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High-pressure minerals in shocked meteorites

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Abstract—Heavily shocked meteorites contain various types of high-pressure polymorphs of major minerals (olivine, pyroxene, feldspar, and quartz) and accessory minerals (chromite and Ca phosphate). These high-pressure minerals are micron to submicron sized and occur within and in the vicinity of shock-induced melt veins and melt pockets in chondrites and lunar, howardite-eucrite-diogenite (HED), and Martian meteorites. Their occurrence suggests two types of formation mechanisms (1) solid-state high-pressure transformation of the host-rock minerals into monomineralic polycrystalline aggregates, and (2) crystallization of chondritic or monomineralic melts under high pressure. Based on experimentally determined phase relations, their formation pressures are limited to the pressure range up to \(
\sim 25 \text{ GPa}
\). Textural, crystallographic, and chemical characteristics of high-pressure minerals provide clues about the impact events of meteorite parent bodies, including their size and mutual collision velocities and about the mineralogy of deep planetary interiors. The aim of this article is to review and summarize the findings on natural high-pressure minerals in shocked meteorites that have been reported over the past 50 years.

INTRODUCTION

The Earth’s crust and upper mantle are mainly composed of silicate minerals. These minerals transform into denser crystal structures, so-called high-pressure minerals, in the deep Earth’s mantle. Here, a high-pressure mineral is defined as one that is thermodynamically stable only under Earth’s mantle pressure conditions (above \( \sim 1 \text{ GPa} \)). The physical and chemical properties of high-pressure minerals are basic and essential parameters characterizing the structure and dynamics of the Earth’s interior. Mineral physicists have been making long-standing efforts to clarify the structural changes and phase equilibrium of silicate minerals based on high-temperature and high-pressure experiments (e.g., Pressnall 1995; Irifune and Tsuchiya 2009). Consequently, a variety of high-pressure polymorphs have been synthesized using a Kawai-type multi-anvil apparatus and a laser-heated diamond anvil cell.

The comparison between experimentally obtained densities and elastic wave velocities of high-pressure minerals and data from seismological observations enables us to elucidate deep Earth’s mineralogy. So far, most of the high-pressure silicate minerals are considered to be major components of the Earth’s deep mantle down to a depth of 2900 km, corresponding to the mantle-core boundary. Despite their geophysical significance, it is almost impossible to directly obtain materials of the deep Earth’s mantle because the maximum depth attainable by borehole drilling is only \( \sim 12 \text{ km} \) (Fuchs et al. 1990). In rare cases, magmatic and tectonic activities transport minerals that formed under high static pressures from the Earth’s upper mantle and transition zone to the surface as inclusions in diamonds (e.g., Moore and Gurney 1985; Walter et al. 2011) and mantle xenoliths (e.g., Collerson et al. 2000).

The first natural high-pressure mineral that was discovered was formed by dynamic compression on the surface of the Earth. In the early 1960s, E. C. T. Chao and his colleagues applied hydrofluoric acid leaching to a large amount of sandstone of the Barringer crater in Arizona, which was the product of an iron meteorite
impact approximately 49,000 years ago. Coesite and stishovite, the high-pressure polymorphs of SiO₂, were identified in the residues by powder X-ray diffraction. The occurrence of coesite and stishovite implies that the quartz in the Coconino sandstone was densified under high-temperature and high-pressure conditions. This was crucial evidence proving that the Barringer crater was formed by an asteroidal impact and was not a result of a volcanic eruption (Chao et al. 1960, 1962).

Meanwhile, high-pressure minerals have been found mostly in extraterrestrial materials. Based on orbital calculations, spectral observations, and the analyses of asteroidal samples obtained during the Hayabusa sample return mission, most of the meteorites are believed to have originated from asteroids (e.g., Brown et al. 2000; Nakamura et al. 2011; Popova et al. 2013). Although asteroids are much smaller than terrestrial planets, their mutual high-velocity collisions achieve high-pressure and high-temperature conditions comparable to the Earth's deep interior. Even during such a short event of no more than several seconds (Ohtani et al. 2004), high-pressure minerals can be produced from the minerals in the host meteorites.

The formation processes of high-pressure minerals are closely related to the pressure-temperature-time history of impact events (Sharp and DeCarli 2006; Gillet and El Goresy 2013). The pressure values deduced from phase equilibria of meteoritic components provide mutual collision velocities of their parent bodies. The shock pressure durations and sizes of impactors have been estimated based on phase transformation kinetics and element diffusion in meteoritic high-pressure minerals (e.g., Ohtani et al. 2004; Beck et al. 2005; Xie et al. 2006b). The combination of this knowledge with the radiometric ages of shock events of meteorites (e.g., Park et al. 2008) and further investigations of the P-T conditions of meteoritic high-pressure minerals provide more robust constraints for the theoretical models of the evolution of the early solar system.

As described above, the first natural high-pressure minerals were discovered from the late 1960s to the late 1970s (e.g., Mason et al. 1968; Binns et al. 1969; Puttnis and Price 1979). However, a long research gap followed after these discoveries due to technical difficulties with respect to the identification of minute crystals. Based on the advancement of instrumentation, the detailed investigations of high-pressure minerals resumed in China, France, Germany, Japan, and the United States in the late 1990s (e.g., Chen et al. 1996b; Sharp et al. 1997; Tomioka and Fujino 1997; El Goresy et al. 2000; Gillet et al. 2000). These active and collective efforts resulted in the discovery of many high-pressure polymorphs of silicates, oxides, and phosphates in shocked meteorites. More than ten high-pressure minerals have been defined as new mineral species by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association since the late 1990s. This article mainly focuses on the description of the occurrences of natural high-pressure minerals in shocked meteorites.

GENERAL OCCURRENCES OF HIGH-PRESSURE MINERALS IN METEORITES

Ringwoodite, a high-pressure polymorph of olivine, is an important indicator of “very strongly shocked” ordinary chondrites of the shock stage S6, which was proposed by Stöffler et al. (1991). It is a high-pressure mineral that is easily identifiable by its characteristic blue color and optical isotropy in the petrographic thin section; other high-pressure minerals have not been considered for shock stage evaluation. However, further detailed and systematic mineralogical and crystallographic studies of shock veins showed that ordinary chondrites classified as S3, S4, and S5 also contain various types of high-pressure minerals (Xie et al. 2006a), in addition to S6.

