Shock-induced P-T conditions and formation mechanism of akimotoite-pyroxene glass assemblages in the Grove Mountains (GRV) 052082 (L6) meteorite

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Abstract: Akimotoite ((Mg,Fe)SiO3-ilmenite) was encountered in shock-induced melt veins of Grove Mountains (GRV) 052082, a highly equilibrated low iron ordinary chondritic meteorite (L6). Coexistence of ringwoodite, majorite and majorite-pyrope solid solution indicates the shock pressure at 18-23 GPa and
temperature of 2000-2300 °C during the natural dynamic event. Most low-Ca pyroxene clasts entrained in the melt veins have been partially or entirely transformed into akimotoite-pyroxene glass assemblages, which contain micron-sized areas with various brightness in the back-scattered electron images, different from the chemically homogeneous grains in the host-rock (Fs_{20.5-21.3}). The transmission electron microscopy study of a focused ion beam (FIB) slice from the heterogeneous areas shows that the assemblages are composed of FeO-depleted and heterogeneous akimotoite (Fs_{6-19}) crystals (100 nm up to 400 nm in size) scattered in FeO-enriched and relatively homogeneous pyroxene glass (Fs_{31-39}). All analyses of the akimotoite-pyroxene glass assemblages plot on a fractionation line in FeO-MgO diagram, with the host-rock pyroxene at the middle between the compositions of FeO-enriched akimotoite and the FeO-depleted pyroxene glass. These observations are different from previous reports of almost identical compositions of akimotoite, bridgmanite ((Mg,Fe)SiO_{3-perovskite}) or pyroxene glass to the host rock pyroxene (Chen et al., 2004; Ferroir et al., 2008; Ohtani et al., 2004; Tomioka and Fujino, 1997), which is consistent with solid-state transformation from pyroxene to akimotoite and preexisting bridgmanite that could be vitrified. The observed fractionation trend and the granular shapes of akimotoite suggest crystallization from liquid produced by shock melting of the host-rock pyroxene, and the pyroxene glass matrix was probably quenched from the residual melt. However, this interpretation is inconsistent with the static experiments that expect crystallization of majorite ((Mg,Fe)SiO_{3-garnet}), instead of akimotoite, from pyroxene liquid (Sawamoto, 1987). Our discovery raises
the issue on formation mechanisms of the high pressure polymorphs of pyroxene and places additional constraints on the post-shock high-pressure and -temperature conditions of asteroids.

**Keywords:** Akimotoite, Pyroxene glass, High pressure polymorphs, Meteorite, Shock, Impact

**Introduction**

Orthopyroxenes [(Mg,Fe)$_2$SiO$_6$] are among the most important components of stony meteorites and the upper mantle of the Earth. At high-pressure and -temperature conditions, pyroxene transforms to high-pressure polymorphs including majorite ((Mg,Fe)SiO$_3$-garnet), akimotoite ((Mg,Fe)SiO$_3$-ilmenite) and bridgmanite ((Mg,Fe)SiO$_3$-perovskite) (Tschauner et al, 2014), which are considered to be among the major constituents of the Earth’s deep mantle (e.g., Liu, 1976; Ohtani et al., 1991; Presnall, 1995). Natural occurrences of these high pressure phases have been mostly discovered in and around shock-induced melt veins of chondrites (Chen et al., 1996; Miyaharaa et al., 2011; Tschauner et al, 2014; Sharp et al., 1997; Tomioka and Fujino, 1997). They provide insight into equilibrium pressure–temperature conditions and the time scale of the dynamic events, and may mimic the phase transformations occurring in the deep Earth mantle and subducted lithosphere (Kerschhofer et al., 1998; Liu et al., 1998; Mosenfelder et al., 2001).
The formation of high-pressure polymorphs of pyroxene in the shock-induced melt veins occurs in various settings and probably involves different mechanisms. The fine-grained crystals in the matrix of the shock melt veins usually result from the crystallization from chondritic melts under high-pressure and high-temperature conditions (Chen et al., 1996; Sharp et al., 1997; Xie et al., 2006b). Large fragments, which were entrained from host rock into the melts, have been generally considered as being in solid-state transformed into polycrystalline assemblages (Ohtani et al., 2004; Tomioka and Fujino, 1997; Xie and Sharp, 2007). In the latter case, the chemical compositions of the high-pressure polymorphs are almost identical to those of the parental pyroxenes in host rock.

