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Back-transformation of high-pressure phases in a shock melt vein of an H-chondrite during atmospheric passage: Implications for the survival of high-pressure phases after decompression

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Abstract

We investigated the H6-chondrite Yamato 75267, in which a fusion crust cuts a shock melt vein. The shock vein region, more than 280 μm from the fusion crust, contains high-pressure phases, such as ringwoodite, majorite-pyrope$_{ss}$ garnet and $NaAlSi_3O_8$ hollandite. However, the shock vein close to the fusion crust entirely consists of the low-pressure polymorphs, olivine, low-Ca pyroxene and plagioclase glass. The boundary between low- and high-pressure phase regions is parallel to the fusion crust. During the atmospheric passage, the peripheral part of the chondrite was melted to form the fusion crust. Our microscopic, laser micro-Raman, electron microprobe investigations and calculations indicate an area up to 300 μm from the fusion crust experienced a temperature of 1400°C after 3 s during the melting of the peripheral part. The high-pressure phases would, at this conditions, quickly transform back to their low-pressure polymorphs. The result obtained here indicates that post-shock temperatures in the interior part of the veins were much lower than 1400°C, thus leading to the survival of high-pressure phases in heavily shocked chondrites.
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Keywords: shock event; H-chondrite; back-transformation; fusion crust; ringwoodite

1. Introduction

Shock-induced melt veins occur in many ordinary chondrites. Especially, the shock veins of some L6-chondrites contain high-pressure phases such as ringwoodite, majorite-pyrope$_{ss}$ garnet and $NaAlSi_3O_8$ hollandite (e.g. [1–4]). The occurrence of these high-pressure phases is of significance to evaluate the pressure and temperature conditions when chondritic parent bodies were subjected to impact events.

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The surface of meteorites experienced heating to form the fusion crusts for short time during the atmospheric passage. We investigated an H6-chondrite bearing a shock vein and a fusion crust, and noticed that the high-pressure minerals in the veins were partially transformed back to their low-pressure polymorphs in the area near the fusion crust. The purposes of this study are: (1) to explore the effect of transient heating on the stability and back-transformation of high-pressure phases in the shock vein, and (2) to understand the *P–T* history of shock veins, because the back-transformation of high-pressure minerals is significant for understanding the post-shock process in the veins. A preliminary report was previously presented by Kimura et al. [5].

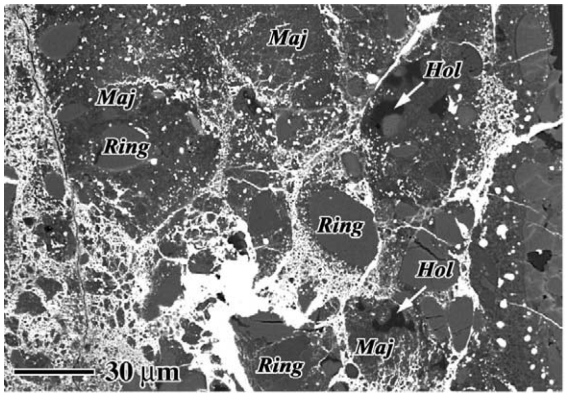

Fig. 1. BSE image of a shock vein in Y75267, showing high-pressure phases, such as ringwoodite (Ring), majorite-pyrope$_{ss}$ garnet (Maj) and $NaAlSi_3O_8$ hollandite (Hol).

2. Sample and experimental methods

We studied the H6-chondrite Yamato 75267 (91-2) (hereafter Y75267). This sample contains the shock melt vein and fusion crust.

Back-scattered electron (BSE) imaging and mineral analyses were obtained using the JEOL 733 electron-probe microanalyzer at Ibaraki University. Quantitative mineral analyses were conducted generally at 15 kV and a sample current of 10 nA. The Bence-Albee matrix correction method was used. Some BSE images were taken by the Hitachi S4700 field emission scanning electron microscope, equipped with a GW Centaurus BSE detector and a PGT IMIX quantitative EDS at the American Museum of Natural History, New York. Raman spectra of minerals were measured by the JASCO NRS-2000 spectrometer with a nitrogen-cooled CCD detector at Tohoku University. A microscope was used to focus the excitation laser beam (514.5 nm lines of a Princeton Instruments Inc. Ar+ laser) to a 2 µm spot. The laser power was 40 mW.

