

## Shock-induced deformation of Shergottites: shock-pressures and perturbations of magmatic ages on Mars

## Shock-induced deformation of Shergottites: shock-pressures and perturbations of magmatic ages on Mars

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Shergottites and Chassignites practiced major deformation effects whose nature, magnitude and relevance were controversially evaluated and disputatively debated. Our studies of many shocked shergottites present, contrary to numerous previous reports, ample evidence for pervasive shock-induced melting amounting of at least 23 vol.% of the original labradorite, finding of several high-pressure polymorphs and pressure-induced dissociation reactions. Our results cast considerable doubt on using the refractive index (R. I.) of maskelynite, in estimating magnitudes of peak-shock pressure in shergottites or ordinary chondrites because R. I. of maskelynite was first established after quenching of the feldspar liquid to maskelynite glass followed by glass dilation after decompression and first at the closure temperature of relaxation. This procedure widely practiced in the past 38 years, revealed unrealistic high-pressure estimates discrepant with the high-pressure mineral inventory in shergottites and with results obtained by robust static experiments. Shergottites contain the silica high-pressure polymorphs seifertite, a monoclinic ultra dense polymorph of silica, stishovite, a dense liquidus assemblage consisting of stishovite + Na-hexa-aluminosilicate (Na-CAS) and both K-lingunite and Ca-lingunite. Applying individual high-pressure silica polymorphs alone like stishovite, previously practiced to estimate the equilibrium shock pressure, is inadequate due to the considerable shift of their upper pressure bounds intrinsically induced by spatially variable absorptions of minor oxides like Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, FeO, MgO and TiO<sub>2</sub>. This revealed variable pressure estimates within the same shergottite subjected to the same peak-shock pressure. Occurrence of Na-CAS + stishovite, lack of NaAlSiO<sub>4</sub> Ca-ferrite structured polymorph or jadeite indicates that the peak-shock pressures barely exceeded 22 GPa. We present convincing evidence to discard the claim that the shock-induced high-pressure inventory in shergottites and ordinary chondrites resulted from local shock spikes in excess of 80 GPa and during the decompression stage. Such scenario calls for a series of incomplete and quenched retrograde reactions starting with Mg-silicate perovskite + magnesiowustite if formed above 80 GPa followed by majorite-pyropess + magnesiowustite below 23 GPa and 2000 degree, ringwoodite above 16 GPa, respectively and finally polycrystalline olivine at ambient pressure. Such incomplete retrograde reactions were never encountered in any shergottite, chassignite or shocked ordinary chondrite so far. Olivine-ringwoodite phase transformation commences with the coherent mechanism producing ringwoodite lamellae with their (111) parallel to the (100) plane of olivine followed by the incoherent mechanism due to build up of strain in the parental olivine. Application of experimentally obtained kinetic parameters of the olivine-ringwoodite phase transitions reveal duration of the natural events for at least several seconds thus refuting the claimed decompression mechanism.

The shock-induced pervasive melting of labradorite and partial melting of clinopyroxene strongly suggests partial to complete resetting of the Ar-Ar, Rb-Sr, Sm-Nd, Lu-Hf, and Hf-W radiometric systems. This also casts considerable doubt on the radiometric ages shorter than 575 Ma reported in the past 38 years to be the igneous crystallization ages. These short ages resulted from partial or total shock-induced age resetting.

## 火星起源シャーゴットイト隕石の衝撃溶融脈およびメルトポケットにおける pigeonite 輝石の分解：火星における衝突イベントへの示唆 Dissociation of pigeonite in shock melt vein/pocket of Martian shergottites: Implications for impact events on Mars

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It is widely accepted that SNC (Shergottites-Nakhlites-Chassignites) meteorites with a meteorite Allan Hills 84001 are derived from Mars. Among the currently recognized 104 Martian meteorites, shergottite is the largest group with 88 members (Meteoritical Bulletin Database). Shergottites are basaltic, olivine-phyric, or lherzolitic igneous rocks probably formed near the surface of Mars. They are characterized by high degree of shock metamorphism [1, 2, 3, 4]. The shock metamorphic features and high-pressure phases in Martian meteorites provide crucial information about the nature and history of impact events on Mars [4]. In this study, we investigated shock-induced features and high-pressure minerals in two basaltic shergottites Northwest Africa (NWA) 856 and Zagami.

We conducted petrographic and mineralogical observations on polished thin sections of the samples using optical microscope, field emission scanning electron microscope (FE-SEM), micro-Raman spectrometer and electron probe micro analyzer (EPMA). Some identified high-pressure minerals were extracted from the thin sections by micro drill and processed by focused ion beam system (FIB) to thin slices. The prepared slices were investigated by synchrotron X-ray diffraction experiments and transmission electron microscope (TEM).

NWA 856 and Zagami have a basaltic texture, mainly composed of two pyroxenes (pigeonite, augite) and plagioclase glass (maskelynite). They contain many shock-induced melt pockets. A shock melt vein is also observed in Zagami. In pigeonite grains adjacent to these melt pocket/vein, we found a dissociation texture of pigeonite not reported so far. The grain margins of the pigeonite adjacent to the melt pocket/vein seem to have dissociated into at least two different phases with different brightness (gray and white) in SEM-BSE images. The gray phase seems to have an idiomorphic crystal habit, whereas the white phase is interstitial. Raman spectroscopy showed that the untransformed part retains the original pigeonite (clinopyroxene) structure, but the dissociated part seems to contain ringwoodite and majorite-pyroxene garnet with pyroxene. The Raman bands of pyroxene associated with this assemblage are relatively broad than that of the original pigeonite. The intensity of the peak at around 1000  $\text{cm}^{-1}$  is significantly weaker than that of the original pigeonite. These features imply that this part contains pyroxene glass [5, 6]. This dissociation reaction is more coarse-grained and advanced in Zagami than in NWA 856.

