Tissint is a Rosetta stone deciphering Noachian magmatic activities and dynamic events in Mars young history

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Tissint is a new witnessed Martian meteorite. NWA 6162 is a new Martian meteorite find. Both are Al-poor ferroan basalts and classified as shocked phric and depleted shergottites. An array of numerous thin shock-melt veins and few thick shock-melt veins pervasively intersect Tissint each containing high-pressure assemblage. Shock features in Tissint could tentatively be assigned to three dynamic episodes on Mars with distinct textural settings, abundance and compositions of the high-pressure inventories.

The first dynamic event induced total melting of feldspar and its quenching at high-pressure to maskelynite glass along with liquidus jadeite, latter confirmed by the characteristic Raman analysis. Pervasive melting of pyroxene, pyrrhotite and titanomagnetite also took place at this episode as deduced from the spatial relationships. Acicular jadeite crystals grew on the pyroxene surface into the maskelynite liquid at high-pressure. Textural and spatial relationship of the maskelynite pools and the bordering jadeite suggests that jadeite was quenched from the plagioclase melt at P: 10-19 GPa and T: 2000 degree. This dynamic event entirely destroyed the original igneous texture and reset the radiometric age at the impact-melting episode.

An array of thin shock-melt veins fan through the whole Tissint. They penetrate Tissint along pyroxene grain boundaries and cut through the jaedite bands. An assemblage of idiomorphic liquidus high-pressure majorite-pyropes and magnesiowustite fill these shock melt veins.

Another type of shock-melt veins that cross cuts pyroxene contains considerably crushed, fragmented and mobilized majorite-pyropes + magnesiowustite grains. Fragmentation and mobilization could have probably taken place in a later dynamic or more likely a Martian tectonic event subsequent to the first vein formation episode.

Fayalite-rich rims of the originally zoned olivine partly inverted to polycrystalline ringwoodite either in coarse ringwoodite domains in the originally fayalite-rich rims or in polycrystallite aggregate in the original olivine suggesting formation by incoherent olivine-ringwoodite phase transition. The Raman spectrum also shows several original olivine crystals adjacent to shock-melt veins were shock dissociated to a fine-grained assemblage of MgSiO\textsubscript{3} perovskite + magnesiowustite. Some olivine grains entrained in the thick shock-melt veins of NWA 6162 depict dissociation textures to MgSiO\textsubscript{3} perovskite + magnesiowustite. This strongly suggests that the olivine dissociation took place at equilibrium peak-shock pressure slightly overstepping 25 GPa and at T above 700 degree. The three deciphered dynamic events on Tissin, and NWA 6162 lithologies entirely erased their igneous integrities.

Tissint and NWA 6162 share many of the encountered pervasive shock-melting effects and high-pressure phase transformations with other phric and basaltic shergottites, unfortunately not recognized by numerous Mars scholars advocating for several volcanic eruptions younger than 575 Ma that is discrepant with the dynamic induced effects documented by us. We cast considerable doubt on the radiometric ages shorter than 575 Ma reported in the past 39 years to be the igneous crystallization ages, especially when considering their coincidence with a well-established late dynamic event. These short ages resulted from partial or total shock-induced age resetting.
Identification of high-pressure silica polymorphs using Raman and cathodoluminescence spectroscopy

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High-pressure silica polymorphs such as seifertite and stishovite are known in Martian and lunar meteorites and the existence and stability provide constraint on condition of shock pressure and post-temperature in impact event that the parent body have experienced. Transmission electron microscopy and Raman spectroscopy have been attempted to identify post-stishovite, whereas it was not successful to determine the structure due to potential vitrification or transition into other phase by the irradiation. Although cathodoluminescence (CL) spectroscopy has been also conducted, no characteristic signal was obtained from post-stishovite. Only XRD analysis allows us to identify the structure, where silica minerals are excavated with a focused ion beam (FIB) system from meteorite. Therefore, it is necessary for identification of micron-order high-pressure silica polymorphs in precious extraterrestrial materials to develop a new method without sample preparation. In this study, Raman and CL spectroscopy has been performed for synthetic and meteoritic silica minerals, the results of which can identify the polymorphs with high-spatial resolution as nondestructive analysis.

The block pieces of silica grains in Zagami, NW A2975 and NW A4734 meteorites, excavated with FIB system, were identified as seifertite, stishovite and cristobalite by a synchrotron X-ray at Spring-8 BL-10 and were employed for Raman and CL spectroscopy. Synthetic seifertite and stishovite were also analyzed as reference materials to compare their CL and Raman data with meteoritic silica polymorphs.

Reflected-light microscopy and backscattered electron image of synthetic seifertite show numerous polycrystalline grains (<50 micrometers in diameter) with two orthogonal sets of bright and dark lamellae. Wedge-shaped silica grains in the meteorites also display the tweedlike internal microstructure and are surrounded by radiating cracks extended from the surface to the neighbor maskelynite or clinopyroxene.

Raman spectra of synthetic seifertite consist of pronounced peaks at 380, 515, 564, 739 and 796 cm⁻¹ and weak peaks at 401, 496, 539, 606 and 749 cm⁻¹, of which the Raman shifts and relative intensities are corresponding to those calculated within the density-functional perturbation theory for seifertite. Similar Raman peaks are also obtained from silica grains in the meteorites, implying characteristic signals of seifertite. Synthetic and meteoritic seifertite has the distinct Raman peaks after the prolonged laser beam, X-ray and electron irradiation. Although seifertite was considered to be highly unstable phase and therefore the post-shock temperature of meteorite containing seifertite was supposed to be relatively low, it might survive post-shock thermal history with a higher temperature than the expected.