In recent years, chemically fractionated ringwoodite-wadsleyite assemblages have been discovered from several highly equilibrated L chondrites. These assemblages were considered to form by fractional crystallization of olivine liquid under high pressure (El Goresy, 2006; Miyahara et al., 2009; Miyahara et al., 2008a). These discoveries address issues on formation processes of high-pressure minerals in heavily shocked meteorites. Is the crystallization of high-pressure polymorphs from mono-mineral melts a unique mechanism for olivine, or a common phenomenon which also occurs in other mineral systems? On the other hand, the high-pressure polymorphs that were quenched from silicate melts provide natural samples to study melting relations of silicate systems under high-pressure and temperature conditions, which is important for understanding the early differentiation processes of the Earth and other terrestrial planets (e.g., Hayashi et al., 1979; Kaula, ...
In this study, we investigated the shock-induced melt veins in the highly equilibrated ordinary chondrite Grove Mountains (GRV) 052082 (L6). Chemically fractionated olivine-ringwoodite and akimotoite-pyroxene glass assemblages (referred to as Aki-Px Glass assemblages) have been encountered. Here we report the textures and compositional features of the Aki-Px Glass assemblages, and discuss their formation mechanisms. Preliminary results were reported by Feng et al (2011a).

Sample and experiments

A polished thin section was prepared from GRV 052082, a 20.4g stone partly covered with fusion crust and recovered from Grove Mountains in Antarctica by the 22nd Chinese Antarctic Research Expedition. GRV 05082 has been classified as a highly equilibrated low iron ordinary chondritic meteorite (L6), with very homogeneous compositions of olivine (Fa24.1) and low-Ca pyroxene (Fs20.7) in the host rock (Connolly et al., 2008). It was heavily shocked, with a shock grade of S4 (Connolly et al., 2008). The sample was firstly investigated and documented with an optical microscope, and a scanning electron microscope (SEM) LEO 1450VP equipped with a back-scattered electron (BSE) detector and an energy dispersive spectrometer (EDS). The high-pressure polymorphs in the shock-induced veins were identified by Laser-Raman spectroscopy Renishaw RM-2000 at the Institute of Geology and Geophysics, Chinese Academy of Sciences, and also a JASCO NRS-2000 at the Institute of Mineralogy, Petrology, and Economic Geology, Tohoku
University. Both of the Raman spectrometers used Ar ion lasers producing 514.5 nm lines as the excitation sources. The laser with power of 20-40 mW was focused to ~1-2 µm on the sample and the acquisition time was 30-90s.

The chemical compositions of silicate minerals were determined by the wave-length dispersive technique by JXA 8100 electron microprobe (EPMA) at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The analyses were operated at 15 kV accelerating voltage and 20 nA beam current. The electron beam was focused to about 1 µm in diameter. Diopside (Ca and Si), jadeite (Na), almandine garnet (Fe and Al), orthoclase (K), rhodonite (Mn), forsterite (Mg), synthetic escolaite (Cr), and rutile (Ti) were used as EPMA standards. The standard ZAF matrix correction program was applied to conduct matrix corrections and obtain the chemical compositions. The detection limits are (1 SD): 0.01 wt% for K₂O, Na₂O, and MgO, 0.02 wt% for SiO₂, Cr₂O₃, Al₂O₃ and CaO, 0.03 wt% for TiO₂, FeO and MnO.

The distribution and textures of high-pressure mineral assemblages in the shock-induced veins were then carefully determined and documented by a field emission gun scanning electron microscope (FEG-SEM) JEOL JSM-71010 at an accelerating voltage of 15 kV. An ultra-thin TEM foil from selected target area was surgically cut by Focused Ion Beam system (FIB) JEOL JEM-9320, and extracted by a micromanipulator installed on an optical microscope. The detailed procedure was described by Miyahara et al (2008b). A transmission electron microscope (TEM) JEOL JEM-2010 operating at 200 kV was used for conventional TEM observation.
and selected area electron diffraction (SAED). We also used a scanning TEM (STEM), JEOL JEM-3000F field emission TEM operating at 300 kV with a JEOL energy dispersive spectrometer (EDS) detector system, for elemental mapping and quantitative analysis. The chemical compositions of individual grains were obtained by EDS under scanning mode at the STEM. The compositions were corrected with Cliff-Lorimer method (Cliff and Lorimer, 1975) using experimentally determined κ-factors (San Carlos olivine). The detection limits are about 0.1 wt% for main elements. The FEG-SEM, FIB, TEM and STEM analyses were carried out at the Institute of Mineralogy, Petrology, and Economic Geology, Tohoku University in Sendai in Japan.

**Results**

Silicates in the host rock of GRV 052082 are homogeneous in chemical compositions. The major mineral constituents include olivine (Fa_{23.2-24.4}), low-Ca pyroxene (Fs_{20.5-21.3}), albitic plagioclase, troilite and metallic Fe-Ni. The EPMA analyses of pyroxene grains in the host rock are listed in Table 1. Shock-induced melt veins are encountered as a network with width up to 2 mm cross cutting the whole thin section (Fig. 1).

Figure 1. Polished thin section of GRV 052082 under transmitted light.