Phase relation of diopside ( $\text{CaMgSi}_2\text{O}_6$ ) shows that diopside dissociates into majoritic garnet + (Ca, Mg) $\text{SiO}_3$ -perovskite at 18-22 GPa and 1400-1800 degree C, whereas into ringwoodite + stishovite at the same pressure and 1000-1400 degree C [7]. The assemblage of ringwoodite + majorite-pyroxene garnet in the basaltic shergottites could be formed by dissociation of pigeonite at 18-22 GPa and around 1400 degree C or in a increasing temperature from <1400 degree C to >1400 degree C. The Raman signals of the possible pyroxene glass might have been derived from that of vitrified (Ca, Mg) $\text{SiO}_3$ -perovskite. Since wadsleyite or akimotoite were not identified, the pressure range may be more restricted to be 19-20 GPa.

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Keywords: dissociation, pigeonite (pyroxene), shergottite, high-pressure, impact events, Mars

## NANOSIMS STUDY OF SHOCK-INDUCED MELT VEINS IN THE ENRICHED LHERZOLITIC SHERGOTTITE GROVE MOUNTAINS (GRV) 020090 NANOSIMS STUDY OF SHOCK-INDUCED MELT VEINS IN THE ENRICHED LHERZOLITIC SHERGOTTITE GROVE MOUNTAINS (GRV) 020090

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Introduction: GRV 020090 is a lherzolitic shergottite found in Antarctica [1]. The lower modal abundance of olivine, higher abundance of plagioclase, more ferroan compositions of ma-fic minerals and higher REE-enrichment of phosphates [2] distinguish it from most lherzolitic shergottites. GRV 020090 shares the same petrography and geochemistry of RBT 04262 [3], probably sampled an enriched upper mantle of Mars or the top stratigraphy of the lherzolitic shergottite igneous unit. Like other lherzolitic shergottites, GRV 020090 experienced heavy shock metamorphism, as indicated by transformation of all plagioclases to maskelynite and the presence of shock-induced melt veins [4]. However, complete extinction of maskelynite in the host rock and preservation of olivine and pyroxene glass in the shock-induced melt veins suggest that GRV 020090 was quenched from the shock event, followed by little post-shock thermal metamorphism. In this study, we applied nanoSIMS to the shock-induced melt veins, in order to constrain the shock metamorphism.

Experiments and Results: A few shock-induced melt veins (up to 100 um wide) were observed in two polished sections of GRV 020090, confined in the poikilitic part that consists of predominant low-Ca pyroxene oikocrysts with less abundant olivine chadacrysts and minor chromite inclusions. Hence, fragments of the melt veins are composed of monominerals. <sup>23</sup>Na<sup>+</sup>, <sup>24</sup>Mg<sup>+</sup>, <sup>28</sup>Si<sup>+</sup>, <sup>40</sup>Ca<sup>+</sup>, <sup>52</sup>Cr<sup>+</sup>, <sup>55</sup>Mn<sup>+</sup> and <sup>60</sup>Ni<sup>+</sup> images of areas of 20x20 um were acquired in multi-collection mode of a CAMECA nanoSIMS 50L at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The O- beam of ~5 pA and ~600 nm in diameter was used, and the mass resolution power was ~6000.

Olivine grains adjacent to or entrained in the veins were transformed to ringwoodite - olivine glass assemblages, surrounded by a layer of olivine glass with a Raman band at 666 cm<sup>-1</sup>. Element mapping revealed enhanced concentrations of Mg, Ca, Mn and Ni in ringwoodite relative to Si and olivine glass, with little variation in Na and Cr. Pyroxene glass with smooth surface was found along the walls of the melt veins. Ca distribution shows presence of lamellae (<1 um in width) in the pyroxene glass, which are continuous to the host pyroxene. Coexisting with ringwoodite and majorite-pyrope solid solution, pyroxene grains were converted to lamellae of akimotoite and amorphous material. Distributions of Ca, Na and probably Mn show lamellae with an orientation different from the akimotoite lamellae.

Discussion and Summary: Presence of high-pressure polymorph assemblages of ringwoodite, majorite-pyrope solid solution, akimotoite and tuite in the melt veins suggests a shock-induced condition of 18-20 GPa, ~1800C. The olivine glass has a Raman band at 666 cm<sup>-1</sup> similar to the olivine dissociation assemblages [5] that composed of magesiowustite+poorly crystallized (Mg, Fe)SiO<sub>3</sub>. The nanoSIMS mapping reveals redistribution of elements during the phase transformation. Preservation of the Ca distribution lamellae in the pyroxene glass suggests that it was formed by solid-solid transformation without melting, or vitrified from (Mg, Fe)SiO<sub>3</sub> perovskite.

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キーワード: meteorite, Mars, high pressure, shock, nanoSIMS, melt vein

Keywords: meteorite, Mars, high pressure, shock, nanoSIMS, melt vein

## 地球惑星物質中の高圧鉱物 High-pressure minerals in the Earth and planetary materials

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Shocked meteorites are the most important sources of high-pressure minerals in addition to impact crater rocks, diamond inclusions and mantle xenoliths. In most cases, natural high-pressure minerals occur as submicron-sized grains. However, state-of-art techniques such as transmission electron microscopy and synchrotron X-ray diffractometry enabled the identification of such small crystalline grains. As a result, many of natural high-pressure phases of silicates and oxides have been discovered in the past 15 years. Textural, crystallographic and chemical characteristics of the natural high-pressure minerals provide us not only the clues to understand the impact events of meteorite parent bodies, but also insights on the structure and dynamics of the deep Earth. In this talk, we summarize the occurrences and discovery histories of the natural high-pressure minerals.