3. Petrography and mineralogy

3.1. Shock vein in Y75267

Y75267 shows a typical texture of H6-chondrite, consisting of anhedral to subhedral olivine and pyroxene with interstitial plagioclase and abundant opaque minerals. No coherent chondrule is encountered in the section studied here. This chondrite contains a shock melt vein of ∼200 µm in average width. The vein consists of two silicate lithologies: (1) coarse-grained aggregates (∼10 to ∼100 µm in size), and (2) fine-grained matrix (below ∼5 µm) (Fig. 1). The vein also contains abundant opaque spherules of submicrons to ∼10 µm in size. The results of phase identification and mineral chemistry are listed in Table 1.

Although the encountered phases in the vein have compositions typical of H-chondrite, most of them are high-pressure minerals. In comparison with L-chondrite, these high-pressure phases were rarely found in H-chondrites [6,7]. Y75267 is the third H-chondrite in which high-pressure phases occur, besides Yanzhuang [8] and Y75100 [9]. The coarse-grained aggregate in the vein contains ringwoodite, wadsleyite, majorite, $NaAlSi_3O_8$ hollandite, and minor akimotoite (Fig. 2). In comparison, the fine-grained matrix mainly consists of majorite-pyrope$_{ss}$ garnet, with minor wadsleyite, ringwoodite and akimotoite.

The chondritic host, outside the vein, consists only of low-pressure phases, such as olivine and low-Ca pyroxene. However, maskelynite of plagioclase composition is encountered everywhere in the host.

Table 1
Selected electron microprobe analysis data of minerals in Y75267

Phase	Occurrence	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	NiO	MnO	MgO	CaO	Na_2O	K_2O	Total	Fo/En	Fs	Wo
Olivine	Fusion crust	38.94	b.d.	0.07	0.54	16.32	1.00	0.09	41.86	0.13	0.08	b.d.	99.03	82.1		
Olivine	Host	39.17	b.d.	b.d.	b.d.	17.41	b.d.	0.56	42.26	b.d.	b.d.	b.d.	99.40	81.3		
Ringwoodite	Vein: High-*P* region	40.14	b.d.	b.d.	b.d.	17.00	b.d.	0.43	42.76	b.d.	b.d.	b.d.	100.33	81.8		
Olivine	Vein: Low-*P* region	39.73	b.d.	b.d.	b.d.	16.74	b.d.	0.32	43.57	b.d.	b.d.	b.d.	100.36	82.3		
Low-Ca pyroxene	Host	55.96	0.14	0.21	0.12	11.09	b.d.	0.52	31.10	0.60	b.d.	b.d.	99.74	82.4	16.5	1.2
Majorite[a]	Vein: High-*P* region	56.59	0.16	0.21	0.09	12.02	b.d.	0.35	30.37	0.75	b.d.	b.d.	100.54			
Majorite-pyrope[b]	Vein: High-*P* region	55.99	0.12	1.27	0.14	11.63	b.d.	0.59	28.28	1.06	0.74	b.d.	99.82			
Low-Ca pyroxene	Vein: Low-*P* region	56.65	0.14	0.10	b.d.	11.09	b.d.	0.49	30.33	0.51	b.d.	b.d.	99.31	82.2	16.9	1.0
Plagiclase glass	Host	64.89	0.08	21.68	b.d.	0.09	b.d.	0.08	b.d.	2.78	9.25	1.17	100.02			
$NaAlSi_3O_8$ hollandite	Vein: High-*P* region	64.90	b.d.	21.96	b.d.	0.40	b.d.	b.d.	b.d.	2.91	9.56	0.96	100.69			
Plagiclase glass	Vein: Low-*P* region	65.34	0.07	21.83	b.d.	0.32	b.d.	b.d.	b.d.	2.92	9.20	1.12	100.80			

b.d.: below detection limits (1σ, wt%), 0.02 for Al_2O_3, MgO, CaO, Na_2O and K_2O, 0.03 for TiO_2, 0.06 for Cr_2O_3, FeO, NiO, MnO.

