* 2010;D66:125–32.
- [34] Dera P. GSE-ADA data analysis program for monochromatic single crystal diffraction with area detector. Argonne: GSECARS; 2007.
- [35] Sheldrick GM. A short history of SHELX. *Acta Crystallogr A* 2008;A64:112–22.
- [36] Zhang L, Yuan H, Meng Y, Mao HK. Discovery of a hexagonal ultradense hydrous phase in (Fe,Al)OOH. *Proc Natl Acad Sci USA* 2018;115(12):2908–11.
- [37] Lundin S, Catalli K, Santillán J, Shim SH, Prakapenka VB, Kunz M, et al. Effect of Fe on the equation of state of mantle silicate perovskite over 1 Mbar. *Phys Earth Planet Inter* 2008;168(1–2):97–102.
- [38] Fei Y, Zhang L, Corgne A, Watson H, Ricolleau A, Meng Y, et al. Spin transition and equations of state of (Mg,Fe)O solid solutions. *Geophys Res Lett* 2007;34(17):L17307.
- [39] Zhang L, Meng Y, Mao H. Unit cell determination of coexisting post-perovskite and H-phase in (Mg,Fe)SiO₃ using multigrain XRD: compositional variation across a laser heating spot at 119 GPa. *Prog Earth Planet Sci* 2016;3(1):13.
- [40] Miyahara M, Sakai T, Ohtani E, Kobayashi Y, Kamada S, Kondo T, et al. Application of FIB system to ultra-high-pressure Earth science. *J Mineral Petrol Sci* 2008;103(2):88–93.