キーワード: 高圧鉱物, 相転移, 隕石, 衝撃変成, 透過電子顕微鏡

Keywords: High-pressure minerals, phase transformation, meteorites, shock metamorphism, TEM

## Jadeite in shocked L6 and H6 chondrites Jadeite in shocked L6 and H6 chondrites

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Feldspar in shocked meteorites transforms to its high-pressure polymorphs or amorphous (maskelynite). Synthetic experiments indicate that jadeite is a dissociation product of albite; albite = jadeite + silica [1]. Jadeite as a dissociation product of albite exists in and around shock-melt veins of shocked ordinary chondrites. However, the natures, occurrences and formation mechanism of the jadeite have not been clarified yet in detail. In this study, we observed jadeite as a dissociation product of albitic feldspar in and adjacent to shock-melt veins of the Yamato 791384 L6 (hereafter, Y-791384) and Yamato 75100 H6 (hereafter, Y-75100) ordinary chondrites by TEM subsequent to micro laser-Raman analysis and SEM observation.

We focused our investigations on six albitic feldspar grains in and adjacent to the shock-melt veins of Y-791384 and Y-75100. Raman spectrum corresponding to jadeite was recorded from the albitic feldspar in the shock-melt veins, implying that jadeite was formed subsequent to the breakdown of the albitic feldspar. Stishovite is the most likely silica phase because estimated shock pressure in the shock-melt veins of the Y-791384 and Y-75100 based on equilibrated high-pressure polymorph assemblage is ~15 GPa or more [2-4]. However, stishovite was not detected from present albitic feldspar including jadeite. TEM images show that many massive or network-like assemblages of jadeite crystal exist in the albitic feldspar. Jadeite crystal is surrounded by amorphous material having pseudomorph texture. The chemical composition of the amorphous material are varied, and plotted between jadeite and silica phase. Recent high-pressure and -temperature synthetic experiments using albite as a starting material demonstrate that the nucleation rate of stishovite is significantly slower than that of jadeite [5]. Jadeite would crystallize from albitic feldspar subsequent to polycrystallization in solid-state. Absence of stishovite is due to the critical differences of kinetics between jadeite and stishovite.

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## Shock History and Formation Mechanisms of High-pressure minerals in Grove Mountains (GRV) L-chondritic meteorites

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**Introduction:** Of 83 shocked Grove Mountains (GRV) ordinary chondrites, 21 L5-6 samples with melt veins were studied with SEM, Raman, EMPA and FIB-TEM, in order to estimate the P-T conditions of the shock events, and discuss formation processes of the high-pressure minerals.

**Results:** The matrix of the melt veins consists mainly of fine-grained majorite-pyroxene solid solution and ringwoodite. The host-rock clasts entrained in the veins are mostly rounded or ovoid. Ringwoodite, majorite, akimotoite, pyroxene glass, jadeite, lingunite and maskelynite were identified by Raman in the clasts.

We encountered abundant Olivine-Ringwoodite (Ol-Rgt) assemblages with novel textures and diverse chemical compositions. These assemblages contain FeO-depleted, dendrite-like Ol cores and FeO-enriched polycrystalline Rgt rims (up to 10 micrometers in width). Nodule-shaped objects of Rgt islands also occur inside the Ol core parts of the large assemblages. The Rgt rims and islands consist of idiomorphic Rgt crystals (~1 micrometer) showing 120° triple junction. The dendritic cores are composed of fine-grained Ol (<= 100 nm) with interstitial Rgt crystallites. Rgt are Fe-enriched (Fa<sub>36-82</sub>), while Ol shows a bimodal Fa-distribution (Fa<sub>8-14</sub> and Fa<sub>22-25</sub>). Difference in the FeO-contents between Rgt and Ol is up to 74 mol%. Intergrowth textures of Ol grains with single crystals of Rgt were commonly observed.

Most low-Ca pyroxene grains entrained in the melt veins have been partially or entirely transformed into akimotoite-pyroxene glass (Aki-Px Gl) assemblages. Idiomorphic Aki grains (100-400 nm, Fs<sub>15-17</sub>) scatter in Px Gl (Fs<sub>31-39</sub>). The CaO contents of Px Gl (0.4-4.5 wt%) are slightly higher than those of Aki (0.1-3.1 wt%) and the Px grains in the host rock (0.8-1.0 wt%). However, the Al<sub>2</sub>O<sub>3</sub> contents of them are almost identical.

**Discussion:** The presence of majorite-pyroxene solid solution and ringwoodite in the melt veins is similar to that reported in other shocked L6 meteorites [1-3], suggestive of a peak shock pressure and temperature of 18-23 GPa and > 2,000°C, respectively, according to the phase diagrams obtained by high-pressure and -temperature melting experiments of Allende and peridotites [e.g., 4].

The textural and compositional features of Ol-Rgt assemblages are suggestive of fractional crystallization from Ol melts [5-6], starting with MgO-rich wadsleyite (Fa<sub>8-14</sub>) followed by relatively FeO-richer olivine/wadsleyite (Fa<sub>22-25</sub>) from the shock-induced Ol melts. Rgt with high FeO-content (Fa<sub>28-82</sub>) crystallized from the residual melt. During the decompression, MgO-rich wadsleyite probably transformed back to Ol of the same chemical composition.

The euhedral grains and heterogeneous compositions of Aki suggest crystallization from pyroxene melts. The FeO content of the Px Gl is significantly higher than the maximum solubility of FeO in perovskite under 18-23 GPa [7], which indicates that the Px Gl could not have been back-transformed from preexisting silicate-perovskite. As crystallization of Aki with high Mg# commenced, the residual melt became enriched in Fe and Ca, which quenched to Px Gl under high pressure.