[a] $Mj_{96.6}Py_{0.7}CaMj_{2.5}Uv_{0.2}$ (Mj: majorite, Py: pyrope, Uv: uvarovite).

[b] $Mj_{88.4}Py_{4.0}CaMj_{0.9}NaMj_{6.4}Uv_{0.3}$.

3.2. Mineralogy of vein near fusion crust

Y75267 is partly covered by a 280-μm-thick fusion crust (Fig. 3). According to Genge and Grady [10], fusion crust of ordinary chondrites is divided into melted crust and substrate from the surface. The melted crust of Y75267 is 60–80 μm wide, and shows a typical quench texture from melt, consisting of euhedral olivine smaller than 10 μm in size, and opaque spherules among glass. These olivines are of Fa_{14-26}, with 0.1–1.4

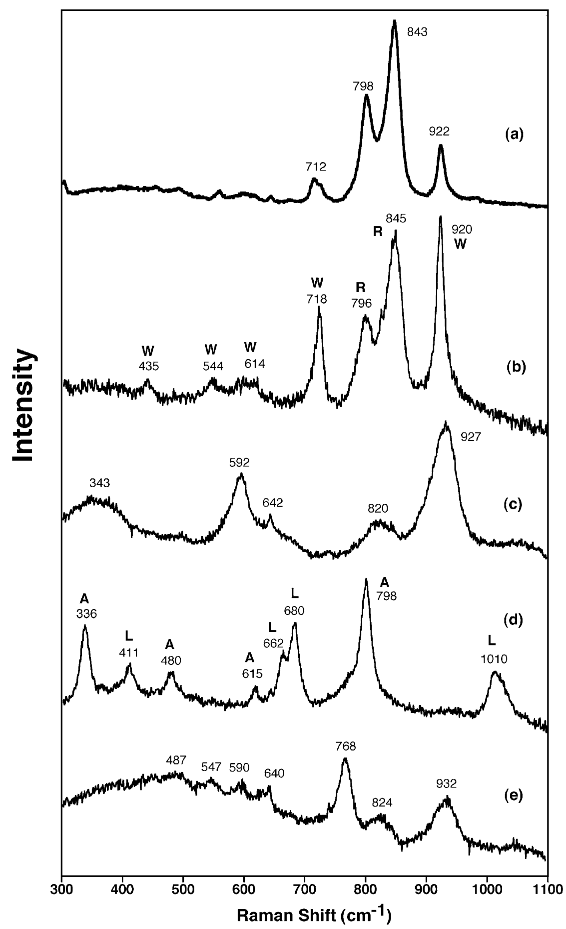

Fig. 2. Raman spectra of high-pressure phases from the shock vein in Y75267: (a) rigwoodite in coarse-grained aggregate, (b) wadsleyite (W) mixed with ringwoodite (R) in fine-grained matrix, (c) majorite-pyrope$_{ss}$ garnet in fine-grained matrix, (d) akimotoite (A) mixed with low-Ca pyroxene (L) in coarse-grained aggregate, and (e) $NaAlSi_3O_8$ hollandite in coarse-grained aggregate.

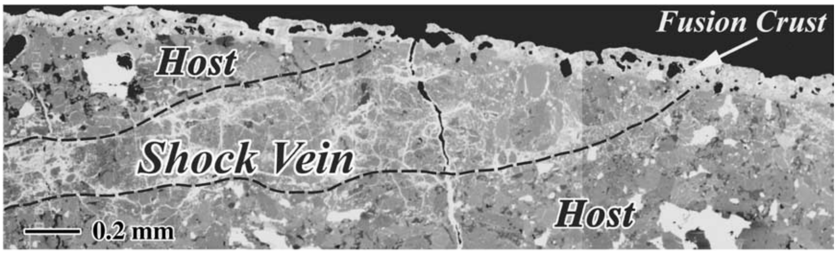

Fig. 3. BSE image showing that portion of shock vein in direct contact with a fusion crust in Y75267.

wt% NiO, in agreement with those given by Genge and Grady [10]. The substrate is observed in the interior part of the fusion crust around the host of Y75267, but is texturally indistinguishable from the shock vein.

