Development of ambient-controlled gas levitation system embedded in tube furnace and its application to chondrule formation

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Chondrules are the most abundant component in chondrites. They are mm-sized round (or irregularly) shaped particles mainly composed of silicates, which formed by the rapid cooling of droplets of molten or partially molten rock in space before they accreted. They show unique and diverse internal micro-textures (e.g., porphyritic olivine, barred olivine, radial pyroxene, etc.), even if they have same bulk compositions. These internal textures, therefore, should reflect not only stating material compositions, but also nebular conditions, such as gas species and their partial pressures, heating and cooling rate. The conditions of chondrule formation, however, remain poorly constrained, because the reproduction of the chondrule formation processes in a laboratory is experimentally difficult, especially in terms of container-less arrangement and reducing (low-fO2) ambient. In the present study, we developed gas-levitation system embedded in ambient-controlled tube furnace in order to reproduce micro-textures of chondrules, and to constrain their formation conditions.

The following is a summary of the newly developed equipment. A vertical tube furnace with a double-helical silicon carbide heating element and an alumina core tube (OD 50 mm, ID 42 mm) is used as a heating source device. An alumina inner core tube (OD 32 mm, ID 26 mm) with a carbon nozzle (blowout hole diameter of 1 mm) at the top is inserted into the outer tube. H2+CO2+Ar mixed gas are separately introduced into the both inner and outer core tubes from a gas port at the bottom, and gas flow rates can be controlled by digital mass flow controllers. The inner tube with the nozzle can move up and down by motor-controlled pantograph, and thereby the seamless switching from a sample exchange positon to a maximum temperature position becomes possible. A levitated sample can be in situ observed by a long focal CCD camera thorough a mirror from the top of furnace. Because thermal radiation light around the heating sample prevents the observation at high temperatures, a dichroic filter that cut >500 nm wavelength light and high power blue (460 nm) LED illumination are installed into the observation optics. Currently, using this system, quenched NaAlSi3O8 glass were successfully collected from 1280 degree Celsius. The developed gas levitation system of the present study show that reducing-gas levitation experiments is a powerful technique to simulate the molten-quenched texture of early solar materials.

Keywords: Chondrule, Gas levitation technique, Crystal growth

Solidification experiments of Fe-FeS melt to estimate the cooling histories of chondrules

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Chondrules are sub-millimeter sized silicate spherules formed by instantaneous heating of solid precursors at the early stage of the solar system evolution [e.g., 1]. In order to constrain the chondrule formation mechanism, it is important to understand the thermal history of chondrules. Crystallization experiments of chondrules have shown that chondrule precursors were heated up to 1800–2200 K and cooled at the rate of 10–1000 K/h [e.g., 2]. The absence of isotopic fractionation of sulfur isotopes in chondrule sulfides indicates that chondrule precursors were heated at the rate of >10^4 K/h [3]. However, there is no tight constraint on the cooling rate of chondrules at lower temperatures (below the solidus of silicates) although it would provide information on formation environments of chondrules. In this study, we focus on eutectic solidification textures of iron and iron sulfides to develop a new cooling speedometer for chondrules.

Powders of Fe metal and FeS were mixed with a ratio close to the Fe-FeS eutectic composition (slightly enriched in S) to prepare starting materials for the experiments. The mixed powder was sealed in an evacuated silica glass tube with graphite, heated at 1400 degree C, and quenched in water. The quenched sample was grinded into 50-300 micron-sized powder. For solidification experiments of Fe-FeS melts, the starting materials were dispersed in silica wool, and sealed in a silica glass tube with FeS and graphite under vacuum. Pieces of FeS and graphite were put in the tube in order to suppress evaporation of sulfur from the sample and to make a reducing environment. The sealed tube was heated at 1330 degree C for 3 hours and cooled down to ~300 degree C with different the cooling rates of 25, 100, 500, and ~10,000 K/h. The run products were embedded in resin, and the polished sections were observed with FE-SEM-EDS (JEOL JSM-7000F, Spatial resolution: ~0.1 micron). The sizes of metallic iron grains were analyzed with the image analyzing software ImageJ.

The size distribution of metal grains changes with cooling rates. Iron metal grains become larger in samples cooled at slower rates. The typical size of metal grains formed below the eutectic temperature is 1-2 microns for the cooling rates of 25 and 100 K/h and smaller than 1 microns for the cooling rates higher than 500 K/h. The quenched sample (~10,000 K/h) contains dendritic/fan-shaped metal grains.

We compared the size distribution of metal grains in run products with those in opaque assemblages in CR chondrules (the images of opaque phases within CR chondrules were kindly provided by Devin Schrader, ASU). With the cooling speedometer developed in this study, we found that a part of the chondrules cooled at a rate slower than 25 K/h and others cooled at the rate faster than 500 K/h.

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Genesis of chemical zoning of asteroid belt and origin of Earth

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Chemical composition of planets in the Solar system is determined by the chemical zoning of protoplanetary disk. There is a region called asteroid belt which is from 2AU to 5AU. In this region there are several tens of thousands of meteorites with various size, and also small planetary bodies with a diameter reaching 1000km. Chemical composition of asteroid belt has been recently investigated in details by telescopes and probes, and it revealed there is systematic distribution in chemical composition of asteroid belt. For example, most inner region of asteroid belt has enstatite chondrite, which is mainly composed of silicate minerals without ice, organic compounds, hydrous silicate minerals, in other words, they are extremely reductive meteorites. On the other hand, outer asteroid belt is dominated by carbonaceous chondrite, and outer side contains more volatiles, which reaches to 20%. This observation indicates there is chemical zoning in asteroid belt and this distribution pattern is same in whole solar system, not only in asteroid belt region. It is thought to be the function of distance from the Sun (= temperature) and reflected to the distribution of minerals and amount of minerals. Grown planetary bodies reflect the chemical composition of growing site of protoplanetary disk. In asteroid belt, small planetary bodies and debris of bodies are remaining as big planet was not formed. Therefore, detailed investigation of asteroid belt will give us original distribution patter of chemical composition of protoplanetary disk.

The Earth was formed from enstatite chondrites existing at 1AU, and bombarded by carbonaceous chondrites to have atmospheric and oceanic components. Primordial atmosphere might have added gradually, so that the surface temperature was low to have glacier probably. Accumulated atmospheric CO2 reacted with primordial continent to fix carbonate minerals, which was carried into deep mantle due to plate tectonics. The thickness of primordial atmosphere is determined by the balance between input by bombardment and fixation of CO2. However, it is generally thought to spend some time to have suitable thickness of atmosphere. But finally, visible sun light became to reach to the surface of the Earth.

Keywords: asteroid belt, chemical zoning, origin of Earth

Secular change of oxygen isotope composition in the solar protoplanetary disk recorded in a fluffy Type A CAI from Vigarano CV3 by Al-Mg chronological study

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Fluffy Type A Ca-Al-rich inclusions (CAIs) containing reversely zoned melilite crystals are suggested to be direct condensates from solar nebular gas (MacPherson and Grossman, 1984). We conducted an investigation of ^{26}Al-^{26}Mg systematics of a fluffy Type A CAI from Vigarano, named V2-01, with known oxygen isotopic distributions of reversely zoned melilite crystals (Katayama et al., 2012); we also conducted oxygen isotope measurements of coexisting minerals. The oxygen and Al-Mg isotope measurements were conducted using SIMS of Hokkaido University (Cameca ims-1280HR). Petrography suggests that the constituent minerals of V2-01 formed in the following order: first spinel and fassaite enclosed by melilite, then reversely zoned melilite crystals, and spinel and diopside in the Wark-Lovering rim. The spinel enclosed by melilite has ^{16}O-rich compositions (Δ^{17}O ~ −24‰) and an initial value of $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$. The fassaite enclosed by melilite crystals shows variable oxygen isotopic compositions (Δ^{17}O ~ −12‰ and −17‰) and plots on an isochron with $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$. The oxygen isotopic compositions of reversely zoned melilite showed continuous variations in Δ^{17}O along the inferred direction of crystal growth, suggesting that surrounding nebular gas, during the formation of the reversely zoned melilite, changed from ^{16}O-poor (Δ^{17}O values larger than −10‰) to ^{16}O-rich (Δ^{17}O ~ −25‰). The six reversely zoned melilite crystals show indistinguishable initial ^{26}Al/^{27}Al values with an average $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ of $(4.7 \pm 0.3) \times 10^{-5}$, which is clearly distinguishable from the value of enclosed spinel and fassaite, indicating a younger formation age than the enclosed spinel and fassaite. The spinel and diopside from the Wark-Lovering rim shows ^{16}O-rich compositions (Δ^{17}O ~ −23‰) with $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0 = (4.5 \pm 0.4) \times 10^{-5}$. The values of $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ are consistent with the formation sequence inferred from petrography. The formation period for the V2-01 CAI is estimated to be 0.18 ±0.07 Myr from the difference in initial ^{26}Al/^{27}Al values. These data suggest that the oxygen isotopic composition of solar nebular gas surrounding the CAI changed from ^{16}O-rich to ^{16}O-poor and back to ^{16}O-rich at least recorded as one cycle during the first ~0.2 Myr of Solar System formation.

Keywords: Al-Mg chronology, Ca-Al-rich inclusion, SIMS, oxygen isotopes, solar protoplanetary disk

Petrography of a Type A CAI evolved by multiple heating.

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Calcium-aluminum-rich inclusions (CAIs) are the oldest solid materials in the early solar system formed at 4567Ma based on the U-corrected Pb-Pb absolute age (e.g., [1]). Coarse-grained CAIs are divided into three groups, type A, type B and type C by the petrography and the bulk chemical composition [2]. Although all type of CAIs has partially melted more than once (e.g., [3, 4, 5]), the petrography and isotopography considering the fractional crystallization with partial melting processes are limited for in-situ chronology (e.g., Al-Mg system). In this study, we try to estimate the crystallization history with petrography and trace elements mapping of wide area by LA-ICP-MS corresponding to the multiple heating process. The major elements mapping were conducted using FE-SEM-EDS at Kyoto University (JSM-7001F and X-max 150). The trace elements mapping were conducted using LA-ICP-MS at Kyoto University (NWR193 Laser Ablation system and iCAP Q ICP-MS).
A large (8 mm ×6 mm) perfect rounded shaped CAI, named KU-N-01, that consists of about 80% melilite, and could be belong to compact type A CAIs. However, KU-N-01 has a bulk chemical compositions between type A and type B on the Stolper’s diagram [6], since the KU-N−01 CAI has spinel-fassaite-rich area that is corresponding to the texture of type B CAIs, even in the core consists of $\text{Åk}_{20\text{-}30}$ melilite enclosed by veined $\text{Åk}_{30\text{-}40}$ melilite.
The trace elements, including rare earth elements (REEs), mappings are obtained by LA-ICP-MS. This mapping applied to the clear partial melting texture at the layered mantle-rim strucure, which consists of fassaite, melilite with zoning of Åk_{20} to Åk_{70}, $\text{Åk}_{15\text{-}20}$ melilite and gehlenetic mantle surrounding Wark-Lovering rim (W-L rim). As results, the REEs excepting Eu (La, Ce, Nd, Sm, Yb, Lu) are enriched in fassiate, whereas Eu are depleted. In contrast the REEs excepting Eu are depleted in the zoning melilite, whereas Eu are enriched. In $\text{Åk}_{15\text{-}20}$ melilite, all REEs are enriched. In the area of gehlenetic mantle with reversely zoned melilite and W-L rim at the most outside, the REEs excepting Eu are enriched in W-L rim and have higher concentration of REEs than the others.
These results suggest that the area of fassaite and melilite with zoning of Åk_{20} to Åk_{70} are crystallized from the pocket of partially melted, however $\text{Åk}_{15\text{-}20}$ melilites are relict, since the REEs are enriched in the melt rather than that of other crystals without Eu. The gehlenetic mantle and W-L rim were formed by condensation, because gehlenetic mantle with reversely zoned melilite is formed by condensation [7] and rim has GroupⅡ REEs pattern [8]. In this talk, through the survey with REEs broad area mapping, we will discuss about new perspective to estimate the partial melting history in CAI formation process.
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Keywords: CAIs, rare earth elements , petrography

Nucleosynthetic Neodymium Isotope Anomalies in Carbonaceous and Ordinary Chondrites.