It is generally accepted that the high-pressure polymorphs encountered in melt veins of meteorites were formed directly via solid-state transformation from their parental minerals [e.g., 8]. Our studies of Ol-Rgt and Aki-Px Gl assemblages from GRV chondrites supply with robust evidence for fractional crystallization from mono-mineral melts [5, 6, 9], which can be another essential formation mechanism of high-pressure minerals.

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## Bhola, Yamato-74442 に含まれるアルカリ元素に富む岩片の Rb-Sr 同位体系 Rb-Sr isotopic systematics of alkali-rich fragments in Bhola and Yamato-74442

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**Introduction:** Alkaline elements (potassium, rubidium, and cesium) are classified as large ion lithophiles and are enriched in residual liquid phase during crystallization. Sodium, potassium, rubidium, and cesium are also classified as moderately volatile elements and large fractionations are expected as a result of evaporation/condensation.

Alkali-rich igneous fragments were identified in the brecciated LL-chondrites, Krahenberg (LL5) [1], Bhola (LL3-6) [2], and Yamato (Y)-74442 (LL4) [3-5], and show characteristic fractionation patterns of alkaline elements (e.g., Na<sup>0.5x</sup>Cl, K<sup>12x</sup>Cl, Rb<sup>45x</sup>Cl, and Cs<sup>70x</sup>Cl [6]). The alkali-rich fragments in Krahenberg, Bhola, and Y-74442 are very similar in mineralogy, petrography, and mineral chemistry, implying that they could have formed from related precursor materials [5]. In order to understand origin of these alkali-rich fragments as well as to constrain timing of their formation and elemental fractionation, we have undertaken Rb-Sr isotopic studies on alkali-rich fragments in Bhola and Y-74442.

**Results and Discussion:** Abundances of rubidium in the whole-rock samples of Bhola and Y-74442 are 2-10 times of those of ordinary chondrites, indicating a contribution of alkali-rich fragments. Rubidium in four fragments from Y-74442 are highly enriched; 20-180 times of those of ordinary chondrites. Two fragments (87-94 and 87-99) show an enrichment of rubidium (~80-180xOC) and a depletion of strontium (~0.2-0.3 x OC).

Alkali-rich fragments (Y-74442, 87-101 and 87-114) yield a two-point isochron age of 4441±30 Ma (2 sigma) with an initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.7082±0.0085, indicating a young age with a slightly high initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio compared with those of Krahenberg (T=4656±33 Ma, (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>I</sub>=0.6994±0.0011; recalculated by (<sup>87</sup>Rb decay constant)=1.402 x 10<sup>-11</sup>a<sup>-1</sup>)[1]. Relatively young <sup>39</sup>Ar-<sup>40</sup>Ar ages of ~4200 Ma were reported for alkali-rich fragments in Bhola [7] and a whole-rock sample of Y-74442 [8], which suggests that they suffered impact event(s) with the partial degassing of argon, and that their alkaline fractionation might have occurred prior to the impact event(s).

An alkali-rich fragment in Y-74442, 101-2 shows porphyritic texture: subhedral olivines are (~50 um in size) embedded in microcrystalline pyroxene (~5 um in size) and alkali-rich glass groundmass, suggesting that the temperature did not exceed liquidus, and that the fragment was cooled more slowly. The difference in thermal history among alkali-rich fragments will provide a clue of their "formation" processes. We suggest one of the possible formation processes of alkali-rich fragments is impact heating.

The alkali-rich fragments in Krahenberg and Bhola possess flat REE patterns [6]. Geochemistry (i.e., solid/liquid fractionation process) could not be responsible for the enrichments of heavier alkalis in the Krahenberg, Bhola, and Y-74442 fragments. Taking into account for the lack of detectable potassium isotopic fractionation in the Krahenberg fragment [9] along with the old formation ages of ~4.56 Ga for the Krahenberg [1], the alkaline elemental fractionation of the precursor materials could have occurred during an early stage of solar system evolution. After the elemental fractionation events, the fragments might be partly melted by impact(s).

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## Insights from silica minerals on chondrule formation, metamorphism and impact processing of EH chondrites

### Insights from silica minerals on chondrule formation, metamorphism and impact processing of EH chondrites

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Unusual sulfide minerals, Si dissolved in metal and the FeO-poor compositions of mafic silicates attest to the formation and metamorphism of enstatite chondrites (ECs) at low oxygen fugacities. Because of these unusual conditions, some metamorphic reactions in ECs are different from those of ordinary and carbonaceous chondrites [1]. Furthermore, shock events have affected the thermal histories of ECs [2]. Therefore, it has been difficult to infer metamorphic sequences for the ECs and to distinguish effects of nebular processes from thermal and shock metamorphism. In this study we focus on textures and phases of silica to distinguish nebular vs. metamorphic crystallization events in three EH chondrites.

Our main results are from three polished thin sections of ALHA81189 (EH3), ALH 84170 (EH3) and St. Marks (EH5). Other enstatite chondrites were used for comparison. Thin sections were examined using petrographic microscopes. Mineral analyses, elemental maps, and back-scattered electron images were collected using a JEOL JXA-8900 electron microprobe at Waseda University. Silica polymorphs were identified by Raman spectroscopy using a Jobin Yvon LabRam 300 Raman micro-spectrometer [Horiba, Ltd.] at Waseda.