High-pressure minerals in meteorites occur in and in the vicinity of shock-induced melt veins (shock veins) and melt pockets up to several mm in width (Fig. 1) and are thought to have formed by two types of mechanisms. One is solid-state transformation of the host-rock minerals. Mineral fragments of olivine, pyroxenes, and feldspars, which are major constituents of stony meteorites, are locally entrapped in shock veins. The fragments are heated up by surrounding chondritic melt during shock compression and first partly and then totally transformed into high-pressure polymorphs (Figs. 1 and 2). The high-pressure minerals form a monomineralic assemblage with nearly the same chemical composition as that of their parental minerals; the grains tend to be submicron sized. The other mechanism is crystallization from shock-induced chondritic melt under high pressure. The “optically black” matrix of the shock veins consists of aggregates of crystals and glasses with euhedral to anhedral shapes that solidified from melt (Figs. 1 and 2). Abundant Fe-FeS globules characterize the petrographic texture of the matrix. The spherical shape of the opaque aggregates clearly suggests immiscible Fe-FeS and silicate melts, which simultaneously melted by shock heating and solidified by subsequent rapid cooling. The silicate and oxide grains tend to be larger (up to several μm in size) than those of the minerals in the host-rock fragments. These grains have variable chemical compositions and often contain Fe-S-O-rich inclusions. The high-pressure minerals that formed by the above-mentioned mechanisms and were found in shocked meteorites are introduced in detail in the following sections.
High-pressure minerals in shocked meteorites

Fig. 1. Schematic drawing of the formation mechanism of high-pressure minerals in shock-induced melt veins (shock veins) in meteorites. High-pressure minerals form by two types of formation mechanisms (1) solid-state high-pressure transformation of the host-rock minerals, and (2) crystallization of chondritic or monomineralic melt under high pressure in the matrix of shock veins. (Color figure can be viewed at wileyonlinelibrary.com.)

Fig. 2. Backscattered electron image of a shock vein in the Y-74445 (L6) chondrite. The bright spherules concentrated at the edge of the shock vein are Fe-FeS assemblages.

ANALYTICAL METHODS FOR HIGH-PRESSURE MINERALS IN METEORITES

Backscattered electron (BSE) imaging with a scanning electron microscope (SEM) and quantitative chemical analysis using an electron microprobe analyzer (EMPA) have been widely used to identify high-pressure minerals in shocked meteorites. However, it is not easy to fully characterize high-pressure minerals in shocked meteorites because of their very small grain size and low abundance. One of the most powerful tools to overcome this difficulty with such samples is the combination of a transmission electron microscope with an energy-dispersive X-ray spectrometer (TEM-EDS). The TEM-EDS allows us to perform textural, crystallographic, and chemical analyses on a micron-to-nanoscale. This technique is especially effective in determining high-pressure phase transformation mechanisms (e.g., Tomioka and Fujino 1999; Miyahara et al. 2010) and deformation processes (e.g., Madon and Poirier 1980; Price 1983).

Conventionally, ultra-thin films (typically ~100 nm) were prepared for TEM by Ar ion milling and ultramicrotomy. In the case of meteorite samples, the target particles for TEM observations are submicron sized. In addition, valuable specimens, such as Martian and lunar meteorites, require special instrumentation to minimize the sample destruction during analysis. For this purpose, focused ion beam (FIB) equipment has been used recently to effectively extract thin foils from desired portions of the meteorites (e.g., Chen et al. 2007; Miyahara et al. 2008; Hu and Sharp 2016).

Electron backscattered diffraction using a scanning electron microscope (SEM-EBSD) has become one of the major techniques for the characterization of high-
pressure minerals because it provides both chemical and crystallographic information on the submicron scale. Compared with TEM, SEM-EBSD has a big advantage in that the whole standard-sized polished petrographic section can be surveyed promptly (e.g., Ma et al. 2014, 2015, 2016).

The first discovery of meteoritic high-pressure minerals was made using conventional powder X-ray diffraction (XRD; Mason et al. 1968). Based on the combination of diffractometry with a focused X-ray beam and mathematical peak deconvolution, XRD provides precise lattice parameters of small mineral aggregates without damaging the sample. To obtain a higher spatial resolution and detect stronger diffraction intensities in XRD measurements, a collimated X-ray beam has been used for laboratory-based micro-area XRD (μXRD; e.g., Gillet et al. 2000). Nowadays, synchrotron X-ray sources are frequently used for μXRD analyses of high-pressure minerals (e.g., Miyahara et al. 2011; Tschauner et al. 2014; Ma et al. 2016).

Laser micro-Raman spectroscopy is also very commonly utilized to determine the high-pressure mineralogy of shocked meteorites (Table 1). This technique allows the identification of high-pressure mineral species in ~1 μm-sized sample spots in standard-sized polished sections within several tens of seconds to seconds (e.g., Gillet et al. 2000; Kimura et al. 2003).

**HIGH-PRESSURE POLYMORPHS OF OLIVINE**

Natural Mg2SiO4-rich spinel, ringwoodite, was discovered in the shock vein of the Tenham chondrite (L6; Binns et al. 1969). Ringwoodite is one of the few high-pressure polymorphs that were also found in terrestrial rocks, as inclusion in a diamond crystal (Pearson et al. 2014). The mineral ringwoodite is named after the experimental geophysicist A. E. Ringwood (Binns et al. 1969). The Fe2SiO4-rich spinel was discovered in the shock vein of a meteorite, the Umbarger chondrite (L6; Xie et al. 2002b). Another occurrence of natural Fe2SiO4-rich spinel was described in the melt pocket of the olivine-phryic shergottite Tissint; it was named ahrensite after the experimental geophysicist T. Ahrens (Ma et al. 2014). Natural (Mg, Fe)2SiO4 with a modified spinel structure was discovered in the shock veins of the Tenham and Peace River chondrites (L6; Putnis and Price 1979; Price et al. 1983) using TEM. The mineral was named wadsleyte after the crystallographer A. D. Wadsley (Price et al. 1983).