CL spectra of synthetic and meteorite seifertite show emission bands at 330 and 380 nm in the UV region, which can be deconvoluted into emission components centered at 3.79 and 3.25 eV. The peak wavelengths are distinct from those obtained from other silica polymorphs such as stishovite (3.15 and 3.04 eV) and cristobalite (3.02 and 2.63 eV). CL images of synthetic seifertite exhibit polycrystalline grains with bright rim and vein-shaped luminescent interior on dull background, which may be caused by formation and elimination of lattice defect due to high pressure and dynamic recrystallization. The components, therefore, may be assigned to pressure-induced defect center. The emission intensities of the components centered at 3.79 and 3.25 eV appear to depend on the inferred shock pressure on the meteorites reported by previous studies and should be closely related to the defect density. Therefore, CL and Raman spectroscopy enables identification of silica polymorphs with high-spatial resolution and without destruction, and provides valuable information on impact history concerning shock pressure and post-temperature.

Keywords: Raman spectroscopy, Cathodoluminescence, High-pressure silica polymorphs, Seifertite, Stishovite, Meteorite
IN SITU ISOTOPE ANALYSES OF ORGANIC CARBON FROM THE TISSINT MARTIAN METEORITE: EVIDENCE FOR A BIOGENETIC ORIGIN

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Introduction: Exploration for paleoenvironment and possible existence of life on Mars are the main goals of Mars missions. Martian meteorites, the only available rocks from Mars, supply us with a unique chance to study these issues using various sophisticated instruments. Tissint is a new witnessed Martian meteorite fall. The unique fresh samples of Tissint are critically important for study of organic compounds in Martian meteorites, since terrestrial contamination is a very serious issue. Tissint is an olivine-phyric shergottite, consisting mainly of olivine phenocrysts, maskelynite (shocked glass of plagioclase) and pyroxenes with minor chromite, ilmenite, sulfide and apatite [1,2]. The meteorite has been heavily shocked, as indicated by presence of shock-melt veins and pockets, maskelynite and various high-pressure assemblages [2,3]. At least 3 shock events were recognized in Tissint [3]. Here we report discovery of organic carbon in this meteorite and the in situ element and isotope analyses. Our observations favor for a biogenic origin.

Results: The organic carbon has two petrographic settings, most fully filling fractures and cleavages in olivine and pyroxenes and a few enclosed in the shock-melt veins. Laser micro-Raman analysis shows that the organic carbon is similar to kerogen. Furthermore, a sharp peak at 1327 cm-1 was detected in some organic carbon inclusions in the shock-melt veins, indicative of formation of diamond by a shock event. The organic carbon of both petrographic settings has been analyzed with the Cameca NanoSIMS 50L. The elemental ratios of H, N, O, S, P and Cl to C of the organic carbon are comparable with the working reference of coal, but distinctly higher than the graphite standards, confirming that the organic carbon is a kerogen-like matter. Except for 4 grains with normal H isotopes, all other 9 analyses are highly D-enriched (deltaD= 324-1183 permil). The organic carbon is characteristic of light C isotopes, with delta13C values of -13.0 - -33.3 permil. The N isotopes are normal within the analytical uncertainty.

Discussion and Conclusions: The presence in the shock-melt veins and the D-enrichment of the organic carbon demonstrate a Martian origin. Furthermore, the clear petrographic settings of the organic carbon evidently indicate depositing from organic fluids, after eruption of Tissint basalt and the following shock event that produced abundant fractures. The organic carbon can not be magmatic in origin claimed by previous work, which was based on its presence in mis-described "magmatic inclusions" [4]. The organic carbon is either unlikely derived from chondritic debris that impacted on Mars, because kerogen is an insoluble organic matter. The significantly light C isotopes of the organic carbon suggest a biogenic origin. Our observations are the currently available evidence for possible biotic activity on Mars.


Keywords: Mars, meteorite, Life, organic carbon, isotopes, SIMS
Evidence for a dynamic event recorded in HED meteorites

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It is expected that HED meteorites originate from one of the largest asteroids in the solar system, 4 Vesta. Recent Dawn mission operated by NASA also supports the prediction [1][2]. Dawn mission clearly revealed the existence of many craters on 4 Vesta, which are the records of heavy meteorite bombardments. The existence of a high-pressure polymorph in a shocked meteorite is a robust evidence for a dynamic event on its parent-body (e.g., [3][4]). A high-pressure polymorph can be used for estimating the magnitude of a dynamic event (e.g., [5][6]). Some previous studies propose that 4 Vesta might suffer from late heavy bombardment (LHB) as well as the moon [7]. However, a high-pressure polymorph has not been found in HED meteorite so far.

We got one of eucrite samples, Bereba to clarify a dynamic event occurred on 4 Vesta using a high-pressure polymorph. Present Bereba sample has several shock-melt veins, implying that it was heavily shocked. Accordingly, we investigated Bereba using Raman spectroscopy, FEG-SEM, synchrotron(s)-XRD and FIB-TEM techniques to clarify a record of a dynamic event occurred on 4 Vesta.