The shock-induced melt veins consist of fine-grained matrix and coarse-grained
silicate fragments. The fine-grained matrix mainly consists of granular or dendritic
majorite-pyrope solid solution with grain-size of 1-3 µm, whose interstices are filled
with metallic Fe-Ni and troilite blebs (Fig. 2a). Feldspathic clasts depict smooth
surfaces on BSE images (Fig. 2a), with some of them converted to maskelynite, and
others to lingunite and minor jadeite as identified by Raman spectra (Fig. 3d, e).
Original olivine fragments entrained in the shock-melt veins have been transformed
into olivine-ringwoodite assemblages, depicting dendrite-like olivine cores (dark)
which are depleted in FeO and surrounded by FeO-rich ringwoodite rims (light grey)
(Fig. 2b). No wadsleyite was observed in these ringwoodite-olivine assemblages. The
textures and chemical fractionation of these ringwoodite-olivine assemblages are also
similar to those observed in the heavily shocked GRV 052049 (Feng et al., 2011b),
but different from coarse-grained ringwoodite aggregates discovered in other shocked
meteorites in previous studies (e.g., Putnis and Price, 1979). Detailed investigation is
needed to clarify the formation mechanism of these highly fractionated
ringwoodite-olivine assemblages.

Original pyroxene mineral fragments and those in chondrule fragments entrained
in the shock-melt veins have been replaced by assemblages of akimotoite crystals and
glassy materials (Fig. 2a). High-magnification BSE images reveal a heterogeneous
distribution of submicron-sized dark areas among light grey amorphous regions, but
more abundant along the rims of the fragments (Fig. 2b and 2d). The boundaries of
these clasts are recognizable, although they are blurred by the fine-grained akimotoite
in contact with the matrix. It is also noticed that Fe-Ni metal spots disperse within
both the dark fine-grained areas and the grey glass regions. These metal spots are elongated, and orientated within the dark areas (Fig. 2d).

Figure 2. BSE images of pyroxene clasts in the shock-induced vein from GRV 052082.

The Raman spectra of the grey matrix of these pyroxene clasts generally display two broad bands at ~680 and 990 cm\(^{-1}\), which are typical for MgO-SiO\(_2\) glasses (Chen et al., 2004b). However, the Raman spectra obtained from the fine-grained dark areas contain a sharp peak of 804 cm\(^{-1}\) (Fig. 3a), the characteristic band of akimotoite. There are few remnant clasts in the enstatite structure (Fig. 3b), or are transformed into poorly-crystallized majorite, as the Raman spectrum shows a low signal/noise ratio (Fig. 3c).

Figure 3. Raman spectra of mineral phases from pyroxene clasts in GRV 052082.

The variation of brightness between pyroxene glass and akimotoite reflects mainly compositional differences. Based on microprobe analyses (Table 1), both phases have low-Ca pyroxene compositions. It is demonstrated that the akimotoite regions are FeO-depleted (Fs\(_{14.0-16.6}\)) whereas the pyroxene glassy areas are FeO-enriched (Fs\(_{19.6-23.0}\)). By measuring the dark and light grey areas in the Aki-Px Glass assemblage in Fig. 2a, the volume fractions of akimotoite and pyroxene glass are
estimated ~62 vol% and 38 vol%, respectively.

Table 1. Compositions of akimotoite region and pyroxene glass by EPMA.

A FIB-TEM slice was made from the Aki-Px Glass assemblage outlined in Fig. 2a. The bright-field images show granular akimotoite crystals, with sizes ranging from tens to four hundred nanometers (Fig 4). Selected-area electron diffraction revealed different orientations of these akimotoite grains, suggestive of random presence in the pyroxene glass. Furthermore, the akimotoite grains clearly distinguish from pyroxene glass matrix in the Mg and Fe elemental mapping images (Fig. 5). No gradual zoning of the major components were observed along the grain boundaries, indicative of no diffusion. The compositional gap between akimotoite grains (Fs6-19) and pyroxene glass (Fs31-39) is confirmed by STEM-EDS measurements (Table 2). The Fs-contents of akimotoite grains obtained by STEM-EDS are comparable with the microprobe analyses, but with a significantly wider range (Fs6-19) compared with the latter (Fs14.0-16.6), which could be due to much smaller excited volumes of the heterogeneous grains by the STEM probe. We also noticed that the Fs-contents of the pyroxene glass obtained by STEM-EDS are significantly higher than those by EPMA, probably due to overlapping tiny akimotoite grains by EPMA.