A portion of the shock vein of Y75267 is cut by the fusion crust (Fig. 3). The texture and grain size inside the vein are homogeneous, regardless of the distance from the fusion crust. The vein region near the fusion crust also consists of two silicate lithologies with abundant tiny opaque grains (Fig. 4).

However, the mineral assemblages evidently depend on the distance from the fusion crust. The vein region, more than 280 μm from the fusion crust, consists of high-pressure phases, i.e. wadsleyite, ringwoodite, majorite, $NaAlSi_3O_8$ hollandite and akimotoite in the coarse-grained aggregate, and mainly majorite-pyrope$_{ss}$ garnet with wadsleyite and ringwoodite in the fine-grained matrix.

The vein region near the fusion crust, less than 280 μm, entirely consists of low-pressure phases such as olivine, low-Ca pyroxene and plagioclase

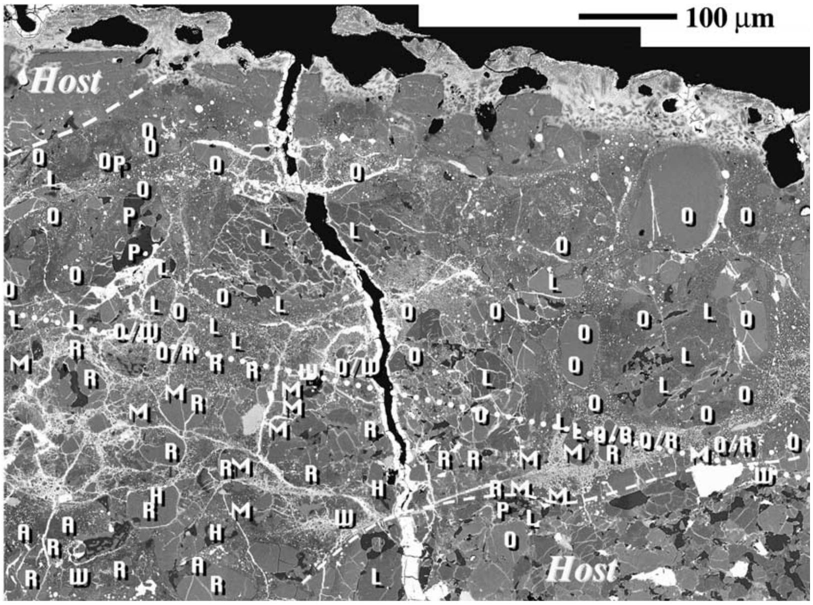

Fig. 4. BSE image of the shock vein with detailed phase identification by laser micro-Raman. The vein region far from the fusion crust consists of wadsleyite (W), ringwoodite (R), majorite or majorite-pyrope$_{ss}$ garnet (M), akimotoite (A) and $NaAlSi_3O_8$ hollandite (H). The vein region near the fusion crust consists entirely of low-pressure phases, olivine (O), low-Ca pyroxene (L) and plagioclase glass (P). Note that the boundary (dashed line) between low- and high-pressure phase regions is sharp, and it is just parallel to the fusion crust at a distance of 280 μm.