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We have performed high precision Nd isotope analysis of chondrites coupled with a new sample digestion technique that confirms complete dissolution of acid resistant presolar grains. We also developed an improved dynamic multicollection method using TIMS to improve the analytical reproducibilities. To test the analytical reproducibility in the dynamic method, we repeatedly analyzed a standard sample (JNdi-1) for eight months. The long-term reproducibilities obtained in the dynamic method were 4.2 ppm, 6.6 ppm and 9.7 ppm for $^{142}Nd/^{144}Nd$, $^{148}Nd/^{144}Nd$, $^{150}Nd/^{144}Nd$ (n = 35), which are 2-11 to times superior to the static and multistatic method.
We analyzed eight ordinary chondrites, showing uniform isotope anomalies for $\mu^{142}Nd$ (-12 ±5 ppm), $\mu^{148}Nd$ (10 ±8 ppm) and $\mu^{150}Nd$ (20 ±12 ppm). Although the $\mu^{142}Nd$ values for ordinary chondrites obtained in this study are generally consistent with those of previous studies, positive anomalies in $\mu^{148}Nd$ and $\mu^{150}Nd$ were not recognized in previous studies. In contrast to ordinary chondrites, carbonaceous chondrites show variable Nd isotope anomalies exceeding analytical uncertainties. individual carbonaceous chondrites are categorized into three groups as a function of $\mu^{142}Nd$; NWA 2090 (-5 ppm), Tagish Lake (-20 ppm), and Allende, DaG 190/082, and Dhofar 1432 (-30 ppm).
The data points for ordinary chondrites are generally plotted on mixing line between the terrestrial composition and the putative *s*-process endmember. This means that the isotope anomalies in ordinary chondrites are induced by the heterogeneous distribution of *s*-process nuclides in early Solar System. By contrast, most of the carbonaceous chondrites deviate from the mixing line towards the direction with lower $\mu^{142}Nd$ values. We presume that the offset from the mixing line is caused by the heterogeneous distribution of *p*-nuclides in the early Solar System, because a part of ^{142}Nd was produced by the *p*-process nucleosynthesis and αdecay of a pure *p*-nuclide ^{146}Sm. Although the Earth and parent bodies of chondrites do not share building blocks with a common Nd isotopic composition, the excess ^{142}Nd signature of the Earth would not necessarily require the existence of a hidden reservoir with a subchondritic Sm/Nd ratio deep in the Earth's mantle as proposed previously.

Keywords: isotope anomaly, presolar grain

The initial abundance and distribution of ^{92}Nb in the Solar System

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Niobium-92 is an extinct proton-rich nuclide, which decays to ^{92}Zr with a half-life of 37 Ma. Because Nb and Zr can fractionate from each other during partial melting of the mantle, mineral crystallization and metal-silicate separation, the Nb–Zr system can potentially be used to determine the timescales of silicate differentiation and core segregation for infant planets. In addition, the initial ^{92}Nb abundance in the Solar System provides constraints on the nucleosynthetic site(s) of *p*-nuclei (*p*- denotes proton-rich). These applications require the initial abundance and distribution of ^{92}Nb (expressed as ^{92}Nb/^{93}Nb) in the Solar System to be defined. Yet previously reported initial ^{92}Nb/^{93}Nb values range from ~10^{-5} to >10^{-3} [1-6], and remain to be further constrained. All but one of the previous studies estimated the initial ^{92}Nb/^{93}Nb using Zr isotope data for single phases with fractionated Nb/Zr in meteorites such as zircons and CAIs, assuming that their source materials and bulk chondrites possessed identical initial ^{92}Nb/^{93}Nb and Zr isotopic compositions [1-5]. To evaluate the homogeneity of the initial ^{92}Nb abundance, however, it is desirable to define internal mineral isochrons for meteorites with known absolute ages. Although Schönbächler et al. [6] applied the internal isochron approach to the chondrite Estacado and the mesosiderite Vaca Muerta, these meteorites include components of different origins and their formation ages are uncertain, which prohibits a precise determination of the solar initial ^{92}Nb abundance.

Here we present Nb-Zr data for mineral fractions from four unbrecciated meteorites, which originate from distinct parent bodies and whose U-Pb ages were precisely determined: the angrite NWA 4590, the eucrite Agoult and the ungrouped achondrites Ibitira. Our results show that the relative Nb–Zr isochron ages of the three meteorites are consistent with the time intervals obtained from the Pb–Pb chronometer for pyroxene and plagioclase, indicating that ^{92}Nb was homogeneously distributed among their source regions. The Nb–Zr and Pb–Pb data for NWA 4590 yield the most reliable and precise reference point for anchoring the Nb–Zr chronometer to the absolute timescale: an initial ^{92}Nb/^{93}Nb ratio of (1.4 ±0.5) x10^{-5} at 4557.93 ±0.36 Ma, which corresponds to a ^{92}Nb/^{93}Nb ratio of (1.7 ±0.6) x10^{-5} at the time of the Solar System formation. On the basis of this new initial ratio, we demonstrate the capability of the Nb–Zr chronometer to date early Solar System objects including troilite and rutile, such as iron and stony-iron meteorites. Furthermore, we estimate a nucleosynthetic production ratio of ^{92}Nb to the *p*-nucleus ^{92}Mo between 0.0015 and 0.035. This production ratio, together with the solar abundances of other *p*-nuclei with similar masses, can be best explained if these light *p*-nuclei were primarily synthesized by photodisintegration reactions in Type Ia supernovae.

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Keywords: achondrite, early Solar System chronology, nucleosynthesis

Os isotope compositions and fractionation of siderophile elements in metal phases from CB chondrites

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Metal is one of the main components of chondritic meteorites and a significant reservoir of Fe along with silicates and sulfides. Metal plays a key role in physicochemical processes that fractionate siderophile elements from lithophile elements in the early solar system, generating variable chemical reservoirs before the onset of planetesimal formation. Highly siderophile elements (HSEs: Re, Os, Ir, Ru, Pt and Pd) have a great affinity for Fe-metal relative to silicate; HSEs are very refractory and exist as gas only at high temperature. Therefore, HSEs in metals in a variety of meteorites can provide an important clue for understanding of high temperature processes in the nebula. Specifically, the ^{187}Re-^{187}Os isotope system yields chronological information regarding the fractionation of HSEs. Numerous studies have conducted comprehensive analyses of HSE abundances in chondritic metals utilizing laser ablation ICP-MS (LA-ICP-MS) [e.g., 1-2]. However, these studies scarcely include *in-situ* Os isotope data due to analytical difficulties. We have developed a technique for *in-situ* measurement of Os isotopes in metal grains using a micro-milling system coupled with N-TIMS. Our previous study reported that individual CB metals have ^{187}Os/^{188}Os ratios close to the bulk CI chondrite value with limited variation [3]. This study is a follow up of our previous investigation that places emphasis on spot analyses of HSEs and other siderophile elements in CB metals where ^{187}Os/^{188}Os ratios have been obtained. We utilize fs-LA-ICP-MS for conducting precise HSEs analysis in metal samples. By integrating overall measurements, we discuss the origin of metal grains in different types of CB chondrites.

We examined multiple metal grains in three CB chondrites: Bencubbin (CB_a), Gujba (CB_a), and Isheyevo (CB_b). The details for Os isotope analysis using a micro milling system and N-TIMS are described in [3]. The concentrations of P, S, Cr, Fe, Co, and Ni in analytical spots adjacent to the sampling pits for Os isotope analysis were determined by EPMA (JEOL-JXA-8530F). The concentrations of HSEs in analytical spots adjacent to the sampling pits were analyzed with fs-LA-ICP-MS (IFRIT, Cyber Laser).

Our Re-Os isotope data are mostly plotted on the 4.567 Ga Re-Os reference line. Nearly homogeneous ^{187}Os/^{188}Os ratios in CB metals indicate that fractionation of Re and Os was minuscule during metal formation at ~4.57Ga. Because Re and Os are ultra-refractory elements with similar 50% condensation temperatures (Re: 1821 K, Os: 1812 K), the limited Re/Os variation may suggest simultaneous condensation of Re and Os from the nebular gas during metal formation. The limited Os isotopic variation suggests that the redistribution of Re and Os during metal formation associated with planetary collision was not significant as are the cases of solidification of liquid metal. A positive correlation of Re/Os ratios calculated from the ^{187}Os/^{188}Os ratios and Os/Ir for CB_a metal grains suggests that the condensation of CB_a metal grains occurred at an equilibrium condition in a cooling gas until the condensation temperature of Ir (~1600 K). Unlike ultra-refractory HSEs, Pd/Fe and Ni/Fe ratios in CB_a and CB_b metals exhibit a strong positive correlation. This positive correlation cannot be explained by nebular condensation but condensation in extremely high gas pressure (10^7 x solar nebula).