We focused our interest on silica phase in this study. Raman spectroscopy analyses show that the silica grains in the host-rock of Bereba are cristobalite, tridymite and quartz. Most quartz grains entrained in the shock-melt veins are partly replaced with coesite. BSE images show that silica grains entrained in or adjacent to the shock-melt veins have network-like and/or lamellae-like textures. Raman spectroscopy, s-XRD analyses and TEM images indicate that such silica grains include coesite, stishovite and silica glass along with quartz.

We found the high-pressure polymorphs of silica from HED meteorites for the first time. The existence of stishovite indicates that pressure condition recoded in Bereba should be 8 GPa at least based on a phase diagram obtained from static high-pressure and high-temperature synthetic experiments [8]. Two giant impact basins on 4 Vesta are depicted by Dawn mission. Crater chronology obtained by Dawn mission reveals that the giant impact basins were formed around 1.0 Ga ago [9]. Its fragments became Vesta family in asteroid belt, and a part of them fell into the Earth as HED meteorites. The existence of high-pressure polymorphs in Bereba may support the giant impact occurred on 4 Vesta.

References:
Iron valences of plagioclase from cumulate eucrites Y-75011 and surface eucrite Y 980433 as inferred from micro-XANES an

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The HED (Howardites, Eucrites and Diogenites) meteorites are the largest group of achondrites and are widely believed to have originated on 4Vesta. Eucrites are mainly composed of pyroxene and plagioclase, and are considered to have been derived from the crust of the asteroid. Recently, the Dawn spacecraft observation has revealed the existence of a metallic core in Vesta and that it experienced early differentiation in the solar system. In this way, Vesta is an important example of early differentiation in the solar system, and thus, HED meteorites may offer substantial information to understand igneous differentiation on Vesta.

The oxidation state of magmas is one of the most significant factors in controlling mineral crystallization and is relevant to the redox state of the parent body. In our previous study, we estimated redox states of six eucrites by using synchrotron radiation (SR) Fe XANES measurement of plagioclase. This study reveals that the Fe³⁺/(Fe²⁺ + Fe³⁺) ratios of plagioclase in cumulate eucrites are higher than those of surface eucrites, which indicates that the deep crust of Vesta was a relatively more oxidized environment. However, this result needs to be reassessed by analyzing minimally metamorphosed samples because most eucrites have experienced significant degrees of thermal metamorphism.

In this study, we focused on surface and cumulate eucrites that were not affected by annealing, in order to compare the XANES results with our previous study. We analyzed thin sections of surface eucrite clast in Y-75011 and cumulate eucrite Y 980433. We first carefully observed them by optical and scanning electron microscopes, and analyzed them by electron microprobe in order to select representative plagioclase grains for SR Fe-XANES. SR Fe-XANES was performed at BL-4A, Photon Factory, KEK, Tsukuba, Japan to measure Fe³⁺/(Fe²⁺ + Fe³⁺) ratios of plagioclase. The SR beam size was about 5 x 6.5 micro meter. The XANES analyses for standard kaersutites with known Fe³⁺/(Fe²⁺ + Fe³⁺) ratios shows a linear relationship between centroid energy position of XANES pre-edge spectra and the Fe³⁺/(Fe²⁺ + Fe³⁺) ratio. Based on this linear relationship, we estimated the Fe³⁺/(Fe²⁺ + Fe³⁺) ratio of samples.

Optical and scanning electron microscope observations show that all samples are mainly composed of pyroxene and plagioclase. The plagioclase abundance in Y-75011 is about 30 vol. % and Y 980433 is about 50 vol. %, respectively. All plagioclase grains analyzed display clear pre-edge peaks in the obtained XANES spectra. The Fe³⁺/(Fe²⁺ + Fe³⁺) ratio of Y-75011 is estimated to be 0.10-0.14 and Y 980433 is 0.48-0.58, respectively.

The Fe³⁺/(Fe²⁺ + Fe³⁺) ratios of plagioclase in two eucrites studied show contrasting values (0.12 vs. 0.52). The Fe³⁺/(Fe²⁺ + Fe³⁺) ratio of the Y-75011 surface eucrite is consistent with our previous study of other surface eucrites (Padvarninkai, ALH 76005, Piplia Kalan and Petersburg) in its low Fe³⁺/(Fe²⁺ + Fe³⁺) ratio. Similarly, the Fe³⁺/(Fe²⁺ + Fe³⁺) ratio of the Y 980433 cumulate eucrite is consistent with our previous study of other cumulate eucrites (EETA 87520 and Moore County).

This study demonstrated that the Fe³⁺/(Fe²⁺ + Fe³⁺) ratios of plagioclase from surface and cumulate eucrites have not been affected by later thermal metamorphism, and they are likely to reflect the redox state of the crystallization environment. Thus, we suggest that there was a heterogeneous redox environment in Vesta, where surface areas were more reduced than the crust and deep interior.

There are two possible scenarios for explaining these features. One is that the oxidizing environment of Vesta's deep crust was caused by water in Vesta’s interior. The other possibility is that the oxidized environment was originally related to the early differentiation of Vesta. Although we cannot determine which model is more likely at present, this study at least reveals Vesta’s deep crust shows a global oxidized environment.