Figure 4. TEM images of FIB slice.
Discussion

Shock-induced P-T conditions of the melt veins

The P-T condition during the shock event can be constrained by the petrographic textures and high pressure mineral inventory in the shock-induced veins of GRV 052082, which are similar to those reported in other heavily shocked ordinary chondrites, e.g. Sixiangkou, Tenham, and Yamaoto 791384 (Chen et al., 1996; Miyahara et al., 2010; Price et al., 1979). Based on the results of high-pressure melting experiments of Allende meteorite and KLB-1 peridotite (Agee et al., 1995), the coexistence of ringwoodite, majorite and majorite-pyrope solid solution indicates the pressure of 18-23 GPa and temperature of 2000-2300 °C, similar to other heavily shocked L6 chondrites. However, if the pyroxene glass was vitrified bridgmanite as suggested in previous reports (Chen et al., 2004b; Tomioka and Fujino, 1997), the peak pressure in the shock veins would have exceed 23 GPa.

Formation of chemically fractionated Akimotoite

This is the first discovery of significant chemical fractionation of akimotoite in
silicate fragments relative to the precursor low-Ca pyroxene, which was probably
formed via a new mechanism instead of solid-state transformation. Natural akimotoite
grains have been reported in and/or adjacent to shock-induced melt veins of heavily
shocked chondrites. They occur as: (1) fine-grained euhedral crystals embedded in the
matrix of shock-induced melt veins, which were generally enriched in CaO, Al_2O_3
and Na_2O because of melted plagioclase. The akimotoite grains have much lower fe#
values (atomic ratio of Fe/Fe+Mg) (0.055) than the host rock low-Ca pyroxene
(0.22), and they were considered to have crystallized from chondritic melts (Sharp et
al., 1997); (2) polycrystalline aggregates in and/or adjacent to the melt veins, which
have nearly the same fe# values of low-Ca pyroxene in the host rocks (e.g. 0.21-0.27
vs 0.22, Ferroir et al., 2008; 0.21 vs 0.22, Tomioka and Fujino, 1997). It suggests no
significant diffusion of Fe and/or Mg during the phase transformation. These
polycrystalline grains of akimotoite have been so far regarded as isochemical grain
boundary or intracrystalline growth of akimotoite at the expense of parental enstatites
at subsolidus conditions (Ferroir et al., 2008; Miyahara et al., 2010; Ozawa et al.,
2010; Ozawa et al., 2009; Tomioka and Fujino, 1997, 1999; Zhang et al., 2006).

The Aki-Px Glass assemblages in GRV 052082 show a similar occurrence as the
polycrystalline grains in shock-melt veins of other meteorites, but these akimotoite
crystals in GRV 052082 have significantly different chemical compositions from the
host pyroxene (Fig. 6). Compared with the homogeneous pyroxene grains in the host
rock (FeO: 13.5 ± 0.3 wt%; MgO: 28.6 ± 0.4 wt%), the akimotoite grains are highly
heterogeneous in compositions: depleted in FeO (4.2 - 11.5 wt%) and enriched in
MgO (29.4 - 35.0 wt%). In contrast, the pyroxene glass became relatively FeO-rich (18.8 - 25.6 wt%) and MgO-poor (21.2 - 24.7 wt%). The compositional gaps among the three phases are obvious, and they cannot be explained by solid-state transformation as proposed in previous studies. Alternatively, the observed compositional fractionation between akimotoite and pyroxene glass (Fig. 6) is difficult to be explained by Fe-Mg partition between akimotoite and preexisting bridgmanite at various temperatures. Although the MgO-enrichment of akimotoite relative to bridgmanite is consistent with the phase diagram by Mao et al. (1982), Ito and Yamada (1982) reported different results. Furthermore, the solid-state diffusion of Fe-Mg between akimotoite and preexisting bridgmanite would have produced a wide compositional range in the pyroxene glass (vitrified preexisting bridgmanite), which is comparable to that of the akimotoite grains.

On the other hand, the heterogeneous and FeO-depleted compositions of akimotoite are readily explained by fractional crystallization of akimotoite from melts. With the partition coefficient of FeO between akimotoite and pyroxene melts (0.20-0.44, see the subsection of Partition Coefficient), the FeO-poor and heterogeneous compositions of akimotoite can be modeled by fractional crystallization from a melt that has the composition of low-Ca pyroxene in the host rock (Fig. 7, see the subsection of Partition Coefficient).

The morphology of akimotoite in GRV 052082 supplies additional evidence for its formation, which also suggests crystallization from melt instead of solid-state transformation that usually leads to production of orientated lamellae in the host.
mineral (Beck et al., 2005; Chen et al., 2004a). The random distribution of akimotoite
grains and the rounded morphology of the clumped grains, confirmed by the
selected-area electron diffraction, are consistent with the homogeneous nucleation
mechanism during crystallization of a silicate melt (Sharp et al., 1997). The elongated
Fe-Ni metal grains in the Aki-Px Glass assemblage (Fig. 2d) are consistent with being
molten due to the high temperature. Orientation of the akimotoite and Fe-Ni metal
crystals suggests plastic deformation by local stress.

Figure 6. FeO- and MgO- contents of akimotoite, pyroxene in host rock, and pyroxene
glass.