The fayalite component of olivine in H, L, and LL-type ordinary chondrites is 16–23 mol%, 23–26 mol%, and 27–32 mol%, respectively (Weisberg et al. 2006). The phase diagram of the Mg2SiO4-Fe2SiO4 system is shown in Fig. 3. Considering the chemical composition of olivine in ordinary chondrites, it is predicted that the olivine in ordinary chondrites transforms into ringwoodite or a wadsleyte-ringwoodite assemblage because of high-pressure and high-temperature conditions induced by an impact event. In fact, 90% of type 5 and 6 ordinary chondrites, which have a shock-induced melting texture (shock-melt vein or melt vein), investigated in previous studies (Table 2 and references therein) contain ringwoodite and ~40% comprise wadsleyite. Ringwoodite also occurs in and in the vicinity of shock veins or melt pockets of heavily shocked shergottite, chassignite, and basaltic lunar meteorites (Table 3). In most cases, wadsleyite does not accompany ringwoodite; the fayalite components of most of the olivine in these achondrites are high (~50 mol%). However, phase transformations from olivine to wadsleyte/ahrensite are rarely observed in shocked chondrites and achondrites, which is mainly due to the Fe-rich chemical composition.

Phase transformation mechanisms from olivine to ringwoodite in shocked meteorites have been enthusiastically investigated because they provide clues about the fate of oceanic plates that are subducting into the deep Earth's interior. The FIB-supported TEM observations revealed that the olivine fragments entrained in shock veins are replaced with polycrystalline ringwoodite (individual crystals are <1 μm in diameter; Miyahara et al. 2010). A ringwoodite-lamellar texture consisting of polycrystalline ringwoodite was observed in an olivine grain adjacent to a shock vein (Chen et al. 2004; Ohtani et al. 2004; Ozawa et al. 2009; Miyahara et al. 2010). The original olivine grain and ringwoodite lamellae show no specific crystallographic orientation (Fig. 4), and their chemical compositions only slightly differ in most shocked ordinary chondrites (Chen et al. 2007; Miyahara et al. 2010). Based on the following features, that are (1) ringwoodite-lamellar texture occurring in original olivine grain, (2) polycrystalline ringwoodite, and (3) no specific crystallographic orientation and little difference on chemical composition between original olivine and ringwoodite, the phase transformation from olivine to ringwoodite is mainly initiated by incoherent grain boundary nucleation and interface-controlled growth mechanisms; the nucleation of ringwoodite occurs along the grain boundaries, fractures, and/or triple points of the original olivine grains; and the interfacial energy between olivine and ringwoodite during the growth is controlled (e.g., Remsberg et al. 1988; Kerschhofer et al. 1996).

Another mechanism is coherent phase transformation (intracrystalline formation) from olivine to ringwoodite. It
Table 1. Major Raman peaks of high-pressure minerals in shocked meteorites.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Chemical compositions</th>
<th>Raman shift (cm⁻¹)</th>
<th>Refs</th>
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<td>Fo₅₂Fa₃₈</td>
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<td>Ringwoodite</td>
<td>Fo₅₂Fa₃₈</td>
<td></td>
<td>1</td>
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<tr>
<td>Ahrensite</td>
<td>Fo₄₈Fa₃₄</td>
<td>213 672 798 843 843</td>
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<td>NaAl₂Si₅O₈</td>
<td>379 438 528 583 700</td>
<td>989 1039</td>
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<td>Tissintite</td>
<td>(Ca, Na, Al)Al₂Si₅O₆</td>
<td>203 377 417 523 573</td>
<td>997 1065</td>
</tr>
<tr>
<td>Majorite</td>
<td>En₉₉Fa₃₉W₀₂</td>
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<tr>
<td>Akimotoite</td>
<td>(Fe₀.₉₉Mg₀.₂₄Ca₀.₀₇Na₀.₁₂)Si₉₉Al₀.₆₄O₆</td>
<td>342 407 477 614 672</td>
<td>796 973</td>
</tr>
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<td>Heimleyite</td>
<td>(Fe²⁺₀.₀₆Mg₀.₇₆Ca₀.₀₈Na₀.₀₈)Al₀.₆₄O₆</td>
<td>342 403 476 611 673</td>
<td>795 973</td>
</tr>
<tr>
<td>Lingurite</td>
<td>Al₂₀₃Mn₉₉O₇</td>
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<td>Coesite</td>
<td>SiO₂</td>
<td>208 272 329 357 429 468 523</td>
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<td>Shishovite</td>
<td>SiO₂</td>
<td>232 587 753 966 10</td>
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<td>CAS³</td>
<td>Ca₁₀₉₉(Al₃₉₉Si₂₀₃)O₃₉₉</td>
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<td>Tuite</td>
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<td>Xlette</td>
<td>(Fe₀.₉₉Mg₀.₃₄Mn₀.₆₄)Ca₀.₈₉Cr²⁺₀.₀₆Fe₂⁺₀.₀₆Cr³⁺₀.₀₆</td>
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<td>TIO₂</td>
<td>152 175 285 315 340 358 428 532 575</td>
<td>14</td>
</tr>
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</table>

³Synthetic sample for the Raman reference.
²Samples from impact craters.
The original olivine grains included in their host rocks do not show chemical zonation (Feng et al. 2011; Pittarello et al. 2015). The rims of the original olivine grains entrained in the shock veins are replaced with polycrystalline ringwoodite. The cores consist of polycrystalline olivine (and minor wadsleyite) with considerable Fe-depletion compared with the original olivine. The polycrystalline ringwoodite is rich in iron compared with the original olivine. The Fe-depleted olivine and Fe-enriched ringwoodite have a fayalite component of approximately 50 mol% (Feng et al. 2011). The iron in the original olivine diffused outward, whereas magnesium diffused inward. This implies that the phase transformation was promoted by a diffusion-controlled mechanism (Pittarello et al. 2015).