Keywords: XANES, Eucrite, Vesta, Plagioclase
Formation of Ca-rich Plagioclase in Meteoritic and Lunar Crust and its Decomposition with Reference to Earth Environment

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In some Antarctic LL chondrites, we found the first evidence of a product of partial melting of the primitive solar materials in Y-74160 [1]. This andesitic material with albite and diopside assemblage, was found in the silicate inclusions in the IAB [2] and IIE irons [3]. In a part of crystalline granulitic clasts in the Y-981971 and Y-793214 LL [4], we found a sizable grain of albite in recrystallized mafic silicates. The presence of the andesitic material suggests that even the primitive solar system material shows evidence of extensive processes of melting and metamorphism. The mineralogy of Vesta, based on data obtained by the Dawn spacecraft's spectrometer [5], is consistent with howardite-eucrite-diogenite (HED) meteorites. Spectrally distinct regions include the south-polar Rhea silvia basin, which displays a higher diogenitic component. This is broadly consistent with our layered crust and magma-ocean models [6]. The unusually low Na in A881394 granuritic eucrite [7] suggests that Na may have been lost by catastrophic bombardment during magma ocean stage to produce Ca-rich plagioclase.

Based on the Th map made by KGRS, Kobayashi et al. [8] showed that the lowest Th regions in the lunar farside occurs north of the equatorial region and noted that the region (FS-DJ region) well correspond to the high Mg number (Mg#) region measured by SP, of the farside crust [9] and consists of rocks that crystallized from less-evolved magma than the nearside crust. The Th concentration of Dhofar 489 [10] are lower than those of the lowest-Th region. Anorthosites composed of nearly pure anorthite (PAN) at many locations in the farside highlands and a map of the Mg#s [9] also showed that the region around the FS-DJ basin is consistent with the Mg#(70 to 76) of the magnesian anorthositic clast in Dhofar 489 [10]. Lunar Magma Ocean (LMO) model deduced from the Apollo samples is not able to explain such dichotomy of the Moon. Convection model [9], or a Procellarum basin impact by Nakamura et al. [11] may explain the problems resulted from the above new findings. A large impact, which excavated a basin of the farside might have produced granulites at a large basin or in deep ejecta of a smaller impact. We investigated a process of decomposition of Ca-rich plagioclase similar to lunar ones by geochemical weathering with fulvic acid. The Ca ion released from plagioclase can be used to fix carbon dioxide as calcite as in oolites. This information is useful for reducing carbon dioxide from the atmosphere on the Earth.


Keywords: Lunar farside, lunar meteorites, lunar crust, Kaguya mission, Vesta, LL chondrite.
Petrology and mineralogy of a new polymict ureilite Yamato 983890

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Introduction

Ureilites are the second largest group of achondrites. They are largely divided into two types: monomict and polymict. More than 90% of ureilites are monomict ureilites, whereas polymict ureilites are relatively rare with only 23 approved meteorites [1]. Polymict ureilites are polymict breccias composed of lithic clasts and mineral fragments of various lithologies, some of which are unlike monomict ureilites [2-5]. Therefore, polymict ureilites provide valuable information about igneous and collisional processes on ureilite parent bodies, which cannot be extracted from monomict ureilites. Yamato (Y-) 983890 is a recently classified polymict ureilite [6]. In this study, we conducted careful petrographic observations on this new polymict ureilite.

Results and Discussions

Y-983890 consists of lithic clasts and mineral fragments which show a large variety of lithologies. Most of them are monomict ureilite-like materials, but some are not. The non-monomict ureilite-like materials include feldspathic clasts, dark clasts (carbonaceous chondrite-like), a chondrule/chondrite fragment, and others.

Monomict ureilite-like clasts/mineral fragments

The monomict ureilite-like clasts/mineral fragments in Y-983890 consist of coarse-grained (up to 1 mm) olivine and/or pyroxene with interstitial dark carbonaceous materials and/or graphite. Olivine has a chemical composition of Fo74−96 with high CaO (0.26-0.46 wt%) and Cr2O3 (0.47-0.91 wt%) contents. Pyroxene is mainly pigeonite (En72−87Wo5−11) and orthopyroxene (En79−85Wo2−5), but minor augite (En55−64Wo33−39) is also present. Chemical compositions of olivine and pyroxene, and Fe/Mg-Fe/Mn relations of olivine are consistent with those of monomict ureilites [4, 7].

Feldspathic clasts

Since monomict ureilites do not contain feldspar, lithic clasts containing feldspar are considered to be of non monomict-ureilite origin. We identified several distinct feldspathic clasts. They show different igneous textures and chemical compositions of constituent minerals (feldspar and pyroxene). Most feldspar has albitic compositions (Ab80−87Or3−8), but more An-rich one (Ab95Or6) is also present in a clast. Pyroxene is mostly augite (En40−62Wo21−38) and some clasts contain enstatite (En100, En97Wo3) and pigeonite (En33Or15). These feldspathic clasts could be basaltic counterparts complementary to monomict ureilites (=ultramafic residues or cumulate).

Dark clasts (carbonaceous chondrite-like)

Y-983890 contains a lot of dark clasts. They mainly consist of fine-grained phyllosilicate-rich matrices with variable amounts of opaque minerals such as magnetite and sulfides. Magnetite occurs as spherical or framboidal grains, or as irregular aggregates. Sulfides such as pyrrhotite and pentlandite occur as euhedral crystals or anhedral polycrystalline aggregates. These dark clasts mineralogically resemble the matrices of CI carbonaceous chondrites.