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Keywords: Chondrite, Metal phase, CB chondrite, Osmium isotopes, Highly siderophile elements, In-situ analysis

Mineralogy of CO3.0-like clasts in the NWA 1232 CO3 breccia: Evidence for aqueous alteration on the parent body

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It is widely believed that CO parent bodies have escaped significant degree of brecciation. However, NWA 1232 is a CO3 breccia consisting of three distinct lithologies (A, B, and C) that have experienced different degrees of thermal metamorphism [1]. Recently, we found that lithology A (whose petrologic type is estimated to be 3.5) contains numerous small (100-1800 μm) clasts [1]. Most of the clasts show CO3.0-like mineralogical characteristics. Type 3.0 chondrites are thought to preserve their primary states when their components were accreted into their parent bodies. Here, we present the results of a mineralogical investigation of the CO3.0-like clasts in lithology A of NWA 1232.
CO3.0-like clasts are widely distributed throughout lithology A. Each of the clasts typically consists of one chondrule surrounded by a fine-grained matrix material, exhibiting the appearance of a chondrule with a rim. Some clasts contain multiple chondrules and CAIs in fine-grained matrix. Most chondrules in the clasts are Mg-rich Type I, and their olivine phenocrysts have homogeneous compositions (~Fa_1), which correspond to type 3.0. It is known that type 3.0 can be subdivided into finer divisions using various mineralogical signatures indicative of metamorphism. Here, we investigated Fe-Ni metal nodules in chondrules to evaluate the metamorphic grade of the clasts using the criteria given by Kimura et al. (2008)[2]. Kimura et al. [2] reported that the textures of metal nodules changed from homogeneous martensite to plessitic intergrowths of kamacite and Ni-rich metal, and to coarser grained intergrowths in the early stage of thermal metamorphism. Our study showed that the metal nodules in the clasts consist of intergrowths of kamacite and Ni-rich metal. The Ni-rich metal grains are intermediate in size (1.63±3.91 μm^2) between Semarkona LL3.01 and type 3.03-3.05 chondrites, whereas their distribution density (0.060±0.079 $N/\mu m^2$) is much lower than Semarkona and similar to type 3.03-3.05 chondrites. In addition, trace element (Si, P, Cr, Co) contents in kamacite and Ni-rich metal are comparable to type 3.03-3.05 chondrites. From these results, we suggest that the clasts correspond to type 3.02-3.05.
The clasts show abundant evidence of aqueous alteration. Phenocrysts and mesostasis in the chondrule peripheries were replaced by fine grains (10-20 nm) of phyllosilicates and an O-Fe-Si-Mg-Al-rich amorphous material. The phyllosilicates replacing phenocrysts are largely serpentine, and those replacing mesostasis are serpentine and smectite. The matrix mainly consists of a O-Si-Fe-Mg-Al-rich amorphous material and contains relatively coarse grains (1-2 μm) of magnetite, forsteritic olivine, enstatite, fine grains (100-500 nm) of olivine, troilite, and finer grains (10-20 nm) of serpentine. In addition, the matrix contains small amounts of C-rich amorphous spherules (100-200 nm in diameter), which have an appearance similar to organic globules that have commonly been found from CI and CM chondrites [e.g. 3].
Our results suggest that the clasts in lithology A of NWA 1232 have experienced aqueous alteration in the least metamorphosed region in the meteorite parent body. The evidence of aqueous alteration has also been reported from other CO3.0 chondrites [4, 5]. These suggest that aqueous alteration occurred generally in the least metamorphosed regions in CO parent bodies. In the NWA 1232 parent body, part (or whole) of the region was brecciated to form many small clasts, and subsequently those clasts were transported and incorporated into lithology A of NWA 1232.
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Keywords: CO chondrite, brecciation, aqueous alteration, thermal metamorphism, Fe-Ni metal, TEM

Aqueous alteration processes of primitive planetary materials with redox conditions controlled by fluid compositions

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Abundance, occurrence, compositions and textures of carbonate minerals and phyllosilicates in carbonaceous chondrites show huge variety depending on aqueous alteration processes in the early solar system. Redox conditions in aqueous alteration processes should be controlled by fluid compositions based on the solar nebula. On the surface of planetesimals and protoplanets, excess H2O may be derived by accumulation of ice-dominated planetesimals. In this study, hydrothermal alteration experiments of Allende meteorite were carried out with fluids containing H2O, CO2 and hydrocarbons.

Hydrocarbon-rich fluid prohibited production of carbonate and phyllosilicate minerals. Excess H2O components promote production of phyllosilicates above 200 degree C. and carbonate minerals at 150 degree C and temporally above 200 degree C. Hydrocarbon-poor fluid estimated on protoplanets can produce Mg-Fe carbonate under 200 degree C and Mg-Ca carbonate over 200 degree C. Phyllosilicate is Fe-rich under 200 degree C and Mg-rich over 200 degree C.

Redox conditions calculated by thermodynamic parameters show higher fO2 in H2O-rich fluid compositions in this study. This estimation is concordant with experimental results on reactivity of metal components and compositions of carbonate and phyllosilicate minerals. Water components strongly promote production of carbonate and phyllosilicates. It is quite distinctive that production of carbonate minerals is stimulated by H2O rather than CO2 compositions in aqueous alteration processes.

Keywords: Aqueous alteration, carbonate, phyllosilicate, oxygen fugacity

Application of scanning-imaging x-ray microscopy to fluid inclusion candidates in carbonates of carbonaceous chondrites.

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In order to search for such fluid inclusions in carbonaceous chondrites, a nondestructive technique using x-ray micro-absorption tomography combined with FIB sampling was developped and applied to a carbanaceous chondrite [1,2]. They found fluid inclusion candidates in calcite grains, which were formed by aqueous alteration. However, they could not determine whether they are really aqueous fluids or merely voids.

Phase and absorption contrast images can be simultaneously obtained in 3D by using scanning-imaging x-ray microscopy (SIXM) [3]. In rrefractive index, $n=1-\delta+i\beta$, in the real part, $1-\delta$ is the refractive index with decrement, δ, which is nearly proportional to the density, and the imaginary part, β, is the extinction coefficient, which is related to the liner attenuation coefficient, μ. Many phases, including water and organic materials as well as minerals, can be identified by SIXM, and this technique has potential availability for Hayabusa-2 sample analysis too. In this study, we examined quantitative performance of d and m values and the spatial resolution in SIXM by using standard materials, and applied this technique to carbonaceous chondrite samples.

We used POM ($[CH_2O]_n$), silicon, quartz, forsterite, corundum, magnetite and nickel as standard materials for examining the $\delta$and μvalues. A fluid inclusion in terrestrial quartz and bivalve shell (Atrina vexillum), which are composed of calcite and organic layers with different thickness, were also used for examining the spatial resolution. The Ivuna (CI) and Sutter's Mill (CM) meteorites were used as carbonaceous chondrite samples. Rod- or cube-shaped samples 20-30 μm in size were extracted by using FIB from cross-sectional surfaces of the standard materials or polished thin sections of the chondrites, which was previously observed with SEM. Then, the sample was attached to a thin W-needle and imaged by SIXM system at beamline BL47XU, SPring-8, Japan. The slice thickness was 109.3 nm and the pixel size was mostly 100 nm.

It was found that $\mu$and d values obtained by SIXM (μ_{SIXM} and d_{SIXM}) are proportional to the theoretical values (m_{calc} and d_{calc}), respectively, exept for large μvalues (>~1000 cm^{-1}), and the following relations were obtained; $\mu_{SIXM} = 0.909(8)\times\mu_{calc}$ and $\delta_{SIXM} = 0.908(6)\times\delta_{calc}$. We can quantitatively identify fluid in inclusions of the terrestrial quartz and organic layers in the shell with the spatial resolution of >~1 μm. If they are less than ~1 μm, we cannot quantitatively identify them due to overlapping of the point spread function.

A hexagonal platy inclusion with facets, or negative crystal (0.7 x 2.3 μm) was found in a calcite grain of the Sutter's Mill meteorite as a fluid inclusion candidate [4]. The δvalue of this inclusion is less than that of water, indicating that any aqueous fluid was not included. As its shape strongly suggests that it was once formed as a fluid inclusion during hydrous alteration in a parent boby, and then the fluid must be escaped. We cannot detect any aqueous fluids in other fluid inclusion candidates, such as a spherical inclusion (~1.8 μm) in a calcite grain of the Sutter's Mill meteorite, which seems to have a bubble inside [1], and a relatively large inclusion with facets in dolomite in the Ivuna meteorite.

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Keywords: Tomography, SPring-8, Hayabusa2, hydrous alteration

HEATING EXPERIMENTS OF TAGISH LAKE METEORITE:
INVESTIGATION OF THERMAL EVOLUTION PROCESS OF THE DEHYDRATED CARBONACEOUS CHONDRITES

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Introduction: More than 20 thermally metamorphosed carbonaceous chondrites (TMCCs) have been identified based on the mineralogy, petrology, and organic materials [e.g., 1]. On the other hand, reflectance spectra of C-type asteroids suggest that some of them have dehydrated surface [2]. Therefore, the asteroids which experienced dehydration caused by heating after aqueous alteration can be the parent bodies of TMCCs. The Belgica group represents strongly heated TMCCs consisting of secondary silicates formed by decomposition of hydrous minerals during heating [e.g., 1]. Although the petrography of the Belgica group is apparently similar to typical CM2 chondrites, they are also similar to the Tagish Lake carbonate-poor lithology with respect to their bulk oxygen isotopic compositions and the chemical composition of the matrix [3]. To understand the formation process of the Belgica group TMCCs, we have performed heating experiments on fragments of the Tagish Lake meteorite and observed the mineralogical changes as a function of temperature and duration of heating.

Experimental procedures: To identify the Tagish Lake carbonate-poor lithology, X-ray computed tomography was carried out. Tagish Lake samples consisting of the carbonate-poor lithology were experimentally heated at four different conditions: 600 ºC for 1 hour (hereafter 600 ºC/1 h), 600 ºC/96 h, 900 ºC/1 h, and 900 ºC/96 h. During the heating period, the oxygen fugacity was kept at the IW buffer in order to reproduce the secondary iron-bearing minerals in the Belgica group meteorites. The mineralogy of the matrix was determined using synchrotron X-ray diffraction (XRD) analysis at KEK BL-3A. SEM/EDS observation was performed for the petrography. Organic materials of the heating experiment products were studied using the STXM technique and XANES analysis at KEK BL-13A. In addition, detailed mineralogy and chemical analysis were obtained by TEM observations.

Results and discussion: The weight loss of the matrix during heating is 11% for the heating products at 600 ºC, 17 % for 900 ºC/1 h, and 20 % for 900 ºC/96 h, respectively. The relative degrees of transformation of the Tagish Lake meteorite can be estimated as following; 600 ºC/1 h ≤ 600 ºC/96 h < 900 ºC/1 h < 900 ºC/96 h. These degrees are obtained by observation of mineralogical changes of opaque minerals and crystallinity of secondary silicates as a heating parameter obtained by XRD analysis and SEM observation. The heating products at lower temperature, the constituent minerals are similar to unheated Tagish Lake. Hydrous minerals and framboidal magnetite can be observed throughout the entire matrix. In the samples heated at 900 ºC, it is quite different from samples heated at 600 ºC. Magnetite and hydrous minerals were not detected. Instead of these common phases, Fe-Ni metal, troilite, and low crystallized secondary silicates, olivine and pyroxene, dominate in the matrix. A comparison of the mineralogy of our experimental results to the Belgica group meteorites shows that the sample heated at 900 ºC reproduces the mineralogical and textural characteristics of the Belgica group meteorites. We will present results of XANES analysis and TEM observation of the matrices in these heating products. The coordinated study of organics and mineralogy in heating products will give us new information to understand dehydration process on C-type asteroids.

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Keywords: Tagish Lake, carbonaceous chondrite, Thermal metamorphism, dehydration

Extraterrestrial organic compound distribution revealed by ultra-high resolution HPLC-MS

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Many soluble organic compounds have been reported from carbonaceous meteorites in various solvent extracts ranging from non-polar hexane to polar water, in which amino acids and carboxylic acids have been targeted in the water-soluble fraction. The compostional and structural diversities of amino acids and carboxylic acids are well documented up to C8 observed with most structural isomers at each carbon number. The non-polar hexane extract contains non-polar components including aromatic hydrocarbons. To date, about a few thousands of soluble organic compounds have been identified in meteorites by GC and/or LC/MS. However, a high-resolution mass spectral study revealed ~160,000 ion peaks in various solvent extracts of the Murchison meteorite by electrosplay ionization using Fourier transform-ion cyclotron resonance/mass spectrometry (FT-ICR/MS) to assign ~50,000 elemental compositions consisting of CHO, CHNO, CHOS and CHNOS (Schmitt-Kopplin et al., 2010). The methanol extracts of carbonaceous meteorites are enriched in organic content with more enriched in D and 15N relative to other fractions, implying more primitive organic compounds. The FT-ICR/MS study did not clarified the detailed chemical structures due to no chromatographic separation. In particular, the organic compounds with their elemental compositions of CH and CHN were not discussed. In the previous study (Yamashita and Naraoka, 2014), homologous series of alkylated pyridines ($C_nH_{2n-4}N^+$ and $C_nH_{2n-6}N^+$) were predominant peaks in the MeOH extract.