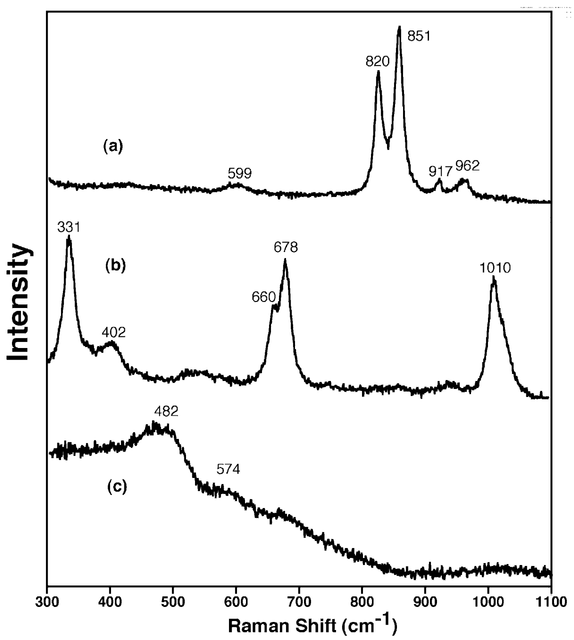

Fig. 5. Raman spectra of low-pressure phases in the low-pressure region from the shock vein: (a) olivine, (b) low-Ca pyroxene, and (c) plagioclase glass.

glass in both lithologies (Fig. 5). The boundary between low- and high-pressure phase regions is sharp, and is parallel to the fusion crust at a distance of 280 μm (Fig. 4).

On the boundary between low- and high-pressure phase regions, we noticed an isolated grain of olivine composition, ∼50 μm in length. This grain consists of olivine portion mixed with a minor amount of ringwoodite in the low-pressure phase region, and a ringwoodite portion in the high-pressure phase region (Fig. 6). The middle part of this grain consists of olivine and ringwoodite.

Ringwoodite and wadsleyite have a similar composition to olivine in the chondritic host with Fa_{18-20} and 0.27–0.6 wt% MnO (Fig. 7). In the coarse-grained aggregate, majorite and akimotoite have the same compositions as low-Ca pyroxene in the host, $Fs_{16-18}Wo_{1-2}$, with <0.5% Al_2O_3 and <0.3% Na_2O (Table 1). However, majorite-pyrope$_{ss}$ garnets ($Mj_{88.4}Py_{4.0}CaMj_{0.9}$-$NaMj_{6.4}Uv_{0.3}$) in the fine-grained matrix are enriched in Al_2O_3 (1.3–4.4%) and Na_2O (0.6–1.3%). The high contents of Al and Na were also reported from such garnets by Chen et al. [1] and Kimura et al. [9], who suggested that garnet is a liquidus phase crystallized from the shock-induced melt at high pressure. Pyroxene in the fine-grained matrix of the low-pressure region have an identical composition to that of majorite-pyrope$_{ss}$ garnet.

$NaAlSi_3O_8$ hollandite in the high-pressure region, plagioclase glass in the low-pressure region, and maskelynite in the chondritic host have similar compositions, $Ab_{76-82}Or_{5-7}$, $Ab_{76-80}Or_{6-8}$, and $Ab_{78-83}Or_{4-7}$, respectively (Table 1).

4. Discussion

4.1. Back-transformation near fusion crust

It is evident that Y75267, like other heavily shocked chondrites, experienced an impact inducing high pressure and temperature, which leads to the formation of high-pressure phases in the vein. The mineral assemblage of wadsleyite, ringwoodite and majorite is indicative of the *P*–*T* conditions of ∼20 GPa at 2000°C, based on the phase diagrams [11,12].

Similarity in texture and chemistry of minerals in the low- and high-pressure phase regions, indicates that the low-pressure phases in the veins were produced through back-transformation of high-pressure phases near the fusion crust. During the atmospheric passage, the peripheral part of Y75267 was melted and quenched to form the fusion crust under atmospheric pressures. Simultaneously, the high-pressure phases near the fusion crust should have been transformed to their low-pressure polymorphs under high temperatures and atmospheric pressure. The composite grain consisting of ringwoodite and olivine described above illustrates such a heat-triggered phase transition. Because of a sharp thermal gradient from the surface to the interior of Y75267 during the atmospheric passage, part of ringwoodite grain near the fusion crust was heated and transformed to olivine, whereas the other part relatively far from the fusion crust remained intact.

In the low-pressure region, we encountered only olivine, low-Ca pyroxene and plagioclase glass.