The phase transformation from olivine to a ringwoodite–wadsleyite assemblage was observed in the shock veins of several ordinary chondrites (Table 2). The original olivine crystals replaced with granular ringwoodite–wadsleyite assemblages in the Peace River (L6), Allan Hills 78003 (L6), and Yamato-74445 (L6) chondrites show a unique feature. The chemical compositions of ringwoodite and wadsleyite in the assemblage significantly differ (up to 32 mol% fayalite component; Miyahara et al. 2008, 2009; Fig. 5). It is difficult to induce such a significant Fe-Mg interdiffusion between ringwoodite and wadsleyite because the Fe-Mg interdiffusion is very sluggish in a solid-state reaction during the limited high-pressure and high-temperature conditions of an impact event. Miyahara et al. (2008, 2009) proposed that the original olivine entrained in the shock vein was melted once and ringwoodite and wadsleyite assemblages subsequently formed from the olivine melt by fractional crystallization.

The phase transformation from olivine to wadsleyite was only observed in the shock vein of Sahara 98222 (L6; Ozawa et al. 2009). The phase transformation occurred without Fe-Mg interdiffusion; wadsleyite nucleated and grew along the grain boundaries and fractures of the original olivine grains, suggesting incoherent grain boundary nucleation and an interface-controlled growth mechanism.

The phase diagram of the system Mg$_2$SiO$_4$–Fe$_2$SiO$_4$ indicates that olivine dissociates into (Mg,Fe)SiO$_3$ perovskite (bridgmanite) and magnesiowüstite (and stishovite) at ~23–25 GPa; however, the dissociation reaction depends not only on the temperature but also on the chemical composition. In general, Martian meteorites record higher shock pressure conditions compared with ordinary chondrites. Miyahara et al. (2011) found evidence for the olivine dissociation reaction in an olivine grain adjacent to the shock vein of the olivine-phyllic shergottite Dar al Gani 735 (Fig. 6). A similar olivine dissociation reaction was found in the olivine-phyllic shergottite Tissint (Walton et al. 2014; Ma et al. 2015;
### Table 2. High-pressure minerals in chondrites.

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*Described as vitrified bridgmanite.


Wds = wadsleyite, Rwd = ringwoodite, Ahr = ahrensite, Jad = jadeite, Maj = majorite, Maj-Prp = majorite-pyrope solid solution, Aki = akimotoite, Hem = hemleyite, Bdg = bridgmanite, Lin = linuginite, Coe = coesite, Sti = stishovite, Tui = tuilite.

The phase transition is kinetically controlled. In several previous studies, researchers tried to estimate the magnitude of an impact event recorded by ordinary chondrites and shergottites using the grain-growth kinetics of ringwoodite. The grain sizes of ringwoodite crystals in shocked ordinary chondrites are similar (up
Table 3. High-pressure minerals in achondrites and iron meteorite.

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Wds = wadsleyite, Rwd = ringwoodite, Ahr = ahrensite, Tis = tissinitc, Maj = majorite, Aki = akimotoite, Bdg = bridgmanite, Lin = lingunite, Lie = liebermannite, Coe = coesite, Sti = stishovite, Sei = seifellite, CAS = Ca-Al-Si-rich phase, Tui = tuite, Xie = xieite.

aDescribed as vitrified bridgmanite.

Fig. 4. Transmission electron micrograph of (a) ringwoodite (Rwd) lamella in an olivine (Ol) grain next to the shock vein of the Y-791384 (L6) chondrite. Ringwoodite platelets (indicated by arrows) also occur. b) Selected area electron diffraction (SAED) pattern indicates that there is a specific crystallographic orientation; (100)_{Ol}//{111}_{Rwd} between the ringwoodite platelets and surrounding olivine. c) SAED pattern indicates that the thick ringwoodite lamella (upper right) consists of unoriented polycrystalline ringwoodite. Ol: olivine, Rwd: ringwoodite. See details in Miyahara et al. (2010).

to 3 μm; Chen et al. 1996b). Accordingly, the estimated shock pressure durations are also similar (less than several seconds; Ohtaani et al. 2004; Xie et al. 2006b). Exceptionally, Baziotsis et al. (2013) proposed that coarse-grained ringwoodite (~75 × 140 μm across) occurs near the melt pocket of the olivine-phryic shergottite Tissint, suggesting the largest impact excavation on Mars. However, detailed TEM observations do not support this hypothesis because the ringwoodite is also fine-grained (≤1 μm) and polycrystalline (Walton et al. 2014; Miyahara et al. 2016).

HIGH-PRESSURE POLYMORPHS OF PYROXENES

Enstatite (MgSiO₃) is a representative endmember component of pyroxenes of terrestrial planets. The phase equilibria of the chemical system have been investigated using high-temperature and high-pressure experiments (Fig. 7). In the high-temperature region above 1600 °C, enstatite (with 4-fold coordinated Si) transforms first into the garnet structure (with both 4- and 6-fold coordinated Si) at ~18 GPa and then into the perovskite structure (with 6-fold coordinated Si ion) at ~22 GPa. In contrast, in the lower temperature region below 1600 °C, enstatite breaks down to wadsleyite (Mg₂SiO₄) and stishovite (SiO₂); the wadsleyite transforms further into ringwoodite. With increasing pressure, these phases return to MgSiO₃ stoichiometry with an ilmenite structure and then to a perovskite structure. The outlines of the phase equilibria in the Fe- and Ca-bearing system are similar to that of MgSiO₃. The Ca-rich pyroxene composition includes an additional phase; CaSiO₃-perovskite also coexists with all other high-pressure polymorphs in the MgSiO₃ phase diagram above ~18 GPa (Fig. 8). So far, the synthesis of the high-pressure polymorphs of pyroxene using shock recovery experiments has been unsuccessful.

A natural high-pressure polymorph of pyroxene was first discovered in ordinary chondrites in the late 1960s (Table 2). Mason et al. (1968) found aggregates with a pyroxene composition in the Coorara chondrite (L6) using powder XRD and identified their crystal structure as a garnet structure (Mason et al. 1968; Smith and Mason 1970). Two years before this discovery, Ringwood and Major (1966) first synthesized garnet from a glass with MgSiO₃ (90 wt%)-Al₂O₃ (10 wt%) composition that was compressed to 20 GPa at 900 °C. The garnet phase had excess Si, corresponding to the MgSiO₃-pyroxene component. The new high-pressure mineral found in Coorara was named majorite after A. Major who greatly contributed to high-pressure mineral
of subcalcic pyroxene in the same chondrite (Xie and Sharp 2007).