In this study, we further examine the distribution of soluble organic compound using ultrahigh-resolution HPLC/MS in order to investigate reaction mechanisms for extraterrestrial molecular evolution. The exact mass between the observed mass and calculated values matched within 1 ppm. Using a hydrophilic interaction liquid chromatography (HILIC) mode, complex compound mixtures were observed with mass peaks between m/z 80 and 1400, where strong ion peaks are distinguished between m/z 90 and 400 with the maximum at m/z ~300. Most peaks have CHN in composition with minor CHO and CHNO compositions. More than ~600 peaks match with the calculated masses for $C_nH_mN^+$ and $C_nH_mN_2^+$ with the range of $5 < n < 33$. Extensive alkylated N-containing cyclic compounds are distinguished by every 14.0156 ($-CH_2-$) difference, which consisted of $C_nH_{2n-4}N^+$, $C_nH_{2n-6}N^+$, $C_nH_{2n-8}N^+$, $C_nH_{2n-10}N^+$ and $C_nH_{2n-12}N^+$ in the earlier retention time, and the $C_nH_{2n+4}N^+$, $C_nH_{2n+2}N^+$, $C_nH_{2n}N^+$, $C_nH_{2n-2}N^+$, $C_nH_{2n+3}N_2^+$, $C_nH_{2n+1}N_2^+$, $C_nH_{2n-1}N_2^+$ and $C_nH_{2n-3}N_2^+$ in the later retention time. In addition to the predominant $C_nH_{2n-4}N^+$ (saturate-alkylated pyridines, $C_nH_{2n-5}N$) and $C_nH_{2n-6}N^+$ (unsaturate-alkylated pyridines, $C_nH_{2n-7}N$), alkylated imidazole homologues were identified by MS/MS analysis. Both alkylpyridines and alkylimidazoles could be produced from aldehydes and ammonia through aldol condensation and imine formation under an alkaline environment. Further redox reactions could have proceeded during water-rock interaction to give alkylpiperidines and pyridine carboxylic acids. Aldehyde polymerization with ammonia is an important pathway to produce the relatively high-molecular alkylated N-containing cyclic compounds on the meteorite parent body.

Keywords: extraterrestrial organic compounds, chemical evolution, carbonaceous meteorite, ultra-high resolution liquid chromatography, ultra-high resolution mass spectrometry

Chemistry of formaldehyde and ammonia in the Solar System small bodies

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Formaldehyde and ammonia is ubiquitous in the universe. Comets contain up to 4% H_2CO and up to 1.5% NH_3 relative to H_2O, and interstellar medium (ISM) contains up to 8% H_2CO and up to 80% NH_3 relative to H_2O [1]. Cody et al. [2] proposed the formation scenario of insoluble organic matter (IOM) in chondritic meteorites, in the presence of liquid water starting with formaldehyde and glycolaldehyde that is the simplest sugar produced by two H_2CO molecules. We have conducted further experimental studies and showed that the presence of ammonia enhanced the IOM like organic solid formation via formose reaction followed by carbonization [3]. These studies were focusing on the solid materials, and now we study the liquid phase of the products with various analytical methods including electrospray ionization mass spectrometry (ESI-MS), X-ray absorption near edge structure (XANES), infrared spectroscopy and amino acid analyses using high performance liquid chromatography (HPLC).

Each starting solution contained 1mL water with 2 mmol formaldehyde, 1 mmol glycolaldehyde, 0.4 mmol ammonia (equivalent to H_2O : C : N = 100 : 7.2 : 0.72) with catalytic amount of $Ca(OH)_2$, and was sealed in a glass tube, then isothermally heated at 90 degrees C up to 250 degrees C. XANES and FTIR analyses showed that aromatic or olefinic C=C bond abundance increased with temperature in the soluble fractions. This indicates that the insoluble residues precipitate as a result of increase in the hydrophobic moieties in the products as the reaction proceeds. This is consistent with the previous results that the amount of insoluble fractions (organic solids) increases with temperature [3]. Acid hydrolysis of the solutions produced various amino acids up to four carbons. Alanine abundance was larger than glycine, and may indicate high abundance of methyl ($-CH_3$) or methylene ($-CH_2-$) substitutions in the amino acid precursor molecules. ESI-MS results suggested that various carbohydrates (CHO molecules) and these with nitrogen containing substitutions. This is somewhat consistent with ultrahigh-resolution ESI-MS analysis of the Murchison meteorite extract that shows various CHO and CHNO molecules [4], although only formaldehyde and ammonia chemistry cannot explain all of the diverse molecules found in this meteorite.

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Keywords: Meteorites, Asteroids, Organic matter

Hydrogen isotopic compositions and Raman spectra of organic particles in NWA 801 CR2 chondrite.

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[Introduction]

Carbonaceous chondrites contain up to 3-4% organic C, which mostly occur as insoluble organic matter (IOM) [1]. Significant deuterium (D)-rich organic globules have been identified from IOM or matrix [e.g. 2, 3]. It is widely accepted that the D-rich organic globules were formed in extreme cold environment in molecular clouds or outer protosolar nebula and record formation and evolution histories of the extraterrestrial organic materials [e.g. 2, 3].

Our previous study identified D-rich organic globules in matrix of Northwest Africa (NWA) 801 CR2 chondrite and revealed their various H isotopic compositions and morphologies [3]. In the matrix of NWA 801, organic particles without large D-enrichment (less D-rich) also occur [3]. Previous studies reported release of D-enrichments of IOM during aqueous alteration and thermal metamorphism [e.g. 4], thus, H isotopic compositions of organic materials are important tracer to understanding their evolution histories. Furthermore, Raman spectra are also useful parameter for metamorphism grade of organic materials [e.g. 5]. In this study, we investigate H isotopic compositions and Raman spectra of the D-rich and less D-rich organic materials in the NWA 801 to understand their evolution histories.

[Experimental]

A polished thin section of NWA 801, covered with a 30 nm thick carbon film [3], was used in this study. In situ quantitative H isotope ratio imaging was performed on matrix regions of the thin section using HokuDai isotope microscope system. The selection criterion for distinguishing D-rich materials that one of their D/H ratios is 2 sigma away from the 3 sigma the distribution of the surrounding matrix. Elemental ratio of H/C for the organic materials were measured using secondary ion intensity of H^- and C^- by SIMS analysis, assuming that average H/C ratio of less D-rich organic materials is corresponding to that of bulk CR2 IOM reported from previous study [4]. Identification and observation of organic materials were performed using FE-SEM-EDS. Raman experiments were performed by Ranishaw Invia Reflex Raman microscope at the Open facility of Hokkaido University. An excitation wavelength is 532 nm (Nd: YVO_4) with spot size of ~1 μm. The laser power on the sample was less than ~300 μW.

[Results and Discussion]

Less D-rich organic particles in NWA 801 occur as sub-micron-sized globules with various morphology that can be classified as follows: ring globule, globule aggregate, round globule, and irregular-shaped globule, that are similar to those of D-rich organic globules in NWA 801 [3]. Although molecular structure of IOM is modified and their H/C ratio is decreased by thermal metamorphism and aqueous alteration [e.g. 4], D-rich and less D-rich organic globules in NWA 801 showed similar H/C ratio, mostly <1.5. Our results imply that the less D-rich organic globules in NWA 801 are not attributed to release of D-enrichment from D-rich organic globules by metamorphism and/or alteration.

Raman spectra obtained from D-rich organic globules, less D-rich organic globule, and matrix showed "D-band" (at ~1400 cm^{-1}) and "G-band" (at ~1550 cm^{-1}). D- and G-band feature of the Raman spectra indicate more metamorphosed feature of D-rich organic globules than that of less D-rich globules and matrix, based on previous results of chondritic IOM [5]. Our results suggest that the D-rich organic globules in NWA 801 would have experienced thermal metamorphism individually, probably in the early solar nebula.

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Keywords: Carbonaceous chondrite, Organic materials, Raman spectrum, Hydrogen isotopic composition

Development FIB-SEM, NanoSIMS and TEM sequential analysis for micrometeorites from Antarctica.

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The sequential analysis using different types of instruments is essential for small and precious sample. For example, Uesugi et al. (2014) proposed a coordinated analytical system for carbonaceous materials found in the Hayabusa returned samples, and successfully obtained maximum chemical, elemental and isotopic information in the materials using micro-Raman spectroscopy, FT-IR, XANES, ToF-SIMS, FIB, TEM/STEM and NanoSIMS. Part of this type of coordinated method has been applied to carbonaceous materials by Stardust cometary dust return mission (e.g., Sandford et al. 2006; Matrajt et al. 2008).

In this study, we focus on the development of coordinated FIB-SEM, NanoSIMS and TEM analysis to obtain the characteristics of isotopic compositions and mineral texture in fine-grained mineral assemblages in few tens to hundreds of micrometer-scale extraterrestrial samples. We, therefore, have chosen Antarctic micrometeorites as an analogue of Hayabusa 2 sample because of their size (10 to 800 μm) and characteristics in terms of isotopes and constituent minerals.

The sample we used in this study is a scoriaceous type micrometeorite, named TT006B101, collected at Tottuki in Antactica in 2000 (Iwata and Imae, 2002), and provided from Antarctic micrometeorite collection in National Institute of Polar Research. The TT006B101 is sphere with ~200 micrometer in diameter, and was mounted on the carbon-nanotube Gecko Tape (Nitto Denko corp.). First measurement by EPMA with EDS (JEOL JXA-8200) was carried out at NIPR for the sample to obtain elemental abundances and BSE image. We, then, prepared a cross-section of the sample (60 x 25 x 5 micrometer) using an FIB instrument (Hitachi SMI4050). The cross-section was transferred into the FIB-SEM instrument (Hitachi SMJ4000L equipped with Oxford X-max150 EDS and Oxford NordlysNano EBSD). Mineral phases of olivine, magnetite and silicate glass were identified by EDS spectra and EBSD patterns on the sample surface. We have applied a rastered ion imaging by the JAMSTEC NanoSIMS 50L to investigate distributions of O isotopes on a part of the sample. All mineral phases showed homogeneous distributions of terrestrial O isotopic ratios. After the O isotopic imaging, we determine the detailed mineralogy and microstructure of the same area that we acquired O isotope map to gain insight into its petrogenesis by TEM (JEOL ARM-200F equipped with EDS) followed by FIB treatment to prepare an ultra thin section (20 x 25 x 0.1 micrometer). We confirmed three different mineral phases that was determined by SEM-EDS system exist in the thin section by mineralogical and crystallographic observation by TEM.

In this talk we will discuss about detailed analytical conditions and results of another micrometeorites (ie., smaller size of ~50 micrometer, unmelted type), and perspective to the Hayabusa 2 sample analysis.

Keywords: NanoSIMS, TEM, FIB, Antarctic micrometeorites, Hayabusa 2

Observation of 3D shapes of olivine negative crystals in equilibrated chondrites:Estimation of equilibrium form and relative ages of healed cracks.