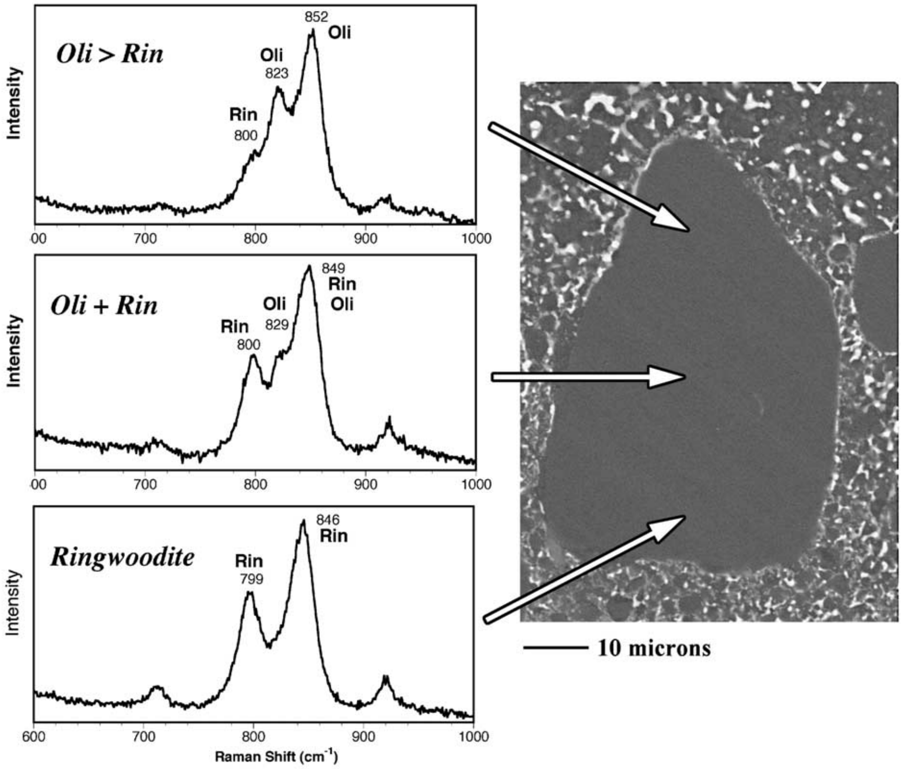

Fig. 6. An isolated olivine grain, ~50 μm in size, at the boundary between low- and high-pressure phase regions. This grain consists of olivine with minor ringwoodite at the low-pressure region, olivine plus ringwoodite, and ringwoodite at the high-pressure region.

According to the experiments of the back-transformation of β-Mg_2SiO_4 to olivine, an unknown intermediate phase was reported [13]. However, we did not identify such a phase. Ming et al. [14] noticed that FeO-bearing silicate spinel decomposed to Fe-oxides and enstatite under atmospheric conditions. However, we did not observe any Fe-oxide in the vein regions containing low-pressure minerals. We suggest that during the atmospheric passage the material in the vein region near the fusion crust was not oxidized. Olivine in this region does not contain NiO (lower than the detection limit, see Table 1), although olivines in the fusion crust contain NiO. Also troilite was not oxidized to form magnetite or wüstite.

In the low-pressure phase region of the vein, majorite-pyrope$_{ss}$ garnet transformed to low-Ca pyroxene. The pyroxene partially inherits the composition of majorite-pyrope$_{ss}$ garnet. It is expected that some of Na and Al were excluded from pyroxene structure to form some other phase, such as plagioclase, during the back-transformation of majorite-pyrope$_{ss}$ garnet. However,

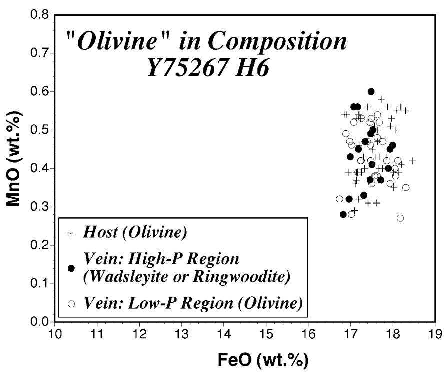

Fig. 7. FeO and MnO contents in the polymorphs with olivine compositions.

we did not identify such secondary phases by Raman spectroscopy, probably because of the fine-grained size and low abundance of these phases. Reynard and Rubie [15] reported the existence of amorphous phase from high-pressure pyroxene polymorph in their back-transformation experiments. But, we did not identify such an amorphous phase with pyroxene composition in the vein.