Another high-pressure polymorph of pyroxene was discovered by a German-American research group while performing detailed TEM analysis on the silicate minerals in Acfer 040 (L5-6; Table 2; Sharp et al. 1997). They found Mg$_2$SiO$_4$-ilmenite in addition to Mg$_2$SiO$_4$-perovskite (as vitrified amorphous Mg$_2$SiO$_4$-rich grains; Sharp et al. 1997). The matrix of the shock veins in Acfer 040 consists mainly of Mg$_2$SiO$_4$-rich amorphous grains (~2 μm in size), ringwoodite, and Mg$_2$SiO$_4$-ilmenite. The Mg$_2$SiO$_4$-ilmenite occurs as plate-like grains and contains considerable amounts of Na$_2$O, Al$_2$O$_3$, and FeO components, while the Mg$_2$SiO$_4$-rich amorphous material comprises significant amounts of Na$_2$O, Al$_2$O$_3$, CaO, and FeO components. Based on the coexistence with high-pressure minerals, such as Mg$_2$SiO$_4$-ilmenite and ringwoodite, it was concluded that the Mg$_2$SiO$_4$-rich amorphous grains initially crystallized as Mg$_2$SiO$_4$-perovskite from the chondritic melt and subsequently vitrified after shock pressure release (Sharp et al. 1997).

Independently, Tomioka and Fujino (1997) reported (Mg,Fe)$_2$SiO$_4$-ilmenite and (Mg,Fe)$_2$SiO$_4$-perovskite in Tenham (Fig. 10). Clinopyroxenate, (Mg,Fe)$_2$SiO$_4$, fragments of the host rock entrapped in the shock veins, directly transformed into aggregates of submicron-sized grains. Some aggregates consist only of column-shaped (Mg,Fe)$_2$SiO$_4$-ilmenite grains smaller than ~1–2 μm in size. Their chemical composition is also identical to that of clinopyroxenate in the host rock. In contrast to Acfer 040, the ilmenite phase is thought to have formed by a solid-phase transition of the host clinopyroxenate. This ilmenite phase was named akimotoite after the experimental geophysicist S. Akimoto (Tomioka and...
Fig. 8. Phase diagram of CaMgSi$_2$O$_6$ (modified after Akaogi et al. 2004). Ca-Pv: CaSiO$_3$-perovskite.

Fig. 9. Transmission electron micrograph of an aggregate of tetragonal (Mg,Fe)SiO$_3$ majorite in the Tenham (L6) chondrite. The TEM sample consists of monomineralic aggregates of euhedral or subhedral grains. SAED pattern is shown in the inset. See details in Tomioka et al. (2016).

Recently, the Fe-rich analog of akimotoite was discovered in Suizhou (L6) and named hemleyite after the mineral physicist R. J. Hemley (Bindi et al. 2017).

Another unique characteristic of akimotoite in Tenham is the topotaxial intergrowth with clinoenstatite. The crystallographic orientations of akimotoite and clinoenstatite crystals show a specific correlation, preserving close-packed layers of oxygen in both structures: (100)$_{Cen}$//(0001)$_{Aki}$ and (010)$_{Cen}$ //(010)$_{Aki}$ (Cen: clinoenstatite, Aki: akimotoite; Fig. 10). The topological analysis based on the relationship of the orientations suggests that the enstatite-akimotoite phase transition is characterized by small displacements of cations associated with the shear of oxygen sublattices of the pyroxene structure, which is called shear mechanism (Tomioka 2007).

As described above, the (Mg,Fe)SiO$_3$-perovskite grains (~0.3 μm in size) in Tenham were identified to be crystalline using TEM (Tomioka and Fujino 1997). The perovskite phase has the same chemical composition as the original clinoenstatite, which is considered to have formed in a solid-phase transition (Fig. 11). Among the high-pressure silicate minerals, (Mg,Fe)SiO$_3$-perovskite is particularly unstable under ambient pressure; it is known to amorphize at ~150 °C (Wang et al. 1992). Furthermore, the (Mg,Fe)SiO$_3$-perovskite grains in Tenham easily vitrified during the TEM observation due to electron-beam irradiation. As mentioned in the previous section, Miyahara et al. (2011) also identified...
fine-grained assemblages of (Mg,Fe)SiO₃-perovskite and magnesioilwüsite as poestringwoodite dissociation products of olivine in the Dar al Gani 735 Martian meteorite. However, crystallographic data on the perovskite phase in Tenham and Dar al Gani 735 are limited. Recently, synchrotron X-ray microdiffraction was used to fully determine the unit cell of natural (Mg,Fe)SiO₃-perovskite in Tenham. The mineral was named bridgmanite after the solid-state physicist P. Bridgman (Tschauner et al. 2014).

A unique occurrence of a MgSiO₃-perovskite-like phase in the carbonaceous chondrite Aefer 094 (ungrouped C2) should also be noted. It is ~300 nm in size and has an oxygen isotope anomaly (Vollmer et al. 2007). Electron diffraction patterns of the particle indicate a superstructure of the orthorhombic perovskite structure. Presolar enstatite particles floating in interstellar space are thought to have transformed into the perovskite-like phase by shock waves before incorporation into Aefer 094.

High-pressure transformations of Ca-rich and subcalcic pyroxenes were also found in shocked ordinary chondrites (Tomioka and Kimura 2003; Xie and Sharp 2007). Figure 12 shows a high-pressure dissociation phase of diopside (CaMgSi₂O₆) in Yamato-75100 (H6). It occurs in the form of submicron scale aggregates of CaSiO₃-rich amorphous grains and Ca-rich majorite. Its bulk composition is close to that of the host diopside. Experimental studies showed that CaSiO₃-perovskite stable at pressures above 11 GPa cannot be recovered under atmospheric pressure but amorphizes upon decompression (e.g., Liu and Ringwood 1975). Therefore, it is considered that the CaSiO₃-rich glass in Yamato-75100 assumes a CaSiO₃-perovskite structure after the dissociation of Ca-rich pyroxene during persisting shock pressure.