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Olivine is one of the most common minerals both in the solar system and circumstellar environments. It is important to understand its crystal shape because anisotropy of the crystal faces affects various physicochemical processes. For example, the IR spectral features of olivine in circumstellar regions depend on the crystal shape, which was controlled by its formation process (e.g., [1]) and the origin of water of the Earth might be affected by anisotropic adsorption of water molecules on olivine surfaces [2]. There are two kinds of crystal forms; growth and equilibrium forms. Growth forms of olivine have been obtained from natural crystals. Recently, its equilibrium form was obtained by *ab initio* calculation [3]. In order to confirm this from natural crystals, we examined the shapes of negative olivine crystals along a healed crack in an equilibrated chondrite [4]. We obtained a shape, which seems to be nearly equilibrium from but is different from the calculated equilibrium form. However, the result was obtained only for one sample. In this study, more number of samples was examined with more detailed crystallographic analysis to discuss equilibrium form. It is also expected that we can estimate relative formation ages of healed cracks if the degree of annealing of negative crystals are different among the healed cracks.

We observed three, two and two samples of the Tuxtuac (LL5), Kilabo (LL6) and Y793214 (LL5) meteorites, respectively. A cube-shaped sample (20-30 um in size) with inclusions was extracted from a polished thin section by using FIB (FEI Quanta 200 3DS). Then, the sample was imaged to obtain three-dimensional structures of negative crystals along a healed crack using imaging microtomography system at beamline BL47XU, SPring-8, Japan with the effective spatial resolution is approximately 150 nm. The crystallographic orientations of host olivine crystals were determined with an FE-SEM/EBSD (JEOL 7001F/HKL CHANNEL5). Then, the lengths along the crystal axes and crystal planes of negative crystals were determined from the CT images together with the EBSD results. Voids with facets, or negative crystals, 0.5–8.0 um in size were present along a plane, suggesting their forms a healed crack. Sometimes two healed cracks were recognized in one sample. The axial length ratios of negative crystals along a healed crack in the Tuxtuac meteorite are almost similar irrespective of their size. This indicates that the negative crystals in this healed crack were most annealed and their shapes changed to near-equilibrium form. The annealing might be caused by thermal metamorphism and/or post shock heating in a parent body. The near-equilibrium form has {100}, {010}and {021} planes with rounded edges. The development of {100} planes is different from the equilibrium form obtained by *ab initio* calculation [3], where (100) plane with a high surface free energy do not appear. Possible causes for this discrepancy are Fe-rich surface composition or adsorption of molecules onto the surface of the negative crystals. Degrees of annealing of healed cracks can be evaluated from deviation of the axial length ratios of negative crystals. More than one healed cracks with different degrees of annealing is present in a single rock fragment, indicating relative ages of healed cracks can be evaluated.

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Keywords: equilibrium form, negative crystal, equilibrated chondrite, olivine, surface free energy, relative age

Lamellar Fe zoning in low-Ca pyroxene in ordinary chondrites

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Diffusion is an important fundamental process for atomic transportation in rocks. It is well known that dislocation (one-dimensional defect) acts a high-speed diffusion pathway of atoms, namely pipe diffusion. Due to larger spatial connectivity within a crystal than dislocation network, two-dimensional defects such as stacking faults and twining are also expected to be effective diffusion pathway. Our current study is focusing on natural occurrences of cation diffusion along planar defects in silicate minerals.

Following previous studies on lamellar Fe zoning found in chondritic low-Ca pyroxene [1, 2], we have investigated two unequilibrated ordinary chondrites, Felt (L3.5) and NWA7676 (LL3.5) by electron microcopies. SEM-EDS analyses clarified that a few of low-Ca pyroxene grains in chondrules of both samples showed bright lamellar contrast less than ~10 μm in width by back-scattered electron imaging. The lamellar zoning is significantly dominant compared to normal core-rim zoning, and it corresponds to Fe concentration in X-ray chemical mapping. The bright portions were further processed into ultrathin films by focused ion beam equipment and examined by TEM-EDS. The pyroxene grains showed numerous stacking faults on the (100) plane. Its orientation is consistent with that of lamellar Fe zoning observed by SEM-EDS. However, such lamellar Fe concentration has not been clearly seen under TEM-EDS analysis. It is probably due to very small Mg-Fe heterogeneity in a sub-micrometer scale. In Felt, low-Ca pyroxene grain also showed high density of elongated dislocations parallel to the (100) plane. The portion showed distinct lamellar Fe zoning even in sub-micrometer scale.

Stacking disorder on (100) in low-Ca pyroxene in chodrules is thought to have formed during inversion from protoenstatite to clinoenstatite mainly due to cooling from above 1000 °C [3]. The straight dislocation microstructure in Felt would have formed by impact deformation based on its shock stage (S4). The lamellar Fe zoning is likely to have been produced by diffusion along stacking fault planes and dislocation arrays, and subsequent volume diffusion along lateral direction to the (100) plane. The present results preliminary imply that planar defects as well as dislocation array is a potential high-speed atomic diffusion pathway in low-Ca pyroxene during heating events in chondrites.

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Keywords: pyroxene, Fe diffusion, planar defect, ordinary chondrite, TEM

Evolution of rheological structure of Mars

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Change of the rheological structure significantly influences the Martian evolution, which might results in the different tectonics operated in between Mars and Earth. Here we show the evolution of rheological structure of Martian lowlands (North Pole) and highlands (Solis Planum) under wet and dry conditions. The thermal state of the past and present planetary interior can be calculated from surface heat flow and the present-day abundance of the radioactive isotopes ^{238}U, ^{235}U, ^{232}Th, and ^{40}K [*Turcotte and Schubert*, 2002]. Rheological structure can be inferred from flow laws that indicate the strength of solids, which is dependent on strain rate, temperature, water content, and chemical composition [*Frost and Ashby*, 1982; *Karato and Jung*, 2003]. In plastic deformation region, power-law creep is generally used to infer the rheological structure and heat flow [*Grott and Breuer*, 2008; *Ruiz et al*., 2008; *Grott and Breuer*, 2010], and this type of flow law is commonly applied to high-temperature creep. However, the Peierls mechanism becomes dominant at low temperatures and high stresses [*Tsenn and Carter*, 1987]. In this mechanism, strain rate is exponentially proportional to applied stress. In this study, the Martian rheological structure is determined not only from Power-law creep but also from the Peierls mechanism and diffusion creep. In brittle deformation region, Byerlee’s law (m=0.6-0.85) is generally used to calculate the rock strength. We took the low frictional coefficient such as clay mineral (m=0.2-0.6) into account [Morrow et al., 2000; Kubo and Katayama, 2015].
The rheological structure of Mars determined in this study indicates that shallow deformation on Mars is mostly controlled by the Peierls mechanism, and that application of power-law creep on its own leads to an overestimation of lithospheric strength. The effect of water is also significant. Our results show that the presence of water would have delayed increases in lithospheric strength on Mars. Moreover recent studies found from the hydrogen isotopes in Martian meteorite that the water loss during the pre-Noachian was most significant [Kurokawa et al., 2014]. Given the evolution of water reservoirs on Mars, the lithospheric strength on Mars may have significantly increased at 4 Ga, suggesting that Mars changed to severe environment in where development of plate boundaries, plate motion, and plate subduction were limited.

Keywords: Mars, Rheological structure, Evolution

A New Interpretation of Pb Isotopic Variation of Shergottites: Evidence for Heterogeneous Mantle and Crustal Assimilation on Mars

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Geochemical studies of shergottites (Martian basalts) based on the Rb-Sr, Sm-Nd, and Lu-Hf isotopic systems have provided clues to understanding of the geochemical evolution of Martian mantle and identification of the source reservoirs. On the other hand, the U-Pb isotopic systematics has been used to a limited extend for the shergottite petrogenesis, because it is generally difficult to discriminate the indigenous magmatic Pb component from secondary Martian near-surface components and terrestrial contamination. This study compiles and reassesses all the available Pb isotopic compositions of shergottites; the datasets include whole-rocks and mineral separates with acid leaching experiments.

Three geochemical groups of shergottites (enriched, intermediate, and depleted) have different Pb isotopic compositions, reflecting different μ(^{238}U-^{204}Pb) values of their sources. The enriched and depleted shergottites individually exhibit distinct linear arrays in the ^{206}Pb/^{204}Pb-^{207}Pb/^{204}Pb diagram, providing apparent isochron ages of ~4.1 Ga and ~4.3 Ga, respectively. These linear arrays in the Pb isotopic diagram are interpreted as reflecting either (1) a Pb-Pb isochron or (2) a mixing of two components with distinct Pb isotopic compositions. Four possibilities have been suggested to explain the linear variations in the Pb isotopic compositions of shergottites: (1a) Pb-Pb isochron representing a shergottite crystallization age, (1b) Pb-Pb isochron for the formation ages of the shergottite source reservoirs, (2a) mixing of a terrestrial Pb component, and (2b) mixing of Martian surficial Pb by alternation. However, these interpretations of the Pb isotopic variations are inconsistent with other isotopic systematics such as Rb-Sr, Sm-Nd, and Lu-Hf for shergottites.

We propose a new model for the shergottite Pb isotopic variations along with other geochemical evidence, in which the two linear arrays defined by the enriched and depleted shergottites represent assimilation of an ancient high-μ crustal component that has high ^{207}Pb/^{204}Pb and ^{206}Pb/^{204}Pb ratios. Differences in the other ends of the linear arrays are interpreted as reflecting the geochemical heterogeneity of the Martian mantle (i.e. enriched and depleted mantle sources). These interpretations of the Pb isotopic variations are consistent with two models proposed by other geochemical signatures of shergottites, “crustal assimilation” and “mantle heterogeneity”.

Keywords: Mars, Shergottite, Pb isotope

In-situ U-Pb dating and hydrogen analyses of apatite in the basaltic eucrites

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Introduction: Water is one of the most important volatiles that determine the planetary environments (e.g. magmatic activities, climates and habitability). Despite its importance, questions concerning its origin, such as when and from where the water was supplied to the inner solar system have been poorly understood. Eucrites, a group of howardites-eucrites-diogenites meteorites (HEDs), are considered to be samples of the ancient crustal components from the asteroid 4 Vesta [1], which experienced planetary differentiation by ~5 million years after CAI [2]. The water records in the early differentiated bodies such as Vesta will provide us the insight to the source and the timing of water supply to the terrestrial planets. Igneous phosphates in the eucrites (e.g. apatite) may have preserved the magmatic water during the Vesta’s crustal formation, as well as U-Pb chronological information. In this study, we conducted the in-situ U-Pb dating and the hydrogen analyses of apatite in the two basaltic eucrites, Agoult and Camel Donga.

Samples: Agoult is an unbrecciated granulite, which experienced the strong reheating with partial re-melting [3]. The Pb-Pb age of its zircon and plagioclase are 4554 ±2.0 Ma [4] and 4532.4 ±0.8 Ma, respectively [5]. Camel Donga is a monomict breccia with abundant Fe metal (~2wt%), associated with the later reduction of igneous phases [6]. The Pb-Pb age of its zircon is 4531 ±10 Ma [7], younger than those of Agoult and other eucrites. By SEM-EDX observation of the polished sections, we identified several euhedral to subhedral apatite grains (20-100μm) in Agoult and anhedral apatite grains (10-200μm) in Camel Donga.