Chondrule textures and the clastic matrix characteristic of type 3 enstatite chondrites [3] are easily identified in ALHA81189 and ALH 84170. These rocks contain coarse olivine. Silica is also present, often as fine-grained rims around chondrules. The presence of olivine with silica is evidence of the unequilibrated state of these two samples. Disequilibrium is also indicated by the wide range in Mg/(Mg+Fe) of pyroxene and olivine. Some of our Raman spectra from silica in the two samples are ambiguous, perhaps due to fine grain sizes, poor crystallinity, or the presence of some glass. Nonetheless, Raman spectra indicate that cristobalite is present in both samples. No other silica polymorph was identified in ALHA81189. Quartz was identified in ALH 84170 and some ambiguous spectra suggest tridymite. Tridymite and quartz, as well as cristobalite and glass, were identified in ALH 84170 by Kimura et al [4], who also used Raman spectroscopy.

In contrast to the two EH3 chondrites, original chondrule/matrix textures have been recrystallized in St. Marks, though some chondrules can still be recognized. No olivine was identified in St. Marks, and almost all of the pyroxene is Fe-poor. Silica occurs as coarse equant crystals. Raman spectra from silica in St. Marks are clear and all of our spectra indicate quartz, consistent with [4].

With the exception of some relict chondrule textures and rare Fe-rich pyroxene, St. Marks has been thoroughly recrystallized during parent body metamorphism. Although we cannot be certain that peak metamorphic temperatures were in the quartz stability field, the universal occurrence of silica as quartz in St. Marks suggests that this is likely.

Only one silica polymorph (cristobalite) was identified in ALHA81189; based on this observation alone, ALHA81189 could be interpreted as an equilibrated chondrite. However, as discussed above, other parameters indicate the unequilibrated condition of this sample. The abundance of cristobalite is due to high temperatures and rapid cooling associated with chondrule formation.

Several silica polymorphs are present in ALH 84170, indicating disequilibrium. Two interpretations are possible. (1) Quartz formed in situ during metamorphism of ALH 84170, and cristobalite, tridymite and silica glass are relict phases from chondrule formation. (2) Quartz in ALH 84170 formed during metamorphism of a previously existing rock and was mixed with the other silica phases during impact processing.

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キーワード: enstatite chondrites, silica, chondrules, metamorphism, shock

Keywords: enstatite chondrites, silica, chondrules, metamorphism, shock

## 強い衝撃を受けたCM炭素質コンドライトの発見 First discovery of a heavily shocked CM carbonaceous chondrite

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Collisional impact events are a fundamental process for the evolution of solar-system small bodies. The impacts on the asteroids result in shock deformation and localized melting in chondritic meteorites. We are able to elucidate the nature of shock events based on the analysis of shock-induced features in meteorites. Cracking, deformation, and phase transformation by impacts are commonly observed in ordinary chondrites. However, carbonaceous chondrites are known to have escaped intensive shock metamorphism. One of plausible explanations for this difference is that large amounts of volatiles in carbonaceous chondrites promote destructive explosion upon impacts and therefore the impacted materials fragmented into small pieces and do not become meteorites (Tomeoka et al.1999).

Some of CV3 chondrites show chondrule flattening and a preferred orientation due to impacts (Nakamura et al., 1992). Experimental impacts on a CV3 chondrite reveals that ~10GPa impact is needed to reproduce recognizable chondrule flattening (1995; 2000). On the other hand, CM chondrites that are more enriched in water than CVs are almost free of shock metamorphism (Scott et al. 1992) and thus no CMs have been found to show chondrule flattening. In the present study, we found CM chondrite MET01072 shows chondrule flattening and high densities of cracking of matrix materials perpendicular to compaction axis. In addition to chondrules, PCPs are heavily compacted and deformed, exhibiting flow-like texture along with chondrule surface. The cracks normal to shock compression axis was reproduced in the impact experiments on Murchison CM chondrite (Tomeoka et al. 1999). The cracks might have been generated due to dehydration of water-bearing minerals during pressure release, but synchrotron X-ray diffraction (S-XRD) analysis indicates that serpentine is still dominant in the matrix of MET01072.

In order to estimate shock temperature, a small piece of PCP (30x15x15 microns) was separated using FIB and exposed to X-rays for diffraction. Tochilinite in PCP has a very low decomposition temperature (~250C) and thus it is the most sensitive temperature indicator. S-XRD analysis showed that tochilinite in the PCP is not completely decomposed and gave broad diffractions. This result suggests that shock temperature might have exceeded tochilinite decomposition temperature, but the duration was too short for complete decomposition.

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## FeCr<sub>2</sub>O<sub>4</sub>の高圧相関係と衝撃隕石中のポストスピネル相への応用 High-pressure phase relations in FeCr<sub>2</sub>O<sub>4</sub> with implications to post-spinel phases in shocked meteorites

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Studies on natural high-pressure minerals in shocked meteorites may provide valuable information on shock events of the meteorites, as well as mineralogy and dynamics of the Earth's deep mantle. High-pressure polymorphs of FeCr<sub>2</sub>O<sub>4</sub>-rich chromite were found in a shocked chondrite by Chen et al. (2003a, b). The polymorphs have structures of calcium-ferrite (CaFe<sub>2</sub>O<sub>4</sub>) type and calcium-titanate (CaTi<sub>2</sub>O<sub>4</sub>) type, the latter of which was named xieite. However, the high-pressure stability relations in FeCr<sub>2</sub>O<sub>4</sub> have not yet been well clarified.

In this study, we have examined the phase relations in FeCr<sub>2</sub>O<sub>4</sub> to apply the results for evaluation of pressure-temperature conditions of formation of the natural FeCr<sub>2</sub>O<sub>4</sub>-rich high-pressure polymorphs in the shocked meteorite. The high-pressure experiments were carried out up to about 27 GPa and 1800 °C, using a multianvil high-pressure apparatus. The quenched samples were examined by microfocus and powder X-ray diffractometers, and the compositions were analyzed by a scanning electron microscope with an energy-dispersive X-ray spectrometer.