Recently, a novel occurrence of a Fe,Al-bearing MgSiO₃-rich pyroxene polymorph was reported; acicular crystals (<0.5 μm in length) are embedded in the glass matrix of shock veins in Tenham (Xie et al. 2011a). Surprisingly, the electron diffraction pattern indicates an olivine structure. The discrepancy between pyroxene and olivine stoichiometry can be reconciled by introducing cation vacancies at the M site of the olivine structure. The estimated density of 3.32 g cm⁻³ is slightly larger than those of enstatite and diopside, and forsterite. Therefore, the mineral is thought to have metastably crystallized from chondrite melt under high pressure during rapid cooling.

**HIGH-PRESSURE POLYMORPHS OF FELDSPARS**

Although the phase equilibrium of feldspar solid solutions for a wide range of temperature and pressure conditions has not yet been established, albite (NaAlSi₃O₈), which is a representative feldspar component in ordinary chondrites, was experimentally investigated (e.g., Liu 1978, 2006; Yagi et al. 1994; Zhou et al. 2017); albite breaks down to jadeite (NaAlSi₂O₆) + quartz (SiO₂) and jadeite + coesite (SiO₂; Fig. 13). Liu (1978) reported that hollandite-type NaAlSi₃O₈ is stable at 21 GPa based on a laser-heated diamond anvil cell study. However, further reevaluation of the system NaAlSi₃O₈-KAlSi₃O₈ using a Kawai-type high-pressure apparatus revealed the absence of the hollandite-type phase in the NaAlSi₃O₈ composition at temperatures up to 2000 °C. Instead of the hollandite-type phase, calcium ferrite (CaFe₂O₄)-type NaAlSi₄O₁₀ and stishovite appear (Fig. 13; Yagi et al. 1994; Liu 2006; Zhou et al. 2017). Therefore, NaAlSi₃O₈-hollandite likely forms under disequilibrium conditions. Similar to pyroxene, high-pressure polymorphs of feldspar have not been synthesized by shock recovery experiments due to sluggish transformation kinetics with respect to microsecond pressure durations.

It is well known that experimentally shocked plagioclase transforms into the amorphous phase with a high refractive index without short-range order loss of its structure (Ostertag 1983). Such a dense plagioclase glass was also found in strongly shocked chondrites and acondrites and has been called maskelynite (e.g., Stöffler et al. 1986, 1991). The glass almost retains the morphology of the original plagioclase but loses its crystallinity. Therefore, it is easily identified based on its optical isotropy under the polarizing microscope. Maskelynite-like NaAlSi₃O₈-rich grains in and in the vicinity of shock veins in Sishangkou (L6) were
monomineralic aggregates of extremely small grains with several tens of nm in size (Fig. 14). The NaAlSi$_3$O$_8$-hollandite was named langunitite after L. Liu who first synthesized the mineral in a laser-heated diamond anvil cell (Liu and El Goresy 2007). The crystal structure of KA$_2$Si$_3$O$_8$-hollandite was characterized using SEM-EBSD and named liebemannite after the high-pressure geophysicist R. C. Liebemann (Ma et al. 2014).

As mentioned above, NaAlSi$_3$O$_8$-rich plagioclase does not have the single-phase stability field of langunitite (Liu 2006; Zhou et al. 2017) but decomposes into jadeite and SiO$_2$ or calcium ferrite-type NaAlSiO$_4$ and SiO$_2$ assemblages with a lesser amount of langunitite under high pressure. These dissociation products do not occur in the shock veins in ordinary chondrites. Even during the shock metamorphism of large meteorite parent bodies, the pressure duration might not be long enough (less than several seconds) to form stable high-pressure phases of plagioclase due to its sluggish reaction. Langunitite in shocked meteorites would have metastably formed due to the hindered dissociation during shock metamorphism. In some cases, jadeite solely occurs in grains of plagioclase origin in L6 chondrites (Kimura et al. 2000; Ohtani et al. 2004; Ozawa et al. 2009). The occurrence was interpreted as plagioclase that transformed into maskelynite due to shock events and subsequently decomposed into jadeite, coexisting with SiO$_2$-rich amorphous material (Miyahara et al. 2013b).

To understand complex high-pressure transitions of plagioclase in shocked meteorites, static compression experiments were carried out using the Kawai-type multi-anvil apparatus (Kubo et al. 2010) and externally heated diamond anvil cells (Tomioaka et al. 2010); a much longer pressure duration time can be achieved with both devices compared with dynamic (shock) recovery experiments. The results of these experiments indicated caveats (1) the kinetic effect must be considered with respect to the high-pressure phase transition of plagioclase during shock metamorphism to explain the formation process of metastable minerals, and (2) the shock pressures of meteorites based on laboratory shock experiments are potentially overestimated.

Ca-rich feldspar produces another kind of high-pressure phase of aluminosilicate. A mineral with (Ca$_{1-x}$Na$_x$)$_{Al_{2+x}}$Si$_3$O$_{11}$ composition was discovered in some shergottites, such as Zagami and NWA 856, by Raman spectroscopy (Beck et al. 2004; El Goresy et al. 2013). The mineral is intergrown with acicular stishovite grains in melt pockets, which formed by crystallization during the partial melting of labradoritic feldspar at high pressure. The mineral was previously synthesized above 16 GPa in phase equilibrium studies of

Fig. 12. Transmission electron micrograph of the Ca-rich majorite (Maj) and Ca-rich glass (Gla) assemblage produced by the high-pressure breakdown of diopside in the Yamato-75100 (H6) chondrite. See details in Tomioaka and Kimura (2003).

Fig. 13. Phase diagram of NaAlSi$_3$O$_8$ (modified after Ozawa et al. 2014; data from Zhou et al. 2017).

sutinized by Raman spectroscopy and µXRD (Gillet et al. 2000); the grains are actually not glass but have a hollandite structure. Because the NaAlSi$_3$O$_8$-hollandite aggregates have a texture flowing into the surrounding minerals and the melting temperature of plagioclase is lower than that of olivine and pyroxene, possibly solely the plagioclase in the host rock was melted and cooled at high pressure, without the incorporation of other mineral components (Gillet et al. 2000).