Analyses: Both U-Pb and hydrogen analyses were conducted using NanoSIMS 50 at AORI, UTokyo. The sample sections were first baked at ~100C in the NanoSIMS air-lock overnight and then kept in the vessel at < 5E-9 torr for 1 week, to remove the adsorbed water. The previously established NanoSIMS analytical methods of U-Pb were applied [8]. For hydrogen analyses, negative secondary ions of H, D, ^{12}C and ^{18}O were collected to calculate water contents and D/H ratios. The background level of hydrogen is ~56 ppm as H_2O.

Results & Discussion: The Agoult apatite has concordant ^{238}U-^{206}Pb and ^{207}Pb-^{206}Pb ages at 4476 ±160 Ma and 4486 ±61 Ma, respectively. The total Pb/U age is 4523 ±13 Ma, significantly younger than Agoult zircon but consistent with the plagioclase and Camel Donga zircon. It is suggested that these younger minerals may have recorded the same reheating event at ~4523 Ma or the slow cooling in the Vesta’s crust. The Camel Donga apatite has U-Pb and Pb-Pb ages at 4478 ±86 Ma and 4474 ±83 Ma, indicating it may have the same thermal records to that of Agoult apatite. The H_2O contents of them are < 100 ppm for Agoult and < 1,000 ppm for Camel Donga. Though their D/H ratios cannot be determined due to the low water contents, such dry apatite is consistent with the reductive conditions, previously estimated from the Agoult zircon [4] and Camel Donga metal [6]. Our results suggest that Vesta’s crust, at least locally, was depleted in water at ~4523 Ma.

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Keywords: eucrite, water contents & hydrogen isotopic ratios, apatite, U-Pb chronology, NanoSIMS

Mineralogical study of quartz and tridymite in cumulate eucrites

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Introduction:Silica mineral is one of the most important rock-forming minerals on the Earth. It has 23 or more polymorphs under various temperature and pressure conditions [Sosman, 1965]. There are not so many silica minerals in meteorites, but some report silica minerals such as α-quartz, tridymite, cristobalite etc. However, in many cases, they are simply described as “silica minerals” alone and their specific mineral species are rarely identified. Tridymite is the most common silica mineral in meteorites. Tridymite has two crystal systems, monoclinic and orthorhombic. Both of them are hexagonal at high temperature, but monoclinic is known to undergo some different orthorhombic systems upon cooling. Their transition processes and relations of crystal structures are very complicated. Most tridymite in meteorites are monoclinic [Graetsch and Florke, 1991]. Although silica minerals have various polymorphs, they are not fully discussed using polymorphic relations in meteorite science. Therefore, in this study, we focus on silica minerals in three cumulate eucrites and discuss their formation conditions and inversion rate of silica minerals considering their cooling histories.

Sample and Method:We analyzed Moore County, Moama, and Y980433. We first located positions of silica minerals using optical microscopy, SEM, and X-ray mapping by EPMA. After that, silica minerals were identified by EBSD patterns and micro-Raman spectroscopy.

Result and Discussion:Tridymite is the only silica mineral in Moore County and Moama. In contrast, Y980433 contains tridymite and quartz. All tridymite in Moore County is monolclinic and larger (~3 mm) than those in other samples. Moore County is estimated to be once cooled from 990 C to 730 C at 0.00016 C/yr and later it was heated up to 930 C and then cooled down to 730 C at a much faster rate of 0.3 C/yr [Miyamoto et al., 1992]. Tridymite in Moore County is larger than other meteorites because initial cooling rate was slower than other meteorites. In Moama, the maximum size of tridymite is about 0.5 mm, but most are less than 0.1 mm. Our observation reveals that most tridymite grains have lamellar texture. Its host is monoclinic but lamella is orthorhombic. Moama is known to have been slowly cooled at 0.0004 ^{o}C/yr [Harlow et al., 1979], which is slightly faster than Moore County. There is a possibility that orthorhombic tridymite lamella in Moama formed by partial inversion from monoclinic to orthorhombic, but it is not clear. Tridymite in Y980433 is euhedral. According to EBSD patterns, it has two different types of crystal structures, monoclinic and hexagonal, but Raman spectra showed that they are all monoclinic. We considered that these two types of EBSD patterns are the result of twinned monoclinic tridymite [Tagai et al., 1977] or fitting error by the analysis software. Y980443 has quartz at the rim of melt vein or grain boundary of pyroxene and plagioclase. We infer from their anhedral shapes that quartz crystallized by a different process from tridymite, for example impact metamorphism. Because plagioclase is partially transformed to maskelynite, melt vein was considered to be occurred by impact.

Conclusion:It is considered that tridymite in cumulate eucrites is the late-crystallization phase, and it is interesting that tridymite is present in different crystal systems probably due to different thermal histories. The lamellar texture of tridymite in Moama may be due to partial inversion of different tridymite crystal structures caused by relatively fast cooling. Unshocked nature of Moama rules out shock metamorphism. Because most quartz grains in Y980433 are anhedral, they would be a product of crystallization from impact melt. It is necessary to elucidate detailed crystal structures of meteoritic silica phases (especially tridymtie) to further understand complicated polymorphic association of silica minerals in light of thermal history of meteorites.

Keywords: silica minerals, eucrite, cooling rate, inversion, tridymite

The origin of primitive achondrites inferred from a mineralogical and isotope cosmochemical study of NWA 6704

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Introduction: NWA 6704 is an ungrouped primitive achondrite found in 2010. It's composed predominantly of low-Ca pyroxene, with less abundant olivine, feldspar, chromite, awaruite, sulfides and whitlockite. The U-Pb dating shows the crystallization age of 4563.75±0.41Ma (Iizuka et al., 2013). This ancient primitive achondrite provides unique insights into the differentiation of asteroids in the very early stage of solar system evolution. To better understand the formation processes of NWA 6704, we've conducted textural and mineral-chemical study of thin sections using SEM-EDS-EBSD and EPMA. Furthermore, we've determined Cr and Ti isotope compositions using MC-ICP-MS to clarify genetic relationships of this unique meteorite and other grouped meteorites.

Results & Discussion: SEM images show that the texture is represented by aggregates of orthopyroxene (opx) megacrysts up to 1.56 cm in length ($Fs_{40-42}En_{53-57}Wo_{3-4}$) with finer interstices including olivine (Fa_{50-53}), chromite (Cr/(Cr+Al)~0.93), awaruite (~80wt% Ni), feldspar ($Ab_{91-93}An_{5-6}Or_{2-3}$) and whitlockite. Feldspars separated with each other share the same optical extinction position over up to 1 cm irrespective of its occurrence either as complete inclusions of or interstitial to opx megacrysts. Feldspars isolated in the megacrysts have apparently euhedral rectangular morphology, but the facets are controlled by crystallographic orientation of opx megacrysts. These observations suggest that opx crystals are actually “hollow” megacrysts so that many interstices are connected with one another. Although most olivines are subrounded and found in the interstices, Fe-rich olivine occurs as inclusions showing vermicular morphology in one place of each opx megacryst. Such vermicular olivine is considered to be the relict decomposition product of the precursor pyroxene through abrupt heating to cause incongruent melting (ca.>1300℃; Tsuchiyama et al., 1986) followed by rapid cooling, which is most plausibly realized by impact-induced heating. This is consistent with the abnormally large size of opx and its hollow morphology and we argue that the initial crystallization occurred under rapid cooling (ca.1-10^2 ℃/hr; Lofgren et al., 1980). On the other hand, later slow cooling is suggested by the existence of pigeonite containing thin augite exsolution lamellae and the relatively homogeneous mineral compositions. Using the geospeedometry based on Mg-Fe exchange between chromite and silicate phases (Fabriès, 1979; Ozawa, 1984), we estimate the cooling rate at 950-850 ℃ to be 10^{-4}-10^{-2} ℃/hr. The olv-spl oxygen geobarometer (Ballhaus et al., 1991) gives fO_2 of FMQ-2.6.

Cr and Ti are successfully extracted with a new five-stage column chromatographic procedure. The Ti isotope analyses yielded $\varepsilon^{50}Ti = 2.28\pm0.23$, which is distinct from differentiated meteorites and ordinary and enstatite chondrites but within the range of carbonaceous chondrites (Warren et al., 2011). Given that the oxygen isotope composition of NWA 6704 is plotted near the fractionation line of CR chondrite (Irving et al., 2011), its carbonaceous chondritic $\varepsilon^{54}Cr$ (Sanborn et al., 2013) and $\varepsilon^{50}Ti$ even more likely support its genetic link with carbonaceous chondites. Our results have indicated that the presence of carbonaceous chondrite-like asteroid at about ≤3.55Ma (after CAI formation; U-Pb age). This is consistent with preservation of ^{26}Al in the undifferentiated parent asteroid at about T=2-3.5Ma (Sahijpal et al., 2007). This and the inferred thermal history suggest high internal temperature of the parent body owing to ^{26}Al decay was augmented by impact to have achieved abrupt heating up to above liquidus, followed by rapid cooling and later slower cooling owing to blanketing effect of impact ejectas pilled up on the parental body.

Keywords: Primitive achondrite, NWA 6704, impact-induced heating, Cr, Ti, stable isotope

Petrological and mineralogical study of a orthopyroxene-rich lodranite Yamato 983119.

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Introduction Primitive achondrites show achondritic textures, but have relatively chondritic bulk chemical features. Acapulcoites and lodranites are a group of primitive achondrites. They suffered few% to <20% partial melting. They are thought that formed in the same parent body which experienced various degree of heating [1]. Therefore they are suitable sample to better understand evolutionary history of a planetesimal.

Yamato (Y) 983119 was collected in Yamato Mountains, Antarctica by JARE39. This meteorite was classified into a lodranite [2]. Although its mg# (molar Mg/(Fe+Mg)) of pyroxene and olivine and O-isotopic compositions are similar to those of acapulcoites and lodranites, it is unusually rich in orthopyroxene (Opx) and poor in olivine. We examined petrology and mineralogy of this meteorite in detail and compared with other acapulcoites and lodranites.

Sample and Methods We analyzed one polished thin section of Y 983119. For comparison, we analyzed thin/thick sections of 3 acapulcoites (Acapulco, Y 74063, Y 981505) and 7 lodranites (Y 74357, Y 791491, Y 791493, Y 981619, Y 981670, Y 981725, Y 981988). These samples are observed by an optical microscope and FE-SEM (JEOL JSM-7100F) at NIPR. Elemental maps were obtained by an EDS-system (Oxford AZtec Energy) equipped with FE-SEM. Modal abundances of each sample were obtained from elemental maps by using of a software ImageJ (NIH). Sizes of the analyzed areas are from ~2 x 4 to 10 x 14 mm. We also performed fabric analysis to reveal lattice-preferred orientation (LPO) of Opx by using EBSD technique. Chemical compositions of constituent minerals were obtained by EPMA (JEOL JXA-8200).

Result Y 983119 has a coarse-grained texture (~0.5-2.0 mm) and composed of Opx (73 vol. %) and plagioclase (14 vol. %), and minor kamacite and taenite (5 vol. %), olivine (4 vol. %), troilite (2 vol. %) and augite (2 vol. %), and traces of phosphate, chromite and schreibersite. Opx has a rounded or tabular shape and some grains have zigzagged rim. Most of them contain numerous augite inclusions (few tens of μm in size) and thin lamellae. There is one rare augite inclusions partly surrounded by K, Al, Si-rich glass in Opx. Olivine and augite show an amoeboid shape. One olivine grain is penetrated by plagioclase and troilite. Plagioclase is distributed interstitially to olivine and Opx grains. Some plagioclase grains enclose olivine and Opx grains. EBSD analysis indicates that Opx grains are randomly oriented.