Chondrule/chondrite fragment

A chondrule fragment was identified in Y-983890. It shows a barred olivine chondrule texture, consisting of barred olivine crystals (Fo79−82) with interstitial devitrified mesostasis with albitic composition (Ab83Or9). The chemical composition of the olivine is in the range of that of H chondrite

The dark clasts and the chondrule/chondrite fragment are considered to be fragments of impactors collided with ureilite parent bodies.

References


Keywords: ureilite, polymict, breccia, Yamato (Y-) 983890
Diamond in ureilites: Formation mechanisms and roles in planetary processes

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Diamond was found in the Novo Urei meteorite, one of typical ureilites, first in meteorites in 1888. Lonsdaleite, hexagonal polymorph of diamond, was found in the Canyon Diablo iron and the Goalpara ureilite first in nature. So far, mineralogical properties of carbon minerals in ureilites have been only roughly determined by using acid-treatment residues because they exist in small quantities in ureilites. Then, the origin of diamonds in ureilites has been controversial.

We observed carbon minerals under an optical microscope under a reflected light and obtained micro Raman spectra of them in polished thin sections. X-ray powder diffraction patterns were obtained from the carbon grains directly taken out of polished thin sections and picked up from disaggregated ureilite samples. Carbon minerals in these carbon grains were also directly observed by TEM and SEM.

In weakly shocked ureilites, diamond occurs with a granular shape of up to a few micron meters in size and shows sharp x-ray diffraction lines and sharp Raman bands at 1332 cm\(^{-1}\), suggesting well-crystallinity of them. Lonsdaleite was not found in weakly shocked ureilites. In heavily shocked ureilites, diamond occurs together with lonsdaleite with a platy shape of up to a few tens micron meters in size and shows very broad x-ray diffraction lines and broad Raman spectra.

Selected area electron diffraction analyses and high resolution TEM observations of carbon grains from the heavily shocked Goalpara ureilite reveal the relative crystal-axes orientations between graphite (Gr), lonsdaleite (Lo) and diamond (Di) as (001)\(_{Gr}\) \(/\/ (100)\_{Lo}\) // (111)\(_{Di}\), [210]\(_{Gr}\) // [001]\(_{Lo}\) // [2-1-1]\(_{Di}\) and (1-20)\(_{Gr}\) // (-120)\(_{Lo}\) // (0-22)\(_{Di}\). The shapes of diffraction spots in the SAED patterns reveal that the transformation of graphite to lonsdaleite and diamond is initiated by sliding of hexagonal carbon planes of graphite along the [210] of graphite structure. These results suggest that lonsdaleite and diamond in heavily shocked ureilites formed directly from graphite through boat-type buckling and chair-type puckering of hexagonal carbon planes of graphite, respectively.

A SEM image of the surface parallel to the basal plane of original graphite from the weakly shocked Y-8448 ureilite is shown in Figure 1. In the figure, triangular crystal faces were observed. BSED patterns reveal that the triangular faces are correspond to (1 1 1) crystal planes of diamond. Such forms of diamond clearly reveal that the diamond crystals have grown on the melt and strongly suggest that diamond in the weakly shocked ureilites was formed through catalytic processes.

In the planetary processes of the ureilite parent body, smelting is thought to be an important process by which the chemical structure of the body was controlled. Ferrous silicates are vulnerable to smelting in the presence of graphite at magmatic temperatures by generic reactions of the sort:

\[
\text{FeO(silicate)} + C(\text{graphite}) = \text{Fe(metal)} + \text{CO}. \quad (1)
\]

On as much as gas of large molar volume appears only on the right-hand side of this reaction, the reaction is expected to be strongly pressure sensitive. Smelting is suppressed at elevated pressure and promoted as pressure falls\(^2\). Then, mg\# of olivine is controlled by the depth at which it has been crystallized. In order to confirm the reaction (1) and the smelting process in the ureilite parent body, it is important to know the relation between mg\# of silicate and the modal abundance of carbon. The modal abundance of original graphite in ureilites was obtained under an optical microscope (Figure 2). Figure 2 shows that the modal abundance of carbon decreases with the increase of mg\# and directly confirms the reaction (1) and the smelting process in the ureilite parent body.


Keywords: ureilite, diamond, lonsdaleite, graphite, transformation
Heterogeneous distribution of noble gases in carbonaceous materials of Shisr 007 Ureilite

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We have characterized carbonaceous materials in Shisr 007 ureilite by multidiscipline techniques for mineralogy and noble gas signatures to gain better understandings of the differentiation process of ureilite parent body and the formation mechanism of carbonaceous materials.

Optical microscope observation revealed that Shisr 007 is an olivine-pigeonite type monomict ureilite. The olivine shows undulatory extinction and planar deformation fractures, corresponding to shock stage S3 (Shock pressure <20GPa). EPMA analysis showed that core composition of olivine (Fo=79) and pyroxene (En=73) in Shisr 007 are close to the average composition of silicates in ureilites and therefore Shisr 007 formed via differentiation process similar to other ureilites.