$NaAlSi_3O_8$ hollandite transformed to plagioclase glass, not to crystalline plagioclase, in the vein during the atmospheric passage. As discussed later, the maximum temperature close to the fusion crust exceeded the melting temperature of albite (1118°C). Plagioclase glass, close to albite composition, might have formed directly from $NaAlSi_3O_8$ hollandite during the atmospheric passage.

4.2. Thermal gradient near fusion crust

Here we discuss the conditions for the back-transformation of high-pressure phases near the fusion crust. The boundary between low- and high-pressure regions is sharp, and is also parallel to the fusion crust. These observations indicate that there was a steep thermal gradient from the fusion crust to the meteorite interior during the atmospheric passage.

Some authors estimated a thermal gradient in the meteorite during its atmospheric passage. Sears [16] calculated that the maximum temperatures of a region about 300 μm distant from the fusion crust lies between 600 and 1500°C. Yabuki [17] estimated that an area 300 μm inwardly distant from the fusion crust experienced 1400°C after 5 s, assuming that the fusion crust melted at 1600°C.

We calculated the temperature distribution as a function of time and distance from the melted surface. We take into account a limited duration for heating the meteorite, because aerodynamic heating is estimated to last only for several seconds (e.g. [18]), which should be significant for back-transformation reaction for high-pressure phases. The thermal conduction of meteorite can be treated as one-dimensional heat flow problem in the semi-infinite solid because the size of meteorite is generally much larger than the heated zone. Time evolution of the temperature distribution of meteorite during the atmospheric passage can be obtained by solving the following diffusion equation:

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} \tag{1}$$

which satisfies the boundary condition that temperature at the surface $\phi(t)$ varies as:

$$\phi(t) = \begin{cases} T_0 \ (t<0) \\ T_1 \ (0<t<\tau) \\ T_0 \ (t>\tau) \end{cases} \tag{2}$$

Here the temperature T is a function of the distance x from the surface $x=0$ and the time t. κ is the thermal diffusivity of the meteorite. The temperature of meteorite is assumed to be T_0 at $t=0$. As described in Eq. 2, the temperature of T^1 at the surface $x=0$ is maintained during the time $0<t<\tau$. The solution of Eq. 1 is given by:

$$T(x,t) = \left(T_1 \mathrm{erfc}\frac{x}{\sqrt{4\kappa t}} + T_0 \mathrm{erf}\frac{x}{\sqrt{4\kappa t}}\right) H(t) + (T_0 - T_1)\mathrm{erfc}\frac{x}{\sqrt{4\kappa(t-\tau)}} H(t-\tau) \tag{3}$$

where $H(t)$ is the Heviside step function which is unity if $t>0$ and zero otherwise and:

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-\xi^2}\, d\xi$$

$$\mathrm{erfc}(x) = 1 - \mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-\xi^2}\, d\xi$$

[19]. Fig. 8 shows the time evolution of the temperature at $x=0.1$–1.0 mm, where we assume that $\kappa=1$ mm^2/s, $\tau=5$ s, $T_0=0$°C, and $T_1=1600$°C.