The outlines of the Aki-Px Glass assemblages can be clearly recognized in the
melt vein matrix. Different from the akimotoite and bridgmanite both crystallized
from chondritic melts (Sharp et al., 1997; Xie and Sharp, 2004; Xie et al., 2006b), the
whole Aki-Px Glass assemblages show a stoichiometric composition of low-Ca
pyroxene and no coexisting ringwoodite was discovered. According to the EPMA
results, the concentrations of minor elements Al and Ca in these assemblages are also
close to those of low-Ca pyroxene in the host rock (Table 1). The presence of minor
Na₂O in the akimotoite grains (Table 1) is consistent with crystallization from
Na-bearing melts, and Na was likely diffused from the surrounding chondritic melt.
Therefore, the Aki-Px Glass assemblages are considered to originate from preexisting
low-Ca pyroxene grains which were little contaminated by the surrounding materials.
Based on the petrographic and compositional features, we propose that the akimotoite in these assemblages were formed by fractional crystallization of nearly pure pyroxene melts, which were produced via melting preexisting low-Ca pyroxene clasts by the shock event. However, we have also noticed that the phase diagram based on static high pressure experiments of pyroxene expects majorite, instead of akimotoite, to crystallize directly from the pyroxene liquid (Sawamoto, 1987). This discrepancy raises the issue of formation mechanisms of high pressure polymorphs of pyroxene.

**Origin of Px Glass and crystallization process of Aki-Px Glass assemblages**

Another key issue related with formation process of the Aki-Px Glass assemblages is the origin of the pyroxene glass. (Mg, Fe)SiO$_3$-glass has been frequently discovered in melt veins of many chondrites, coexisting with high pressure polymorphs of pyroxene, i.e. majorite and/or akimotoite (Chen et al., 2004b; Ferroir et al., 2008; Miyahara et al., 2010). The (Mg, Fe)SiO$_3$-glass in these petrographic settings has nearly identical chemical compositions of low-Ca pyroxene in the host meteorites, and it was considered to be vitrified bridgmanite that formed by solid-state transformation at high pressures $>23$ GPa. The amorphization of bridgmanite is likely due to irradiation of laser or electron beam during measurement of this phase, as suggested by recent discovery of bridgmanite in similar assemblages (Tschauner et al., 2014). The bridgmanite grains have nearly identical compositions of the coexisting
akimotoite, and both are similar to that of the low-Ca pyroxene in the host rock (Tschauner et al., 2014). The latter study confirms the solid-state transformation of bridgmanite. Although the Aki-Px Glass assemblages in GRV 052082 show a texture similar to that of coexisting akimotoite and bridgmanite (or vitrified bridgmanite) reported in other meteorites, the akimotoite and pyroxene glass in the Aki-Px Glass assemblages are highly fractionated in compositions, different from the previous results mentioned above. Therefore, these Aki-Px Glass assemblages in GRV 052082 should not have been formed by the same mechanism of solid-state transformation.

Alternatively, the pyroxene glass in the Aki-Px Glass assemblages could be vitrified bridgmanite that crystallized from silicate melts. Amorphous (Mg,Fe)SiO$_3$-grains coexisting with akimotoite and ringwoodite were reported in shock-induced melt vein matrix, and they were considered as vitrified bridgmanite crystallized from melts (Sharp et al., 1997). The amorphous (Mg,Fe)SiO$_3$-grains are idiomorphic, surrounded by crystals of akimotoite and/or ringwoodite (Sharp et al., 1997; Xie et al., 2006b). This is obviously different from the granular grains of akimotoite embedded in the pyroxene glass matrix in GRV 052082 (Figs. 2 and 4), arguing for their distinct forming mechanisms. Furthermore, experimentally determined high-pressure and -temperature phase diagrams also forsee bridgmanite crystallization prior to akimotoite during pressure release (e.g., Hirose et al., 2001). Hence, the phase diagrams argue against the possibility that the pyroxene glass was vitrified from preexisting bridgmanite. Furthermore, FeO is significantly enriched in the pyroxene glass (18.8-25.6 wt%) compared with the pyroxene in the host rock
(13.5±0.3 wt%). According to the analyses of bridgmanite in fine-grained melt veins in shocked chondrites (Sharp et al., 1997; Xie et al., 2006b) and that recovered from the high-pressure and -temperature experiments (Asahara et al., 2004; Corgne et al., 2005; Hirose et al., 2004; Liebske et al., 2005; McFarlane et al., 1994; Tange et al., 2009; Trønnes and Frost, 2002), the partition coefficients of FeO between bridgmanite and chondritic/silicate melts are less than 1. Hence, bridgmanite first crystallized from the chondritic/silicate melts would be FeO-depleted, different from the significant FeO-enrichment of the pyroxene glass.