Compositions of mafic silicates are within the ranges of acapulcoites and lodranites: Opx ($Wo_{2.3}$ $En_{94.2}$ $Fs_{3.6}$), augite ($Wo_{45.4}$ $En_{53.1}$ $Fs_{1.5}$) and olivine ($Fa_{3.0}$). However, the Mg/Mn ratios of Opx are significantly higher (molar Mg/Mn = 189) than the other samples we examined (molar Mg/Mn = ~100-120). Plagioclase has relatively anorthitic composition ($Or_{1.7}$ $Ab_{69.6}$ $An_{28.7}$) than those of the others ($An_{\sim 10\text{-}20}$).

We conclude that Y 983119 is classified into acapulcoites and lodranites clan but has unusually high abundance of Opx (73 vol. %) and low abundance of olivine (5 vol. %). This rock might have been cumulates crystallized from melt formed by larger degree of partial melting.

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Keywords: Primitive Achondrites, Acapulcoite-Lodranite Meteorites, Planetesimals

Numerical study on chemical zoning of olivines at chondrule formation

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Chondrules are millimeter-sized and spherical silicate objects contained in chondritic meteorites. It is considered that chondrules were formed from dust aggregates (precursors), which experienced melting and subsequent rapid solidification in some flash heating events. Chondrules include some silicate minerals such as olivines, in which chemical zoning is observed. The chemical zoning reflects environmental change during solidification. However, it has not been understood what zoning profile is recorded in minerals when the actual thermal history experienced by chondrules is considered.

In this study, we carried out the numerical simulations of melting and growth processes of an olivine crystal in a flash heating event in order to investigate the zoning profile recorded in the crystal. Because the chemical composition of the growing crystal differs from that of the ambient liquid phase, incompatible elements are swept out to the liquid phase (element partitioning). We considered the element partitioning at the crystal-liquid interface and the element diffusion in the solid and liquid phases at the calculation. As the numerical method, we adopted a phase-field method combined with the ideal solution model of Mg-Fe olivine.

First, we considered a simplified thermal history, which is divided into three periods: heating at a constant rate, isothermal at peak temperature, and cooling at a constant rate. Olivine was melted at the heating and isothermal periods. At the cooling period, olivine was turned to growth and the chemical zoning was formed. The zoning profile did not depend on the heating rate and the duration of the isothermal period significantly, but varied with the cooling rate. In addition, we confirmed a local minimum in the Fe concentration at the position where the olivine was turned to growth.

Second, as the more realistic situation, we considered the thermal history predicted by a shock-wave heating model. We found that the slope of the zoning profile agreed with that predicted by a theoretical model [1], which considered the cooling period only. These results suggested that the chemical zoning of olivine crystals formed during chondrule formation mainly reflects the cooling condition.

References: [1] H. Miura and T. Yamamoto (2014), The Astronomical Journal 147, 54 (9pp).

Keywords: chondrule, chemical zoning

Formation Process of Compound Chondrules: Collision-Induced Crystallization of Supercooled Droplets

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Some chondrules are composed of two (or more) chondrules fused together. They are called compound chondrules. Compound chondrules have several remarkable features. In this study, we focus on three features; (1) textural types, (2) the size ratio between two components, and (3) the fraction of compound chondrules. In previous studies, these three features are remained to explain.
Textural types of chondrules originate from their thermal histories. Non-porphyritic chondrules (e.g., barred olivine, radial pyroxene, and cryptocrystalline) are formed from completely molten precursors, while porphyritic chondrules are formed from partially molten precursors. As for single chondrules, the majority is porphyritic type (84%) and non-porphyritic ones are rare (16%). In contrast, more than 80% of all the compound chondrules have non-porphyritic textures. This significant feature suggests that compound chondrules are crystallized from completely molten precursors.
Experimental studies revealed that floating completely molten precursors turn into supercooled droplets without crystallization, and non-porphyritic chondrules are produced by crystallization of supercooled droplets triggered by contact with something. In addition, theoretical studies suggest that the duration of supercooling can be long.
Here, we propose a new model for the compound chondrule formation: compound chondrules are formed by collision-induced crystallization of supercooled droplets. This model is based on the feature (1) and experimental facts. Additionally, we can obtain the feature (2) that larger ones of compound chondrules keep round shapes while smaller ones are deformed. This feature is explained by the reason that larger ones are likely to be collided more than smaller ones.
We also estimate the product of the number density of precursors n and the duration of supercooling t for reproducing the fraction of compound chondrules. Then the product of the number density and the duration is $n\ t = 0.1\ \mathrm{cm}^{-3}\ \mathrm{s}$. Thanks to the supercooling, we can explain the fraction of compound chondrules with large t and low n.

Keywords: compound chondrule, supercooling, crystallization, collision

Oxygen and carbon isotopic ratios of calcite in the Nogoya CM chondrite

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CM chondrites exhibit evidence for aqueous alteration to variable degrees. Carbonate is a secondary mineral of aqueous alteration. Detailed petrological and mineralogical observations along with O-isotope measurements have been carried out by previous studies. These studies have suggested that carbonates in CM chondrites did not form in a single event but formed intermittently (Tyra et al., 2012; Lee et al., 2013). In this study, we conducted in-situ O- and C-isotope measurements on calcite grains in the Nogoya CM 2.2-2.3 chondrite. Isotope measurement on carbonates in multiple “generations” could shed light on the evolution of O and C isotopic compositions during aqueous alteration.

We found many calcite grains by SEM observation. As reported in the previous studies (e.g., Lee et al., 2014), two types of calcite grains with distinct mineralogical characteristics were found. Following the definition by Lee et al. (2014), we describe these calcite grains as type 1 and 2 grains. Most type 1 grains are single crystals and have serpentine/tochilinite rims. On the other hand, type 2 grains are polycrystalline and microporous, and do not have rims.

Oxygen isotopic compositions are highly different between type 1 and 2 grains, but similar within each type ($d^{18}O$ = 34.7 ‰(type 1) and 19.3 ‰(type 2) on average). The average $D^{17}O$ values are -2.5 ‰ (type 1) and -5.4 ‰(type 2). The $d^{18}O$ and $D^{17}O$ values indicate that type 2 calcite formed later than type 1 calcite, because progressive alteration led to O-isotope exchange between water and anhydrous silicate with lower $d^{18}O$ and $D^{17}O$ values than water. Carbon isotopic ratios of type 1 grains are similar ($d^{13}C$ = 31.8 ‰on average), whereas type 2 grains have variable $d^{13}C$ values ranging from 28.8 to 61.2 ‰. These observations indicate an increase in $d^{13}C$ values in later stages of aqueous alteration.

It has been suggested that the Rayleigh-type isotopic fractionation driven by the escape of ^{13}C-poor CH_4 could have led to ^{13}C enrichments of the dissolved inorganic C (Guo and Eiler, 2007). The observed $d^{13}C$ increase of ~30 ‰can be explained if ~28 % of the dissolved C was reduced to produce CH_4 and was lost at 28 ^{o}C. If true, aqueous alteration in CM chondrites would have occurred in an open system at least in later stages.

Keywords: calcite, oxygen-isotope, carbon-isotope, CM chondrite

Dehydration process of hydrous asteroids inferred from mineralogy and noble gas signatures of dehydrated CI and CM chondrites

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CI and CM carbonaceous chondrites are the most primitive materials in the solar system in terms of their unfractionated chemical compositions. But they have experienced aqueous alteration to various degrees and thus retain little or no primordial mineralogy. Their parent bodies are believed to be hydrous C-type asteroids based on the similarity of reflectance spectra between the meteorites and the asteroids [1]. However, reflectance spectra of a subset of hydrous C-type asteroids are similar to those of hydrous carbonaceous chondrites that experienced heating and dehydration [2] and thus it was suggested that dehydration has occurred in hydrated asteroids. Since more than 20 meteorites showing evidence of dehydration have been found, dehydration is a common process of primitive hydrous asteroids. However, dehydration process especially for CI chondrites and the heat source for dehydration remain unknown. The purpose of this study is to evaluate the degrees of heating and to constrain the heating temperatures based on mineralogical properties and noble gas signatures of the two meteorites. In this study, we used two samples; Yamato (Y)-982086 and Y-980115, which are classified as CM and CI chondrites, respectively.

The two meteorites were analyzed using an optical microscope, a field-emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometry (EDS), an electron probe micro-analyzer (EPMA) and synchrotron X-ray diffraction (S-XRD) for petrology and mineralogy. Y-980115 was analyzed for noble gas isotopes.

Petrologic observation indicates that Y-982086 has experienced a moderate degree of aqueous alteration and is classified to CM 2.3 based on the classification scheme [3]. S-XRD shows that matrix phyllosilicate exhibits no 001 basal reflection, but remains prism reflections and secondary olivine is not identified, suggesting that phyllosilicate starts to decompose to be poorly crystalline. Based on (1) the presence of pentlandite and pyrrhotite with pentlandite lamellae and (2) the mean and standard deviation of Cr_2O_3 contents in FeO-rich olivine [4], it is suggested that the meteorites was heated at a temperature of 400 to 450 °C, which corresponds to the heating stage II [5].

Y-980115 contains coarser phyllosilicates and higher abundance of Fe sulfide than the Orgueil CI chondrite, suggesting that Y-980115 has not experienced advanced aqueous alteration compared with Orgueil, because it is known that phyllosilicate becomes smaller and Fe sulfide becomes less abundant with progressive aqueous alteration of CI chondrites [6]. Very weak 001 reflection of matrix phyllosilicate suggests that phyllosilicate is poorly crystalline, like Y-982086. Coexistence of carbonate and carbonate-decomposed product, periclase, suggests a heating temperature of 520 to 550 °C, which corresponds to the heating stage II to III [5]. This is consistent with similarity of noble gas release patterns of Y-980115 to those of CM chondrites of heating stage II [7]. Cosmic-ray exposure age estimated from cosmogenic ^{3}He (0.16 Ma) is shorter than that from cosmogenic ^{21}Ne (0.48 Ma). We argue that thermal dehydration occurred along with diffusive loss of cosmogenic ^{3}He not on its parent asteroid but during transit to the Earth by solar heating.

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Keywords: hydrous carbonaceous chondrite, aqueous alteration, thermal metamorphism

Be-B systematics of refractory inclusions in CO and CH chondrites

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Observations of solar-type Young Stellar Objects (YSOs) have shown enhanced and frequent X-ray flares accompanied by intense flux of accelerated particles [1]. The powerful X-ray activity around newborn stars suggests that intense irradiation from the proto-Sun has also occurred in the early solar nebula. Be-B systematics of refractory inclusions, the first solids in our solar system [2, 3], can potentially shed light on irradiation processes in the early solar system.

Previous studies have demonstrated that a short-lived radionuclide ^{10}Be, which decays to ^{10}B with a half-life of 1.4Myr [4], was present in the early solar system with initial ^{10}Be/^{9}Be ratios ranging from 10^{-4} to 10^{-2} [5-13]. However, most of the data come from refractory inclusions in CV3 chondrites. To further investigate the distribution of ^{10}Be and irradiation conditions in the early solar system, we conducted Be-B isotopic measurements using a NanoSIMS 50 (at AORI, Univ. of Tokyo) on compact melilite-rich CAIs in primitive chondrites, Y81020 (CO3.05) and SaU290 (CH3).