Diamond, graphite, and compressed graphite, which is an intermediate phase formed during graphite-diamond phase transition, are identified in carbonaceous materials by SR-XRD. Shisr 007 contains a large carbonaceous material (BCM ; 1000 x 1500 microns on a polished section). It has rectangular, blade-like shape.

implying that it was a large single crystal of graphite, as is observed in ALH 78019. Using an edged tool, BCM was separated into small pieces typically 200-300 micron in diameter. A amoeboid-shape carbonaceous materials (ACM; typically 100-400 micron in size) commonly occur and were separated from the polished section with HF/HCl. Individual 17 pieces of the BCM were first measured with Si-std by synchrotron X-ray diffraction (SR-XRD) to determine their diamond abundances. The data show that diamond abundance is roughly proportional to the weight. After the SR-XRD analyses, noble gas compositions of 10 ACMs and 16 BCMs were analyzed by stepwise heating method (600, 1300, 1900, and 2100C) using Pot-pie furnace designed for small sample analysis. In addition, 2 samples of BCMs are measured in 6 steps adding 1000 and 1600C fraction. The ACMs have relatively constant 36Ar contents (30-200 x 10-6ccSTP/g) and 36Ar/132Xe elemental ratios (100-200), while BCMs show a wider range of 36Ar contents (3-400 x 10-6ccSTP/g) and a higher 36Ar/132Xe ratios (150-450). A major part (70-95%) of primordial 36Ar, 84Kr, and 132Xe was released at 1600-2100C fraction. To identify where the carrier of noble gases are, we performed the heating experiment of CVD diamond synthesized by the hot filament method. CVD diamonds were started to decompose at 1600C, confirmed by their Raman spectra and microscopic observation, which is consistent that the main gas carrier phase of Shisr 007 is diamond. However, diamond abundances and gas concentrations did not correlated, indicating that diamonds have variable gas contents: Some diamonds contain large amounts of noble gases, but the other diamonds are almost free of gases. The heterogeneous noble gas compositions of the BCMs and ACMs imply that they have formed from multiple stages of thermal and shock metamorphism.

Keywords: Ureilite, Noble gases
Reduction, oxidation and sulfidation in ordinary, enstatite and R chondrites based on speciation of iron

Timothy Fagan

Speciation of iron plays the pivotal role in distinguishing the H, L, LL groups of ordinary (O) chondrites and O vs. enstatite (E) and R chondrites [1,2]. The variations in Fe-bearing minerals among these chondrite groups reflect variable physical conditions from different locations and times in the inner solar nebula. Most previous work has focused on speciation of Fe between silicates and metals as an indicator of oxygen vs. reduction [e.g., 1,2]. This project considers the role of sulfidation as well as reduction and oxidation in chondrite-forming regions of the solar nebula.

This approach depends on determining the speciation of Fe between silicates, metallic minerals and sulfides (mostly troilite). Data set (1) is based on modes and mineral compositions from thin sections of H, L, LL, E and R chondrites. These include: Ben-sour (LL6, fall); Mt. Tazerzite (L5, fall); Tamdakht (H5, fall); St. Marks (EH5, fall); Lewis Cliff 88180 (EH5, find); Northwest Africa 974 (E6, find); Northwest Africa 753 (R3, find). Meteorite falls and type 5 and 6 chondrites were emphasized in order to minimize heterogeneity of mineral compositions and effects of terrestrial weathering. In Data (1), modes were determined from manual counting of grids overlain on elemental maps, and mineral compositions were determined using a JEOL JXA-8900 electron microprobe at Waseda University. Data set (2) is based on whole-rock wet chemical analyses conducted and compiled by E. Jarosewich [3,4]. We used falls for LL (n = 17), L (n = 57) and H (n = 31) and all of the E (1 fall, 3 finds) chondrites from the Jarosewich compilation. Data set (3) is based on similar whole-rock analyses conducted by H. Haramura of NIPR and compiled by Yanai and Kojima [5]. This data set consists of Antarctic finds (59 LL, 158 L, 162 H, 6 E).

This project also requires an understanding of reactions that transfer Fe between the silicate, sulfide and metal subsystems within whole-rock reacting systems of O, E and R chondrites. A reaction space [6,7] approach was used to identify the main reactions that change mineral abundances in these rocks: (R1) NaAlSi3O8 = NaAlSi2O6 + SiO2; (r2) Mg2SiO4 + SiO2 = 2 MgSiO3; (R3) FeSiO3 = Fe-metal + SiO2 + 0.5O2; (R4) FeSiO3 + 0.5 S2 = FeS + SiO2 + 0.5 O2. R1 does not appear to be important in most chondrites. R2 is very important as it describes variations in abundance of olivine vs. pyroxene, but this reaction occurs entirely within the silicate subsystem. Reduction of Fe occurs with progress on R3, so forward progress on R3 can be estimated from the ratio of metallic Fe to all Fe, and can be used as a monitor of reduction. Likewise, forward progress on R4 can be used as a monitor of sulfidation. In this framework, if R3 = 1, all Fe occurs as Fe-metal; if R4 = 1, all Fe occurs as Fe-sulfide; if R3 = R4 = 0, all Fe occurs as FeO in silicates.

The three data sets all show a wide range of reduction and little variation in sulfidation for O chondrites (R3 from 0 to 0.7; R4 ~ 0.2). E chondrites appear to be more reduced and sulfidized (R3 from 0.7 to 0.8; R4 from 0.2 to 0.3). The R chondrite of this study is oxidized and somewhat sulfidized (R3 = 0; R4 ~ 0.3). Most deviations from these patterns occur in Data (3) and are probably due to terrestrial weathering. Results suggest that an oxidant (or reductant) was independent of sulfur fugacities in the regions where ordinary chondrites formed.