The hollandite phases in shocked meteorites were also investigated by TEM; NaAlSi$_3$O$_8$-hollandite and KA$_2$Si$_3$O$_8$-hollandite were found in shock veins in ordinary chondrites (e.g., Tomioaka et al. 2000; Xie and Sharp 2004) and a basaltic shergottite (Langenhorst and Poirier 2000a), respectively (Tables 2 and 3). Both form
High-pressure polymorphs of silica

Dense crystalline silica was first synthesized at 3.5 GPa using a Bridgeman-type high-pressure apparatus by Coes (1953; Fig. 15). Subsequently, natural dense crystalline silica akin to the synthesized one was discovered in sandstone distributed around the Barringer crater and named coesite (Chao et al. 1960). Another crystalline silica phase with rutile-type structure was synthesized at ~7 GPa by Stishov and Popova (1961; Fig. 15). Similar to coesite, a natural analog was discovered in the Barringer crater; it was named stishovite (Chao et al. 1962). Stishovite has been synthesized not only by static high-pressure experiments but also by shock recovery experiments (DeCarli and Milton 1965). Both terrestrial coesite and stishovite were identified in a xenolith (e.g., Smyth and Hatton 1977) in addition to rocks distributed around craters (e.g., Stähle et al. 2008; Chen et al. 2010). At much higher pressure, α-PbO₂-type silica was synthesized in shock recovery experiments of quartz up to 90 GPa (German et al. 1973). Based on TEM observations, Sharp et al. (1999) first reported silica similar to the α-PbO₂ type from Shergotty. Dera et al. (2002) concluded that the silica in Shergotty has an α-PbO₂-type structure based on detailed crystal structure refinements with Rietveld XRD analysis. The mineral was named seifertite after mineralogist F. Seifert (El Gorey et al. 2008). Another poststishovite phase with baddeleyite (ZrO₂)-like structure has been reported in Shergotty (El Gorey et al. 2000).

High-pressure polymorphs of silica have not been found in chondrites, except for Asuka-10164 (EH3), Gujba (CB), and Khatyryka (CV3; Table 2). Silica phases (cristobalite, tridymite, quartz, and silica glass) are common both in EH- and EL-enstatite chondrites (Kimura et al. 2005). Distinct shock veins occur in Asuka-10164 (EH3; Kimura et al. 2017). Raman spectroscopy clearly indicates that coesite occurs in silica grains entrained in shock veins. Kimura et al. (2017) proposed that the parent body of Asuka-10164 was subjected to high-pressure conditions of ~3–10 GPa during impact. In general, carbonaceous chondrites are expected to be less shocked compared with ordinary chondrites. However, some of them show heavily (or moderately) shocked features, which has previously been overlooked (e.g., Ishida et al. 2012; Forman et al. 2016). Gujba (CB) consists mainly of Fe-Ni metallic iron and chondritic fragments. Weisberg and Kimura (2010) identified coesite in addition to wadsleyite and majorite in the chondritic fragment portions and estimated the shock pressure conditions to be at least ~19 GPa. Bindi et al. (2014) and Hollister et al. (2014) reported the existence of coesite and stishovite in
addition to quasicrystals in Khatyryka (CV3). Although the shock degree in Khatyryka is heterogeneous, the portion including coesite and stishovite was subjected to high-pressure conditions above 5 GPa during the impact (Bindi et al. 2014; Hollister et al. 2014).

Many kinds of achondrites (Martian, lunar, HEDs, and iron meteorites) contain high-pressure polymorphs of silica (Table 3; Figs. 16a and 16b). In particular, stishovite occurs in many shergottites (Table 3); a small amount of cristobalite is present in some shergottites. Raman spectroscopy revealed that parts of the silica grains near melt pockets transform into stishovite (e.g., He et al. 2015). As described in the previous section, plagioclase in shergottites dissociates into CAS and stishovite at ~22 GPa and 2000–2200 °C (Akaogi et al. 2010). Stishovite, as a dissociation product of plagioclase, is needle-shaped in habit (Beck et al. 2004; El Goresy et al. 2013). The TEM observations revealed that seifertite also occurs in shergottites, as a replacement of cristobalite (Sharp et al. 1999; El Goresy et al. 2013). Seifertite always shows a unique characteristic in the backscattered electron image, a tweed-like texture, which is one of the diagnostic features for the identification of seifertite (Fig. 16c).

With respect to meteorites other than shergottite, high-pressure polymorphs of silica have been discovered only in basaltic lunar meteorites, although both basaltic and feldspathic breccia lunar meteorites include silica. Silica in and around the shock veins or melt pockets of basaltic lunar meteorites transforms into coesite, stishovite, seifertite, and/or silica glass (Ohtani et al. 2011; Miyahara et al. 2013a; Kayama et al. 2016). Kaneko et al. (2015) discovered stishovite in the regolith breccia Apollo 15299. This was the first time that a high-pressure polymorph was discovered in extraterrestrial rocks from sample return missions. Basaltic (monomict or polymict) eucrites, which are assumed to originate from 4 Vesta in the asteroid belt, contain cristobalite and tridymite fragments. Shock veins were observed in some basaltic eucrites. Cristobalite and tridymite, which occur in and around the shock veins of the basaltic eucrites Bêrêba and NWA 8003, transform into coesite and/or stishovite associated with silica glass (Miyahara et al. 2014; Pang et al. 2016). The Muonionalusta iron meteorite (IVA) shows a deformation texture and is associated with a small amount of silica fragments (Hollstam et al. 2003). Stishovite accompanying silica glass and quartz occurs in one of the silica grains.

The TEM analyses of high-pressure polymorphs of silica are difficult because the polymorphs are very sensitive to electron-beam irradiation. The formation mechanisms of high-pressure polymorphs of silica in shocked meteorites are, therefore, not well understood. In addition, high-pressure syntheses of silica revealed that the phase equilibrium conditions are complex because the products depend on the silica phases of the starting materials and impurities therein (e.g., Lakshman et al. 2007; Kubo et al. 2015). Accordingly, the phase diagram of the high-pressure polymorphs has not been well established. The estimates of shock-pressure conditions using the conventional phase diagram of silica have, therefore, some uncertainties (Fig. 15).

HIGH-PRESSURE POLYMORPHS OF ACCESSORY MINERALS

High-pressure polymorphs of accessory minerals were also found in shocked chondrites. Xie et al. (2002a) reported that mineral fragments of the phosphate mineral merrillite (Ca9NaMg[PO4]2) in the Suizhou chondrite (L6) were entrapped in shock veins and transformed into a phase with a γ-Ba3(PO4)2 structure. This phase is known to be stable in the apatite field >10 GPa (Murayama et al. 1986). The γ-Ca9(PO4)2 mineral was named tuite after the geochemist G. Tu (Xie et al. 2003). Tuite is thought to be a major host of rare earth elements with large ionic radii in the deep mantle.