Above about 14 GPa, FeCr<sub>2</sub>O<sub>4</sub> chromite with the spinel structure dissociates into an assemblage of a new Fe<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> phase and Cr<sub>2</sub>O<sub>3</sub> with corundum structure. The new Fe<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> phase has the same structure as a high-pressure form of Mg<sub>2</sub>Al<sub>2</sub>O<sub>5</sub> found recently by high-pressure experiments in MgAl<sub>2</sub>O<sub>4</sub> (Enomoto et al., 2009, Kojitani et al., 2010). The two phases combine at 16-19 GPa into the FeCr<sub>2</sub>O<sub>4</sub> polymorph with the calcium-ferrite structure below about 1300 °C, while they combine into the other polymorph with the calcium-titanate structure above about 1300 °C. Both of the calcium-ferrite and calcium-titanate phases are stable up to at least 27 GPa. These results suggest that the natural FeCr<sub>2</sub>O<sub>4</sub>-rich calcium-ferrite and calcium-titanate were formed at pressure above 19 GPa at temperature below and above 1300 °C, respectively, during the shock event. This is generally consistent with the texture observation of the two FeCr<sub>2</sub>O<sub>4</sub> polymorphs in the shocked meteorite.

キーワード: 隕石, 衝撃圧縮, FeCr<sub>2</sub>O<sub>4</sub>, ポストスピネル, 高圧

Keywords: meteorite, shock compression, FeCr<sub>2</sub>O<sub>4</sub>, post-spinel, high pressure

## 準安定なゼイフェルタイトの形成 Formation of metastable seifertite

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Seifertite is a polymorph of silica with alpha-PbO<sub>2</sub> type structure that was found in the heavily shocked Martian meteorite (e.g., El Goresy et al., EJM2008). This phase is thermodynamically stable at more than 90 GPa corresponding to the base of Earth's mantle (Murakami et al., GRL2003). However it has also been known that this phase metastably appears from cristobalite at around more than 40 GPa and room temperature (Dubrovinsky et al., CPL2001). In this study, we focus on the kinetics of metastable formation of seifertite as important constraints on shock conditions of meteorites containing silica phase.

We have carried out high-pressure and high-temperature in-situ XRD experiments of quartz and cristobalite using a Kawai-type apparatus (SPEED-1500) at BL04B1 of SPring-8. Diffraction peaks of both quartz and cristobalite became very broad with pressures during cold compression, suggesting that the partially amorphization occurred. In the experiments of quartz, we observed sharpening of diffraction peaks and complete amorphization when heating at around 19 and 23 GPa, respectively. In both cases, stishovite appeared at more than 500-600C without formation of seifertite. Whereas in cristobalite, we observed formation of seifertite before appearance of stishovite when heating at 11-23 GPa. In the time scales of tens of minutes, the formation temperatures decrease from 500C to 200C for seifertite and increase from 600C to 800C for stishovite with pressures. As a result, the metastable field of seifertite can be kinetically defined, which expands to much lower pressures than previously thought. Further analyses of kinetic data obtained enable to estimate the P-T-t conditions for the presence of seifertite in shocked meteorites quantitatively.

## Vaporization of MgSiO<sub>3</sub> from First Principle Molecular Dynamics Simulations and Implications for Planetary Impacts

### Vaporization of MgSiO<sub>3</sub> from First Principle Molecular Dynamics Simulations and Implications for Planetary Impacts

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During the planetary impacts, large amounts of vaporized debris can be generated by releasing highly compressed materials adiabatically and intersecting the liquid-vapor phase envelope. They have long been recognized to be important for the chemical equilibrium and dynamics in the aftermath of giant impacts. However, present knowledge of the liquid-vapor phase equilibria and vapor phase speciation of silicates is extremely scarce or completely unknown over much of the relevant range, which makes the degree of impact-induced vaporization impossible to estimate accurately and therefore hinders our understanding of planetary formations and evolutions.

In this study, we have studied the vaporization of liquid MgSiO<sub>3</sub> from first principle molecular dynamics simulations over unprecedentedly high temperature regime (from 4000K to 8000K). Heterogeneous simulations involving two coexistence phases have been carried out with initial conditions prepared by first running a one-phase liquid simulation and then embedding the final snapshot in a large simulation cell that consists mostly of vacuum. The interfaces between the phases were then identified via the Gibbs criterion, which allows us to determine the densities and compositions of liquid and vapor phases in each snapshot. Speciations in the gas phase were inspected through bond-length criteria and analysis of the charge densities. The location of the critical point was finally estimated.

While the finite-size effects and phase behaviors of the other systems await further investigations in our subsequent studies, the *ab initio* simulation results in this study provide new constraints on silicate vaporizations and substantially reduce current uncertainties on the critical temperature and speciation. These may greatly affect the amount of vapor produced in giant impact, the composition of the first atmosphere overlaying the hadean magma ocean and potentially alter the accretion history of terrestrial planets.

キーワード: vaporization, first principle, impact, heterogeneous, phase equilibrium, silicate  
Keywords: vaporization, first principle, impact, heterogeneous, phase equilibrium, silicate

## 月面の複雑クレーターの衝突メルト分布からみる中央丘形成のタイムスケール Timescale of the central peak formation suggested by impact melt distributions within lunar complex craters

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**Introduction:** There have been many studies on impact cratering, but the formation process of complex craters with central peaks has not been understood well. The timescale for the rise of central peaks has been discussed on the base of observation of the terrestrial impact structures whose impact melt sheets surround the central uplift [1, 2]. However, recent studies suggest that there seems to be smooth surface material not only on the floors but also on the central peaks in several lunar craters, suggesting an impact melt [3, 4]. But there is little description that how impact melts extend on the central peaks. In this study, we analyzed both occurrences and the composition of impact melts on the central peaks of two relatively fresh lunar complex craters, Jackson (22N, 197E, 71km diameter) and Tycho (43S, 11W, 85km diameter), in attempt to constrain cratering formation.