Keywords: chondrites, oxygen fugacity, sulfur fugacity, solar nebula
K-Ca systematics of alkali-rich fragments in LL-chondritic breccias

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**Introduction:** Alkali-rich fragments in LL-chondritic breccias, Kraehenberg, Bhola and Y-74442 are very similar in mineralogy and petrography, suggesting that they could have come from related precursor materials [1,2]. Recently we reported Rb-Sr isotopic systematics of alkali-rich igneous rock fragments in Y-74442 [2]. The extremely high Rb/Sr value (2.58 at 4.429 Ga ago) of this source can be explained by mixing of a chondritic component with an alkali-rich component formed in the early solar nebula. Since alkali-rich fragments in the LL-chondritic breccias are highly enriched in K, we can expect enhancements of radiogenic \(^{40}\text{Ca}\). The decay of \(^{40}\text{K}\) to \(^{40}\text{Ca}\) has not been widely used for dating due to the high abundance of \(^{40}\text{Ca}\) along with the fractionation of Ca isotopes during analysis in the mass spectrometer. Here, we report preliminary results of K-Ca isotopic systematics of alkali-rich fragments in Y-74442.

**Results and Discussion:** The Ca abundances in samples were calculated from their \(^{48}\text{Ca}/^{44}\text{Ca}\) ratios, normalized to \(^{42}\text{Ca}/^{44}\text{Ca} = 0.31221\) [3]. While the Ca abundances in alkali-rich fragments of Y-74442 are almost constant and chondritic (1.3-1.8 x CI), the fragments show enrichments of K (5-15 x CI) [2]. Over time, the enrichment of K in alkali-rich fragments of Y-74442 result in large epsilon \(^{40}\text{Ca}\) values (epsilon \(^{40}\text{Ca} = 2-7\)) relative to other planetary materials [4,5]. The data of Y-74442 fragments yield a K-Ca age of 4.51 +/- 0.23 Ga (2 sigma, MSWD = 3.5, n = 6) for lambda \(^{40}\text{K}\) = 0.5543 Ga\(^{-1}\) [6,7] with an initial \(^{40}\text{Ca}/^{44}\text{Ca}\) = 47.1587 +/- 0.0032 (2 sigma) using the Isoplot/Ex program [8]. Since K-Ca data for one fragment of Y-74442 deviates from the isochron, we exclude the data from the calculation. This age is within error of the previously reported Rb-Sr age of 4.429 +/- 0.054 Ga [2]. We could obtain a mean initial \(^{40}\text{Ca}/^{44}\text{Ca}\) ratio of 47.1597 at 4.429 Ga (the more reliable Rb-Sr age). Then, using the initial \(^{40}\text{Ca}/^{44}\text{Ca}\) value of bulk silicate earth at 4.568 Ga, the source \(^{40}\text{K}/^{44}\text{Ca}\) ratio of 0.00162 for the fragments is obtained. This source for alkali-rich fragments is about 4.5 times higher than that of the LL-chondrite parent body \(^{40}\text{K}/^{44}\text{Ca} = 0.00035\) [9]. It is consistent with the Rb-Sr systematics of Y-74442 fragments [2] and suggesting that the K enrichment may have also occurred by vapor/solid (or liquid) fractionations in the early solar system. A mixture of the alkali component (early nebular condensates) and the ferromagnesian component could reflect flash heating induced by impact on an LL chondritic parent body at least 4.429 Ga ago, and further enrichments of K and Rb relative to Ca and Sr, respectively, could have occurred during this event. The resulting impact-melt rocks could have been fragmented by later impact event(s) and finally incorporated into the Y-74442 parent body.


Keywords: chondrite, alkaline elements, chronology
A primitive mesosiderite NWA 1878

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The silicate part of mesosiderites is similar to HED achondrites. The parent body solidified early. Mesosiderites were located close to the surface of the parent body as evidenced by rapid cooling rates after a reheating event (Delaney et al., 1981) and also by excess neutron fluence (Hidaka and Yoneda, 2011). Hence mesosiderites may remember the early solar nebula environment which was very energetic as suggested by chondrule formation. In fact, mesosiderites were reheated to high temperatures after the mixing of silicates and metal. The heat source of this reheating event is not well established and mesosiderites may have been heated by an external (nebular) heat source. For understanding mesosiderite formation and the reheating event we need to study the most primitive mesosiderites. The following features can be used as criteria for primitiveness. They are plagioclase composition heterogeneity, pyroxene lamellae width, metal grain size and olivine corona development. Plagioclase compositions in mesosiderites are in a restricted range (Delaney et al., 1981). The compositional variation was probably inherited from the precursor materials though it may be partly due to evaporative loss of Na at high temperatures. In either case, the heterogeneity would be reduced during subsequent cooling in a closed system. A wider compositional range could be an indicator for weaker reheating. Plagioclase in NWA 1878 shows the widest range in composition, ranging from An79 to An99. This was measured with SEM-EDS and need to be confirmed by EPMA. Pyroxene lamellae width seems to be a promising criterion because this is not affected by original heterogeneity of brecciated samples. But in order to make this a quantitative criterion, bulk pyroxene composition effects have to be corrected because the exsolution temperature depends on the bulk pyroxene composition. In the case of NWA 1878, pyroxene lamellae are observed only in Fe-rich pyroxenes (Fs38’-Fs43). This suggests relatively rapid cooling, although the exact cooling rate has not been established yet. The metal grain size seems to be a good criterion for relatively primitive mesosiderites which show spheroidal metal grains. The size determination was made by fitting spheroids to spheroidal grains. This procedure is somewhat subjective because grains are not perfectly spheroidal, somewhat sintered with each other. As the grain size grows by metamorphism, the metal shape becomes more irregular and quantitative size determination becomes more difficult. In spite of such difficulties, metal grain sizes could be determined precise enough for the purpose of sub-classification of primitive mesosiderites. The metal size is ~250 micrometer in diameter in NWA 1878 which is the smallest among the mesosiderites in this study. Incipient corona formation around an olivine grain ~2 micrometer in size is observed in NWA 1878. Fe-poor pyroxenes occur close to the olivine, followed by anorthite. Chromites are located farther away in Fe-rich pyroxenes. Many phosphates are found on metals grains facing the olivine. These are in contrast with stage I corona described by Nehru et al., (1980) and Delaney et al., (1981) where chromites are located in a distinct corona layer next to the olivine and many phosphates are also located close to the corona. The locations of chromite and phosphate in NWA 1878 suggest that both Cr and P did not diffuse over long distances during the reheating event. This petrographic feature cannot be quantized, however, and should be used as supporting evidence for primitiveness. Based on the four criteria, NWA 1878 appears to be the most primitive mesosiderites among 7 mesosiderites I observed so far.