Another formation scenario of the pyroxene glass is that it was quenched from the residual melts after fractional crystallization of FeO-depleted akimotoite, which had become FeO-enriched as precipitating of the latter. This scenario is consistent with all observations, including the occurrence of the granular akimotoite crystals in the pyroxene glass, the FeO-depletion of the akimotoite and the FeO-enrichment of the pyroxene glass. These Aki-Px Glass assemblages can be elucidated as following: The original pyroxene fragments were selectively molten during the peak shock pulse (18-23 GPa) around 2300 °C, because it contains 20 mol% of FeSiO₃ that lowers its melting temperature comparing with pure MgSiO₃-pyroxene (Fei and Bertka, 1999; Huebner and Turnock, 1980; Presnall, 1995). Akimotoite with low FeO-contents crystallized from the pyroxene melts as the temperature decreased rapidly to the akimotoite stability field, i.e. lower than 2000 °C at ~20 GPa (Gasparik, 1990; Presnall et al., 1995; Wentzcovitch et al., 2004). With crystallization of FeO-poor akimotoite, the residual melt became enriched in FeO, which finally was quenched to
The heterogeneity of pyroxene glass in the same assemblages suggests that the quenching was very fast due to heat waste.

Normally, shock-induced melt veins and pockets in meteorites are fine-grained mixtures of melted regions and have compositions close to the bulk meteorites. As discussed above, the Aki-Px Glass assemblages likely crystallized from nearly pure pyroxene melts. The presence of pyroxene melts was probably due to large sizes of the precursor pyroxene fragments, which could help the melts to preserve their original compositions without mixing surrounding material. In addition, crystallization of akimotoite first along the boundaries of the pyroxene melts formed “wall” of the assemblages, further protecting from mixing the surrounding material. Similar features have been observed in ringwoodite-olivine assemblages in the shocked Grove Mountains ordinary chondrites (Feng et al., 2007 and 2011) and in the ringwoodite-wadsleyite assemblages reported by Miyahara et al. (2009). In these assemblages, ringwoodite was proposed to crystallize from pure olivine melts.

**Partition coefficient of FeO between Akimotoite and Pyroxene melt**

According to the formation process outlined above, the chemical compositions of akimotoite grains are constrained by the FeO partition coefficient between akimotoite and pyroxene melt. Because no melting experiment of akimotoite has been conducted so far, the partition coefficient of divalent cations between akimotoite and pyroxene melt need to be experimentally determined. However, the small and euhedral grains of akimotoite in shock-induced melt veins were previously proposed to crystallize from
melts with chondritic compositions (Sharp et al., 1997; Xie and Sharp, 2004). We tested the possibility of obtaining the partition coefficient of the divalent cations into akimotoite using the obtained data of the bulk composition of an L- chondritic melt (Chen et al., 1996) and the chemical compositions of akimotoite embedded in the melt vein matrix (Sharp et al., 1997; Xie and Sharp, 2004). We calculated the partition coefficients (K) of FeO between akimotoite and chondritic melt as: 

\[ K_{\text{Aki-melt}} = \frac{M_{\text{Aki}}}{M_{\text{melt}}} \]

where M is FeO wt%. The obtained \( K_{\text{Aki-Melt}} \) is in the range of 0.20 - 0.44.

According to the fractional crystallization process of akimotoite from pyroxene melt in GRV 052082, we calculated the partition coefficient of FeO between akimotoite and pyroxene melt with the following two methods. Assuming that akimotoite of lowest Fs value was crystallized first from the pyroxene melt, \( K_1 \) can be defined as: 

\[ K_1 = \frac{M_{\text{Aki of lowest Fs value}}}{M_{\text{pyroxene in host rock}}} \]

In the second method, the akimotoite and the pyroxene glass of highest Fs value can be considered to have formed at the end of crystallization sequence, therefore we calculated \( K_2 \) by:

\[ K_2 = \frac{M_{\text{Aki of highest Fs value}}}{M_{\text{px glass of highest Fs value}}} \]

As a result, \( K_1 \) is 0.31; \( K_2 \) is 0.44, respectively. Both of them are in the same range as that of akimotoite in melt vein matrix of L chondrites.