With respect to double-oxide minerals, high-pressure phases of chromite (FeCr2O4) with CaFe2O4-like and CaTi2O4 structures were discovered in Suizhou. These high-pressure minerals have a lamellar morphology and occur in the host chromite grains (Chen et al. 2003a, 2003b). High-pressure experiments confirmed that CaTi2O4 is stable at pressures above 17–18 GPa and 1300 °C, while CaFe2O4 is stable at pressures above 17–18 GPa and below 1300 °C. However, the CaFe2O4 phase is unquenchable and converts into a modified CaFe2O4 structure upon decompression (Ishii et al. 2014); CaTi2O4-type FeCr2O4 was named xieite after the mineralogist X. Xie (Chen et al. 2008).
Ries crater in Germany is one of the most investigated impact structures with respect to the high-pressure mineralogy. Baddeleyite (ZrO$_2$)-type and scrutinyite (α-PbO$_2$)-type TiO$_2$ were discovered in the heavily shocked gneisses in the Ries crater suevite by microbeam XRD (El Goresy et al. 2001a, 2001b). High-pressure phase equilibria of TiO$_2$ have not yet been established; however, the formation pressure of these minerals was deduced to be \( \lesssim 22 \) GPa based on their coexisting high-pressure minerals (El Goresy et al. 2010). The baddeleyite-type TiO$_2$ was named akaogite after the experimental mineral physicist M. Akaogi (El Goresy et al. 2010).

The high-pressure phase of zircon (ZrSiO$_4$) is also a key to understanding shock metamorphism in impact craters. The scheelite (CaWO$_4$)-type ZrSiO$_4$ was discovered in the upper Eocene impact ejecta layer in marine sediments by XRD (Glass and Liu 2001) and named reidite after the mineralogist A. F. Reid who first synthesized this phase (Glass et al. 2002). Reidite was subsequently found in impact craters including the Chesapeake Bay (Malone et al. 2010), Xiuyan (Chen et al. 2013), Rock Elm (Cavosie et al. 2015), and Ries (Erickson et al. 2017) craters. Shock recovery experiments of zircon indicate that the transition to reidite starts at \( \sim 30 \) GPa and is completed at \( \sim 53 \) GPa (Kusaba et al. 1985). In contrast, static high-pressure experiments demonstrated that the stability field of the phase is in the pressure range of \( \sim 8 \)–25 GPa (Ono et al. 2004; Tange and Takahashi 2004). Because the kinetic effect of the high-pressure transformation on the transformation of zircon is poorly understood, the formation pressure of reidite is still not robust.

**SUMMARY AND PROSPECTS OF HIGH-PRESSURE MINERALOGY IN NATURALLY SHOCKED ROCKS**

Based on the advances in analytical techniques, including electron microscopies, X-ray diffractometers, and micro-Raman spectroscopy, many of the high-pressure minerals that previously were only known as synthetic minerals have been discovered in shocked meteorites. Their formation processes have been studied extensively in the past two decades. Natural high-pressure minerals found in terrestrial impact craters and other high-pressure minerals in shocked meteorites are not described sufficiently in this article because of space limitations; however, more information can be found on the following website: High-pressure Mineral Database, https://sites.google.com/site/highpminal.

High-pressure minerals have been considered to mostly occur in limited types of meteorites especially in

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**Fig. 16. Transmission electron micrographs of (a) coesite (Coe) in the eucrite Béréba (see details in Miyahara et al. 2014), (b) stishovite (Sti) in Apollo 15299 (Kaneko et al. 2015), and (c) seifertite (Sei) in the lunar meteorite NWA 4734 (Miyahara et al. 2013a). All are associated with a high-density silica glass. Qtz: quartz.**
ordinary L chondrites and shergottites. However, current investigations reveal that high-pressure minerals more widely occur in various types of shock-metamorphosed materials (carbonaceous chondrites, lunar meteorites, iron meteorites, and impact crater rocks) than as previously thought (Tables 2 and 3). Further detailed investigations will provide more statistical occurrences of high-pressure minerals in all types of shocked minerals in meteorites and impact crater. Moreover, new high-pressure minerals might be found in meteorites such as calcium-aluminum-rich inclusions in carbonaceous chondrites, which have not been well investigated with respect to shock metamorphism. Drilling core samples from impact crater (e.g., Morgan et al. 2016) might be also promising samples for search for high-pressure minerals.

The comparison of the above-mentioned information on natural high-pressure minerals with experimentally determined phase equilibria and transformation kinetics of meteoric and terrestrial minerals will lead to a more robust understanding of the pressure-temperature history in naturally shocked materials.

Because they are analogs of deep Earth’s minerals, meteoritic high-pressure minerals also draw special attention from mineral physicists. In addition to theoretical and experimental studies, the textural, crystallographic, and chemical characteristics of high-pressure minerals provide profound information about high-pressure transformations, formation kinetics of metastable phases, and deformation microtextures under Earth’s deep mantle conditions.

For instance, dislocations in ringwoodite (Madon and Poirier 1980) and stacking faults in wadsleyite and ringwoodite (Madon and Poirier 1983; Price 1983) were first characterized by TEM observations of meteorite samples. These defect structures are essential parameters to discuss the rheology and transformation mechanisms of the olivine polymorphs in the upper mantle. Another example is a new transformation model of pyroxene under high pressure proposed based on the crystallographic analysis of a shocked meteorite. The enstatite-akimotoite intergrowth in the Tenham chondrite, as described in the previous section, suggests a “diffusionless” shear transformation mechanism from enstatite to akimotoite. This mechanism potentially plays an important role in the enhancement of transformation kinetics of low-Ca pyroxene in oceanic plates subducting into the lower mantle (Tomiyama 2007).

Previously, in almost all cases, high-pressure minerals have been synthesized prior to the discovery of natural samples. However, some high-pressure minerals are yet to be synthesized in the laboratory. Such high-pressure minerals stimulate experimental studies of the deep Earth’s mineralogy.

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