Keywords: mesosiderite, reheating, primitive
Origin of igneous clasts with graphite-bearing and graphite-free lithologies found in NWA801 (CR2) chondrite

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Introduction: We found three igneous clasts in a primitive CR2 chondrite, NWA801. The clasts contain eclogitic mineral assemblages (garnet and omphacite), suggesting formation at a high pressure [1]. The origin of the high pressure could be either due to shock loading or static pressure in deep interior of a large planetesimal. We discuss here the origin of the clasts based on mineralogy, bulk chemistry, oxygen isotopes and REE abundances. Preliminary results and arguments are given in [2]. Analytical procedures for oxygen isotopes using a CAMECA ims-1280 ion microprobe at the University of Wisconsin-Madison are given in [3] and those for REE and Ba abundances are briefly described in [2] (also see [4]).

Two lithologies: The igneous clasts have two different lithologies: graphite-bearing (GBL) and graphite-free (GFL). The constituent minerals are olivine, Ca-poor pyroxene, Na-Al-rich pyroxene (omphacite) and garnet, with minor minerals such as graphite (in GBL), phlogopite (in GFL), chlorapatite, Fe-Ni metal, troilite and pentlandite. The mineral assemblages and compositions are similar to those in terrestrial eclogite. The formation condition of the clasts is estimated to be ~3GPa and ~1000C based on a set of conventional geothermobarometers [1].

Bulk chemical compositions of both GBL and GFL are nearly chondritic (not very different from those of CR chondrites). This suggests that the igneous fractionation is not as extensive as that of ureilites.

Phosphate shows very high LREE abundances (140-200 x CI) and gradual decrease from Gd to Lu (down to 30-50 x CI). Garnet shows rapid increase toward HREE with Lu abundance ~100 x CI for GFL garnet (consistent with garnet/melt partition) but only to ~20 x CI for GBL garnet. Omphacite in GFL shows REE abundances of ~1 x CI. The estimated bulk REE abundances for GFL and GBL show almost flat patterns with ~2 x CI and ~1.5 x CI, respectively. This also suggests that the igneous fractionation is not as extensive as that of ureilites.

Oxygen isotopic compositions of olivine and pyroxene are distributed along a slope ~0.6 line with one end near the ureilite field [5] and the other near the CR chondrite field [6]. The GFL data are tightly clustered at the upper-right end of the distribution (delta-18O ~5 permil and delta-17O ~0.7 permil), whereas the GBL data are more scattered along the line (with delta-18O from +2.4 to +4.3 permil and delta-17O from -1.0 to +0.2 permil). There is no particular difference between olivine and pyroxene data.

Discussion: The formation conditions estimated from several geothermobarometers gave consistent results (~3GPa and ~1000C [1]). This suggests that equilibration has been attained among different mineral assemblages. This favors a static high pressure model. However, the REE and oxygen isotope data show noticeable heterogeneity within and/or between the two lithologies. This seems to support a shock-induced high pressure model, though it is not certain if a shock heating event with a rather short heating duration (~10 sec) could produce all the observed features of the igneous clasts. In any case, rather large planetesimals and their disruptions must be required to produce two different lithologies of the igneous clasts, to stick them together, and mix them with chondrules and matrices to form a CR chondrite.


Keywords: CR chondrite, igneous clast, graphite, oxygen isotopes, REE, SIMS
Heterogeneous impact processes and shock scale problem

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Shock processes are time-, space-, and initial state-dependent so that they display complicated and non-equilibrium phenomena. In order to understand them from the meteorites that experienced impacts, it is not so simple as we can image based on the detailed observations of meteorites. We need to develop more models to help us to know the basis of shock-induced chemical, mineralogical, and physical processes of various states of meteorite materials. Heterogeneous conditions generated by shock wave are to be characterized by the initial state of pre-impact body. Local temperature rise due to local energy deposition makes more difficult to interpret the phenomena. We consider some heterogeneous heating mechanism during shock process.

Keywords: Shock processes, Impact, Experiments, High pressure and high temperature