Based on the Rayleigh Law, the ratio of element concentration in the residual melt over the initial concentration in the melt can be expressed as:

\[ C_L = C_0 F^{(k-1)} \]  \( (i) \)

where \( C_L \) = concentration of the element in the residual melt, \( C_0 \) = initial concentration of the element in the melt, \( F \) = fraction of the melt that remains, and \( K \)
= bulk partition coefficient for the crystallizing solids. Using the determined $K_1$ and $K_2$ values of FeO, with the chemical composition of pyroxene in host rock, we can model the compositional path of akimotoite crystallizing from pyroxene melt under high pressure and temperature conditions in GRV 052082. The curves of FeO contents in akimotoite and residue melt are shown in Figure 7. It is noticed that the measured values for akimotoite are consistent with the predicted trend while values obtained for the pyroxene glass are close to that of the residual melt. The upper limits of FeO in both akimotoite and pyroxene glass intersect the $K_2$ curves at the same points (black arrows on Fig. 7), which represents that based on $K_2$, the FeO-enriched akimotoite and pyroxene glass formed at the same stage of akimotoite crystallization when ~30% melt was left as residual. The residual melt was probably quenched fast, without more FeO-enriched akimotoite crystallized. Although we ignored the temperature and pressure variation during the crystallization, the simplified modeling results are basically consistent with our observations. The predicted abundances of akimotoite (~70%) and pyroxene glass (~30%) are also close to the measurements, 62 vol% akimotoite and 38 vol% pyroxene glass.

Figure 7: Variation of FeO concentrations during fractional crystallization of akimotoite from the pyroxene melt

Melting of silicates and crystallization of high-pressure minerals

Fractional crystallization of ringwoodite-wadsleyite assemblages from olivine
melt has been reported in heavily shocked L6-chondrites (Miyahara et al., 2009; Miyahara et al., 2008a). Our study also shows that melting of a single silicate mineral and subsequent fractional crystallization of high-pressure polymorphs are not restricted to olivine-material minerals, but also take place in other constitutes of chondrites. Melting of enstatite under high pressures (~2400 °C at 18 GPa) (Ohtani and Kumazawa, 1981; Presnall and Gasparik, 1990) slightly exceeds the estimated shock-induced temperature of the melt vein (18-23 GPa, 2000-2300 °C). But with the increase of FeO content, the melting temperature of pyroxene decreases (Huebner and Turnock, 1980), which could lead to the formation of (Mg, Fe)SiO$_3$-melt from parental low-Ca pyroxene grains enclosed in the shock-induced melt veins.

Akimotoite has been considered as a high-pressure, low-temperature mineral, since it is stable under pressures of >20 GPa and temperatures of <1800 °C (Fei and Bertka, 1999; Sawamoto, 1987). It was determined as a subsolidus phase and is not predicted to crystallize from chondritic or mono-pyroxene melts based on high pressure experiments (Sawamoto, 1987; Agee et al., 1995; Gasparik, 1992; Zhang and Herzberg, 1994). Therefore, it was suggested that akimotoite discovered in the matrix of shock-induced melt veins crystallized metastably from a supercooled melt during fast quenching (Sharp et al., 1997; Xie and Sharp, 2004; Xie et al., 2006a; Xie et al., 2006b), which is supportive of our model. Crystallization and preservation of akimotoite indicates that the temperature decreased fast; in the meantime, the duration of high pressure (~20 GPa) in the shock event on asteroid parent body was long enough (Beck et al., 2005) to allow the growth of high pressure minerals up to
hundreds of nanometers. Another scenario is that akimotoite might be in solid-state transformed from preexisting majorite that first crystallized from the pyroxene melt.

**Implications**

Chemically fractionated akimotoite-pyroxene glass assemblages were discovered in shock-induced melt veins in the L6 chondrite GRV 052082, associated with ringwoodite-olivine assemblages that suggested a pressure of 18-23 GPa and a temperature of 2000-2300 °C produced by a shock event. Detailed study of these assemblages suggest that the akimotoite grains crystallized from mono-pyroxene melt and the pyroxene glass was quenched from the residual melt. However, crystallization of akimotoite directly from liquid is inconsistent with the phase diagram of pyroxene (Sawamoto, 1987). This discrepancy may be explained by crystallization of supercooled melts or solid-state transformation of preexisting majorite.

This work suggests a new mechanism for the formation of akimotoite besides the solid-state transformation and crystallization from chondritic melts reported in previous studies. The significantly fractionated akimotoite-pyroxene glass assemblages provide with natural samples for elemental partition between akimotoite and pyroxene glass, and the results will shed light on the high-pressure experiments of the Earth’s and planetary mantle. Furthermore, the significant chemical fractionation between akimotoite and residual melt will constrain the P-T-t track during asteroid impact events, if the partition and diffusion coefficients will be determined.
Acknowledgements:

The meteorite sample was supplied by the Polar Research Institute of China. Our study was supported by the Natural Science Foundation of China (41430105, 41273077, 41203048, 41521062). L. Feng was also financially supported by Tohoku University Global COE program “Global Education and Research Center for Earth and Planetary Dynamics” and the Max-Planck Society Foundation. We would like to thank M. Kimura and other four anonymous reviewers and the Associate Editors Dr. Sergio Speziale and Dr. Liu for their useful comments that led to significant improvement of this paper.

Reference


United States of America 101, 15033-15037.