**Method:** Each mineral or impact melt exhibits unique spectral absorption depending on their compositions. We used the nine spectral bands data (415-1550nm) of the Multiband Imager (MI) on SELENE [4] to estimate mineralogy by comparing with the data from the RELAB Spectral Database (Apollo samples) [5]. Topographic data was also derived from MI. In addition, we used Lunar Reconnaissance Orbiter Camera (LROC) image data whose resolution is 0.5m per pixel [6] to identify impact melts with flowing structures or droplets.

**Results:** Based on the MI spectral and topographic data, there are primarily three zones on the central peaks: the steepest slope zones with the plagioclase spectral absorption pattern, the intermediate slope zones with the pyroxene pattern, and the gentler zones with the impact-melt-glass pattern like floor-melt pattern. There is no clear boundary of absorption patterns between pyroxene and melt-glass zones, but they change continuously.

LROC data revealed smooth surfaced melt patches, melt lobes, and cooling cracks on the central peaks as well as in the floors and on the wall terraces in both of Jackson and Tycho, and there was no droplet pattern. Many of these melt-related features were found in the zones which have melt-glass spectral pattern and were also observed in the pyroxene zones.

**Discussion and Conclusions:** The extent of the melting features observed by LROC and the MI spectral data of the two craters demonstrate that there are impact melts on the central peaks. Since impact-melt-glass zones and pyroxene zones exhibit spectral continuities and melting morphologies, we consider that both of these zones are impact melt origin. Therefore, the central peaks uplifted from under the impact melt sheets because massive, homogenous melts covered the peaks, and there are no droplet features.

Melosh and Ivanov (1999) explained that central peaks had formed before impact melt sheets solidified, since melt sheets extend around the peaks [2]. This study, however, exhibits the impact melts on the top of the central peaks. Therefore, we consider that central peak formation of craters of these size are not before melts solidification but almost same timescale within a few minutes.

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キーワード: 衝突クレーター, 衝突メルト, 中央丘, 月, かぐや

Keywords: impact crater, impact melt, central peak, moon, SELENE

## 蛇紋石の衝撃回収実験と衝撃脱ガスプロセス Impact water release mechanism of antigorite

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蛇紋石は隕石、特に炭素質コンドライト中に豊富に含まれ、隕石衝突や海洋プレート沈み込みによる温度の上昇により脱水反応を起こす。そのため、地球に飛来した隕石中に含まれていた蛇紋石の脱水反応が地球の海洋形成や大気形成に大きく関わった重要な物質と考えられている。そのため、蛇紋石の衝撃実験は数多く行われている中でもマーチソン隕石中のサーペンティンに関する実験結果では、約10~30GPaまでの衝撃圧力では一部が分解し、36GPaで完全に分解するという結果がでている。このような衝突による脱水反応で脱水メカニズムを定量化する為に、本研究は粉末試料を用いて、試料密度1.6-2.0 g/cm<sup>3</sup> (空隙率24-40%)、衝撃ピーク圧力20-35 GPaで行なったので、その結果を報告する。いるも

衝突実験は一段式火薬銃を用いて、アンティゴライトの粉末を金属試料容器に封入し、衝撃回収実験を行った。回収試料は光学顕微鏡観察、粉末X線回折(XRD)法、分析透過電顕観察(TEM, EDS)、熱重量示差熱分析(TG-DTA)で調べた。

回収試料容器は(i)密閉したまま回収できたものと、(ii)容器の衝突面に開口部ができたが試料は回収できたもの、(iii)容器底(衝突面)が破裂して試料が回収できなかったものに分けられた。回収できた試料にかかった圧力は約20~32GPaだった。XRD分析の結果、20~25GPaの圧力を受けた試料はほとんど蛇紋石のまま残っており、約30GPa圧力を受けた試料はほとんどがフォルステライトとエンスタイトに分解していることがわかった。約30GPaの圧力を受けた試料のうち、試料粉末密度が高い試料を用いた場合開口部が存在している試料は開口部がなかった試料に比べ、分解が進んでいなかった。TG-DTAによる分析の結果、いずれの試料も約550℃から脱水反応による質量欠損が確認された。衝突による質量欠損は、20~25GPaの圧力を受けた試料は1%程度しか起こっておらず、約30GPaの圧力を受けた試料は約6%起こっていたことがわかった。約30GPaの圧力を受けた試料のうち、密度が低い試料はサーペンティンの脱水反応とは異なる重量変化質量欠損が見られ、サーペンティンは衝突でほとんど分解していた。TEM観察では試料容器の状態に違いがあるものを観察し、XRD、TG-DTAでは変化が見られなかった約20~25GPaの圧力を受けた試料の違いを明らかにした。容器に開口部がない容器内の試料には、開口部がある容器内の試料に対してアモルファス物質が多かった。しかし、開口部のある容器内の試料からは開口部のない容器内の試料には見られなかった発泡の跡が残った粒子が観察された。観察された試料はいずれも衝撃により細粒化していることが観察された。特にアモルファス物質は蛇紋石に比べると細粒なものが多く観察された。光学顕微鏡の観察では、衝撃により細粒化が起こっていることが明らかになり、また衝撃圧力の増加に伴い粒子はより細粒化していくことがわかった。

これらの結果から、蛇紋石の粉末試料は20GPaですでに分解が始まっており、23~32GPaの圧力で大きく分解が進むことがわかった。空隙率の少ない試料のアンチゴライトに対する自由空間中で分解する状態に近い条件での同様な実験結果と比べて、大きな変化はなく、衝撃圧力が分解の重要なパラメータであることを示している。これらの実験結果は、地球を含む惑星の水の起源を理解する手掛かりになるだろう。