From our results, an area 300 μm distant from the melted surface is heated to 1400°C after 3 s. This temperature value hardly depends on the initial temperature T_0. The temperature difference is within ~2% even in an extreme case of $T_0=-273$°C. Aerodynamic heating is estimated to last only for several seconds. It is, therefore, probable that even at the region near the fusion crust, the high-temperature conditions lasted for a short time, possibly less than several seconds as

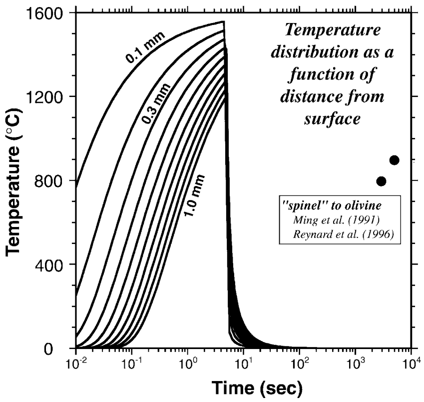

Fig. 8. Temperature distribution as a function of time (s) and distance form the melted surface (0.1–1 mm) during atmospheric passage of meteorite, assuming that the initial temperature of meteorite and heating duration were 0°C and 5 s, respectively. The calculation equations are shown in text. The results of back-transformation experiments of silicate spinel to olivine are also plotted.

shown in Fig. 8. High-pressure phases near the fusion crust in Y75267 should have quickly transformed to their low-pressure polymorphs in such a short time under high temperatures and atmospheric pressure condition.

In contrast, the vein regions, more than ~300 μm distant from the fusion crust, should not have been heated up to ~1400°C. Therefore, high-pressure phases survived during the atmospheric passage in short time.

Some back-transformation experiments on high-pressure phases have been made. Suzuki et al. [20] found that β-Mg_2SiO_4 promptly transformed to olivine at 900°C and atmospheric pressure. Ming et al. [14] showed that silicate spinel transforms to olivine in ~1.4 h at 900°C (Fig. 8). Our results indicate that the back-transformation of high-pressure phases takes only a few seconds at high temperatures. Our calculation is consistent with the previous experimental work. Reynard et al. [13] suggested that the time for back-transformation strongly depends on the magnitude of the temperatures. Although no experimental work was done for the back-transformation of majorite or majorite-pyrope$_{ss}$ garnet, our results suggest that they would also transform instantaneously to pyroxene, like silicate spinel at high temperatures.

4.3. Significance of the back-transformation

The pressure and temperature conditions for crystallization of high-pressure phases in the vein have been estimated based on phase equilibria (e.g. [1–4]). However, post-shock conditions in the vein have not yet been quantitatively estimated.

Some shock veins in chondrites consist mainly of low-pressure phases transformed from their high-pressure polymorphs at the pressure release stages [21–23]. Thus, the survival of high-pressure assemblage in the vein depended on the cooling rate. Our results may be used for the estimation of post-shock conditions. If the pressures were immediately released after the formation of high-pressure phases, the temperatures decreased far below ~1400°C in a few seconds. Otherwise, the high-pressure phases should transform to their low-pressure polymorphs. The shock-induced melt vein might have been instantaneously quenched through heat waste to the cold meteoritic matrix within the low-temperature chondritic host after the formation of high-pressure phases, as suggested by Langenhorst and Poirier [24] and Sharp et al. [25]. Therefore, our results could not favor the model that the high-pressure phases formed at the decompression stage [26,27], because only several seconds are sufficient for phase transitions from high-pressure phases to low-pressure polymorphs at a high post-shock high temperatures after pressure release.

Chen et al. [28] and Ohtani et al. [29] recently investigated the occurrence of high-pressure mineral assemblages in heavily shocked L6-chondrites, and suggested that a time period of up to several seconds could be required to quench the veins before decompression at a temperature at which high-pressure phases survived on release of pressure. Their suggestion is consistent with our results obtained here.

5. Summary

1. We reported evidence for the back-transformation of high- to low-pressure phases in a shock vein near a fusion crust in an H-chondrite.

2. The back-transformation should have taken place in few seconds under high temperatures and low pressures during atmospheric passage of the meteorite.
3. The dense polymorphs in the vein evidently crystallized under high pressures and temperatures. However, our results strongly indicate that post-shock temperatures should have been considerably low, leading to the conservation of the high-pressure phases in the shock veins.

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