Tschauner O., Ma C., Beckett J. R., Prescher C., Prakapenka V. B., and Rossman G R. (2014) Discovery of bridgmanite, the most abundant mineral in Earth, in a


Table 1. Compositions of akimotoite region and pyroxene glass by EPMA, in comparison with pyroxene grains in host rock, in wt%.

<table>
<thead>
<tr>
<th></th>
<th>Akimotoite</th>
<th>Pyroxene glass</th>
<th>Pyroxene in host</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>n=8</td>
<td>n.d.</td>
<td>SD</td>
</tr>
<tr>
<td>SiO₂</td>
<td>57.4</td>
<td>56.4</td>
<td>56.1</td>
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<tr>
<td>TiO₂</td>
<td>0.18</td>
<td>0.16</td>
<td>0.19</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.15</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.11</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>FeO</td>
<td>9.37</td>
<td>12.6</td>
<td>13.7</td>
</tr>
<tr>
<td>MnO</td>
<td>0.42</td>
<td>0.61</td>
<td>0.68</td>
</tr>
<tr>
<td>MgO</td>
<td>31.9</td>
<td>28.8</td>
<td>26.9</td>
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<tr>
<td>CaO</td>
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<td>0.83</td>
<td>0.94</td>
</tr>
<tr>
<td>Na₂O</td>
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<td>1.27</td>
<td>1.67</td>
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<tr>
<td>Total Si</td>
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<td>100.86</td>
<td>100.08</td>
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<tr>
<td>Total Fe</td>
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<td>Total Ca</td>
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<td>Total Na</td>
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<td>Total K</td>
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<tr>
<td>Total FS mol%</td>
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<tr>
<td></td>
<td>Ti 0.005</td>
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<td></td>
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<td></td>
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Table 2. Compositions of akimotoite grains and pyroxene glass obtained by STEM-EDS, normalized to 100%

<table>
<thead>
<tr>
<th></th>
<th>Akimotoite</th>
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<th>Pyroxene glass</th>
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<td>CaO</td>
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<td>0.4</td>
<td>0.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.5</td>
<td>3.5</td>
<td>3.3</td>
<td>3.2</td>
</tr>
<tr>
<td>MgO</td>
<td>30.0</td>
<td>33.0</td>
<td>29.4</td>
<td>23.1</td>
</tr>
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<td>Total</td>
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Formula (O = 6)

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<th>Ca</th>
<th>Al</th>
<th>Mg</th>
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</tr>
<tr>
<td>FeO</td>
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<td>Total</td>
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</tbody>
</table>

Note: The analytical uncertainties were estimated <5% (1SD), based on repeated analyses of a small region of the pyroxene glass.
Figure Captions

Figure 1. Polished thin section of GRV 052082 under transmitted light. The shock-induced melt veins are opaque (arrows).

Figure 2. BSE images of pyroxene clasts in the shock-induced vein from GRV 052082. (a) High-pressure mineral assemblages from a chondritic clast. The FIB-TEM slice is shown in the dashed-line frame. White box locates image (b). (b) High magnification image of bright pyroxene glass area (Fs23.2) and the dark akimotoite grains (Fs17.3). (c) High-pressure mineral assemblages in the shock-induced vein. White box locates image. (d) High magnification image of bright pyroxene glass area (Fs21.4) and dark akimotoite crystals (Fs15.5). Note the black arrow pointing to the direction of elongation of akimotoite and metal. Abbreviations: Mas = Maskelynite; Hol = Lingunite; Px Glass = Pyroxene Glass; Aki = Akimotoite; Ol = Olivine; Rgt = Ringwoodite; Jad = Jadeite.

Figure 3. Raman spectra of mineral phases from pyroxene clasts and those of lingunite and jadeite in GRV 052082.

Figure 4. (a) Bright-field TEM (BF-TEM) image of FIB slice from Aki-Px Glass assemblage. Idiomorphic crystals of akimotoite (Aki) embedded in amorphous pyroxene glass (Px-Glass). (b) SAED pattern of an akimotoite crystallite along the
zonal axis \([\overline{300}]\).

Figure 5. A bright-field (BF)-STEM image and Si, Mg, Fe, Al and Ca maps of Aki-Px Glass assemblage. The arrows in Mg-K\(_\alpha\) and Fe-K\(_\alpha\) maps point to the akimotoite crystallites. Color bars on the left are intensity of K\(_\alpha\) lines of the elements.

Figure 6. Plots of FeO- and MgO- contents of akimotoite, pyroxene in host rock, and pyroxene glass.

Figure 7: Variation of FeO and MgO concentrations in akimotoite (Aki) and pyroxene melt (Px melt) vs. fraction of melt remaining based on equation (\(i\)). Solid lines are calculated curves of pyroxene melt and dashed lines are of akimotoite. Green and yellow areas are compositional ranges of akimotoite and pyroxene glass detected in GRV 052082.
Fig. 1

Shock-induced melt veins

2mm

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