## 隕石およびインパクトに含まれるマスクェリナイトのカソードルミネッセンス Cathodoluminescence of maskelynite in meteorite and impactite

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Maskelynite is an important material in planetary sciences to interpret shock metamorphic effects on impactite and meteorite. Recent scientific interests, therefore, focus on the formation processes of maskelynite by shock metamorphism, but it has been uncertain whether maskelynite is produced by shock-induced amorphization of plagioclase in solid-state reaction or by quenching from shock-induced dense melts of plagioclase at high-pressures. Cathodoluminescence (CL) spectroscopy can reveal crystal-chemical properties for the existence and distribution of defects and trace elements in materials with high-spatial resolution, which should be more informative to shock-induced minerals. This technique is expected to clarify a formation process of maskelynite from feldspar. In this study, CL analysis of maskelynite and K-rich feldspar glass in impactite and meteorite, as well as diaplectic glass derived from shock experiment for feldspars has been conducted to interpret shock-induced effects on a glassification of the feldspar.

Maskelynite and K-rich feldspar glasses originated from K-feldspars (K-feldspar glass) in amphibolite from Ries crater and in Martian meteorites of Dhofar 019, Shergotty, Zagami and NWA 2975 and lunar meteorite of NWA 4734 were employed for CL measurements. Single crystals of sanidine from Eifel, Germany, albite from Minas Gerais, Brazil and andesine from Bekily, Madagascar were selected as starting materials for shock recovered experiments at pressure of 40.1 GPa. Synthetic hollandite-KAlSi<sub>3</sub>O<sub>8</sub> and meteoritic Na-lingunite from Y-790729 were analyzed as reference materials to compare their CL data with those of the feldspar glasses.

CL spectra of maskelynite and K-feldspar glasses in impactite and meteorites consist of emission bands at 330 and 380 nm. Similar UV and blue CL emissions are also recognized in CL spectra of diaplectic glasses derived from the shock recovered sanidine, albite and andesine. The deconvolution of CL spectra in the UV-blue spectral region for maskelynite, K-feldspar glass and diaplectic glasses originated from shock experiment indicates Gaussian components at 3.88 and 3.26 eV, which have been undetectable in the unshocked feldspars. The emission components are, therefore, characteristic CL signals of maskelynite, K-feldspar glasses and diaplectic glass derived from the shock recovered feldspars. CL spectra of the hollandite-KAlSi<sub>3</sub>O<sub>8</sub> and Na-lingunite also show emission bands at 330 and 380 nm, which can be deconvoluted into the components at 3.88 and 3.26 eV. These emission intensities are appreciably higher than those of maskelynite, K-feldspar glass and diaplectic glass obtained from shock experiment. This might be responsible for octahedral coordination of all Si and Al atoms in the former and some of them in the latter. The facts imply that the emission components might be assigned to shock-induced defect centers in the Al and Si octahedra produced at high pressure. Furthermore, diaplectic glasses from disordered feldspar tend to exhibit higher intensities of the components at 3.88 and 3.26 eV than those from ordered feldspar at same shock pressure, possibly arising from a difference in the transition shock pressure into diaplectic glass among the feldspars. Accordingly, the CL signals can be applied as an estimation method for the degree of Si-Al order in the original feldspar affected before shock impact.

CL images of the lunar meteorites revealed that the maskelynite contacted with or located near melt pockets has a dull CL emission compared to those far from ones. This might be explained by either an elimination of the shock-induced defect centers in diaplectic glass by annealing or a difference in the formation process between dull and bright CL areas, that is, diaplectic glass and glass quenched from a shock-induced dense melt at high pressure.

キーワード: カソードルミネッセンス, マスケリナイト, 隕石, インパクト, 衝撃実験, リンガナイト

Keywords: Cathodoluminescence, Maskelynite, Meteorite, Impactite, Shock experiment, Lingunite



## オーストラリア、クイーンズランド州で発見されたL6コンドライト中ショックベインの組織解析および高圧鉱物解析 High-pressure phase analyses in shock-melt veins: New L6 chondrite in Queensland, NE Australia

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We investigate the high-pressure mineral phases in the shock-induced melt veins in new L6 chondrite obtained from Queensland in NE Australia. The preliminary research shows that the shock veins contain a number of high-pressure phases including ringwoodite, majorite, akimotoite, hollandite-structured plagioclase, which are fragments of the solid-state transformation of chondrite matrix. We conducted petrographic observations and laser-Raman micro-analyses for high-pressure mineral phases in/adjacent the melt veins of new chondrite to estimate the pressure- and temperature- conditions during shock event. The melt-veins show three distinct textures corresponding to distance from host chondrite; 1) vein edges 30-um-wide show mineral assemblage of majorite + ringwoodite + akimotoite with minor rounded metal-sulfide, 2) the middle of the vein 730-um-wide contains majorite + magnesiowustite with irregular-shaped metal-sulfide, 3) the outer rim of the melt vein consists of glass which can represent silicate melt under high-pressure and temperature conditions. These distinct differences of texture and constituent indicate heterogeneity of quench rate in the melt vein. Although the mineral assemblages in the vein edge and centre are distinctly different, the pressure range of both assemblages are consistent with crystallization from similar pressure conditions. The matrix in the vein edge crystallized at about 23-25 GPa and in the vein center crystallized at about 21-25 GPa. The estimation of crystallization pressure suggests that silicate melt with high-pressure phases in the vein quenched and consolidated during pressure pulse remained.

キーワード: ショックベイン, L6 コンドライト, レーザーラマン分光分析  
Keywords: Shock-melt vein, L6 chondrite, laser-Raman spectroscopy