The melilite-rich CAI in Y81020 yields an isochron with the initial ^{10}Be/^{9}Be ratio comparable to those of CV CAIs within uncertainties. The results suggest that CO CAIs have also experienced irradiation processes similar to CV CAIs. In contrast, a melilite-rich CAI in SaU290 shows no resolvable excesses in ^{10}B from the terrestrial value. Previous studies have demonstrated that hibonite-rich inclusions in CMs and FUN inclusions in CVs typically show lower ^{10}Be/^{9}Be ratios than those of most normal CAIs [7, 9, 12, 13]. In addition, these inclusions are known to have low ^{26}Al abundances, which is interpreted as their formation prior to the injection of ^{26}Al into the solar system [e.g., 14]. These observations may suggest that FUN-like inclusions record irradiation history in the protosolar molecular cloud [9, 15] and/or heterogeneous distribution of ^{10}Be in the early solar system [12, 13]. A substantial fraction of CH CAIs also has little ^{26}Al [16], suggesting possible relevance to FUN-like inclusions. The low ^{10}Be/^{9}Be ratio of the CH CAI observed in this study could, therefore, support the above hypothesis.

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Keywords: early solar system, irradiation processes, Be-B isotopes

Reflectance spectra, mineralogy, and chemistry of experimentally heated Tagish Lake carbonaceous chondrite

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C-, P-, and D-type asteroids, orbiting at the outer asteroid belt, are important objects for understanding of the evolution of outer solar nebula. A subset of these asteroids shows evidence of thermal evolution such as dehydration (Jones et al., 1990), though the thermal effects on reflectance spectra, mineralogy, and chemistry are not fully understood. The purpose of this study is to reproduce the spectral, mineralogical, and chemical changes of D-type asteroids caused by heating events, using the experimentally heated samples from Tagish Lake meteorite which is believed to have derived from a D-type asteroid (e.g., Hiroi et al., 2001). Besides, this study was performed to identify constituent minerals of Martian moons, Phobos and Deimos. The spectra of Phobos and Deimos are similar to that of D- and T-type asteroids (e.g., Rivkin et al., 2002). However the 3.0-μm absorption band is shallower than these asteroids, suggesting that they are heated D-type objects.

The Tagish Lake carbonaceous chondrite fragments were experimentally heated in a vacuum at temperatures of 400, 600, and 900°C for 50 hours. Unheated and heated samples were analyzed using the powder and synchrotron X-ray diffraction (XRD) methods for bulk mineralogy, field-emission scanning electron micro scope (FE-SEM) for texture, elemental analyzer for C, N, S contents, mass spectrometer for carbon isotope ratios, and FT-IR for reflectance spectra.

XRD patterns and FE-SEM observation showed that the unheated Tagish Lake sample consists of saponite, Mg-Fe carbonate, pyrrhotite, olivine and magnetite. Saponite was replaced by olivine, and recrystallization of secondary olivine was proceeded from 600°C to 900°C. Similarly, by heating at 600°C, Mg-Fe carbonate was decomposed into magnesiowüstite, which was reduced into taenite by heating at 900°C.

Carbon content and isotope ratio ($\delta^{13}C$ values) start decreasing from the temperature of 600°C. Decomposition of carbonate, which has $\delta^{13}C$ value of ~+67‰ (Grady et al., 2002), is responsible for the decrease of carbon content and $\delta^{13}C$ value up to 600°C. Meanwhile, from 600 to 900°C, carbon content and $\delta^{13}C$ value decreased due to gasification of organic carbons ($\delta^{13}C$ of ~-9‰; Grady et al., 2002) by thermal cracking and oxidation taken place during heating at 900°C.

The 3.0-μm absorption band in a reflectance spectrum is responsible for interlayer and structural water of saponite and absorbed water. The 3.0-μm band of the unheated sample was deep and broad, which becomes shallower and shaper with increasing heating temperatures. Interlayer water was dehydrated up to 600°C, and structural water was dehydrated up to 900°C. In contrast, structural water of serpentine in the Murchison carbonaceous chondrite, which is derived from a C-type asteroid, was dehydrated at lower temperature of 600°C (Yamashita et al., 2015). Therefore, it may be possible that C- and D-type asteroids have different water content when they are heated at the same temperature.

Mineralogical, chemical, and spectral changes of Tagish Lake proceed with increasing heating temperatures; (1) saponite is dehydrated and recrystallized into olivine, (2) interlayer and structural water of saponite are dehydrated step by step, (3) Mg-Fe carbonate is replaced by magnesiowüstite and finally reduced into taenite, and (4) volatile elements including carbon, nitrogen, and sulfur are gasified and C isotope ratios are changed accordingly.

Comparison to Phobos and Deimos spectra suggests that 400°C and 600°C heated samples of Tagish Lake matches better. But 0.65-μm absorption band that is characteristic absorption of the Phobos red areas was not reproduced. Therefore, the reproduction of 0.65-μm absorption requires additional conditions, if Phobos was originally D-type asteroids.

Keywords: Tagish Lake, dehydration

A primitive chondrite, NWA 8613 chondrite, CV3.1-3.2

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Carbonaceous chondrites are primitive meteorites, and they give important information about the early processes in the solar system. Especially one of them, CV chondrites are characterized by the occurrence of large refractory inclusions and chondrules. They are classified into three subgroups: two oxidized groups, CV_{oxA} and CV_{oxB}, and a reduced group, CV_{red} [1]. Oxidized CVs were subjected to the secondary metasomatic reactions and partly aqueous alteration. On the other hand, CV_{red} chondrites preserve their primitive nature, although most of them partly experienced the secondary reactions [2]. Here we present our petrographic results on a new CV chondrite.

We studied NWA 8613. This is a newly classified CV chondrite. The shock stage is S1, and the weathering grade is W3. It consists of large chondrules (0.84 mm on average diameter, and 38 vol.% in modal composition), refractory inclusions (13 vol.%), and matrix (41 vol.%). Magnetite and phyllosilicate are not encountered, but kamacite is abundant. All these features indicate that the NWA 8613 is classified as CV_{red}.

Chondrules in NWA 8613 do not show preferred orientation, and are mostly porphyritic olivine and olivine-pyroxene type (89%). Mesostasis phases are mainly anorthitic plagioclase often with diopside. Olivine phenocrysts are mostly magnesian ($Fa_{2.1}$ on average). The width of ferroan rims of olivine gains is below 1 μm in general. Low-Ca pyroxenes are also magnesian ($Fs_{1.7}$). Chondrules contain kamacite and troilite.

Type A CAI and AOA are most common refractory inclusions. Melilite is the most abundant mineral, and gehlenitic (Geh_{72-93}). Magnesian spinel (mostly <0.3 wt.% FeO) is abundant in many inclusions. A few CAIs contain ultrarefractory metal nuggets. Olivines in AOAs hardly show chemical zoning, and the width of ferroan rims is smaller than 1 μm. Matrix comprises fine-grained minerals, mainly ferroan olivine with spinel, metal and sulfides. Matrix contains Ni-rich metal, troilite, and pentlandite.

Kimura and Ikeda [2] showed that even chondrules in CV_{red} chondrites experienced the secondary reactions, such as replacement of low-Ca pyroxene by ferroan olivine, secondary zoning of olivine, and exchange of Ca-Na to produce nepheline and sodalite. Chondrules in NWA 8613 hardly show the evidence for all these reactions. Only very thin nepheline lamellae (<0.5μm in width) and narrow ferroan rims of olivine grains are noticed in chondrules.

Metamorphic degree (petrologic subtype) can be estimated for CO and partly CV chondrites by several methods. One of them is the grain size of matrix olivine [3]. That of NWA 8613 is <0.9 μm on average. The width of ferroan olivine rims in AOAs is also a key for the classification [4], and is <1 μm in NWA 8613. Although Fe-Ni metals in chondrules do not show typical plessitic texture in Semarkona (type 3.01) [5], tiny Ni-rich metals are encountered within host kamacite. All these features indicate that NWA 8613 is classified as type 3.1-3.2.

We conclude that NWA 8613 hardly experienced shock metamorphism, thermal metamorphism, and metasomatism. This is one of the most primitive CV chondrites so far. Therefore, NWA 8613 is a significant sample to classify CV chondrites, and to clarify the processes in the early solar system.

Acknowledgements: Dr. A. Yamaguchi in NIPR helped us to analyze and observe this sample.

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Keywords: Carbonaceous chondrite, Petrologic type

The differences among CO3 chondrites from the X-ray diffraction

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1. Introduction

The X-ray diffraction method is one of a powerful tool for studying the subtle differences of thermal metamorphism and initial condition of unequalibrated chondrites. The X-ray gives the global feature of constituent mineral phases including submicron-sized matrices. The petrologic type of the CO chemical group, constituting a group of carbonaceous chondrites, is three, which is subdivided into 3.0-3.9. In the present study, the X-ray powder diffraction patterns were obtained from the polished thin sections of the CO3 chondrites, and new insights were obtained on the differences among the subtypes.

2. Experiments

The X-ray diffractometer, SmarLab (RIGAKU), at National Institute of Polar Research installed in 1994 was used for the present study. The sample stage of the automatically sample change (ASC10) was used for the sample holder of the polished thins sections (PTSs), Y-81020 CO3.0, Colony CO3.0, Y-791717 CO3.3, Lance CO3.5, ALH-77003 CO3.6, Isna CO3.8, A-882094, and Y983589. The X-ray was generated from the Cu target and K beta was removed using the Ni filter. Tube voltage and tube current were 40 kV and 30 mA, respectively. The scan speed of the solid-state detector (D/tex Ultra 250) was 0.4degree/min. The width of the incident X-ray was 10 mm. The PTS was rotated within the plane during the measurements at 100 rpm. It was confirmed that the method gives the consistent diffraction pattern with the powder X-ray diffraction method (Imae, 2015). The half width and intensity of the diffraction was analyzed using the program by the software Visual Basic 6.0 runtime.

3. Results and discussion

The diffraction of olivine (130) is doublet when the subtype is less than 3.5, corresponding to ferroan olivines in matrices (Fa~35-45) at lower diffraction angle and magnesian olivines in the type I chondrules at higher diffraction angle. It is single when the subtype is more than 3.6. In more detail (Fig. 1), the half width increases and the peak position shifts lower (to ferroan) at higher diffraction angle when the subtype changes from 3.0 to 3.5, but the peak vanishes more than the subtype of 3.6. On the other hand, the half width decreases and the peak intensity increases at lower diffraction angle when the subtype changes from 3.0 to 3.8. The series of sensitive change occurs during the weak thermal metamorphism accompanying the Mg-Fe diffusion in olivines and bulk sample.

The (22-1) of clinoenstatite was detected irrespective of the subtype, and the (321) of orthoenstatite was also identified irrespective of the subtype (Fig. 2). It is considered that the orthoenstatite in lower petrologic subtype is high temperature type formed during the chondrule formation although that in higher subtype may be low temperature type formed during the thermal metamorphism on the CO parent body. The unique occurrence of the orthoenstatite phases would suggest that the thermal history during the chondrule formation is different from that for the ordinary chondrites. The result is consistent with that by Imae et al. (2013) based on the EPMA.

4. Acknowledgment

NI is grateful to Dr. Shugo Ohi in Shiga Univ., who indicated the diffractions of clinoenstatite.

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Keywords: X-ray diffraction, CO3 chondrite, olivine, pyroxene

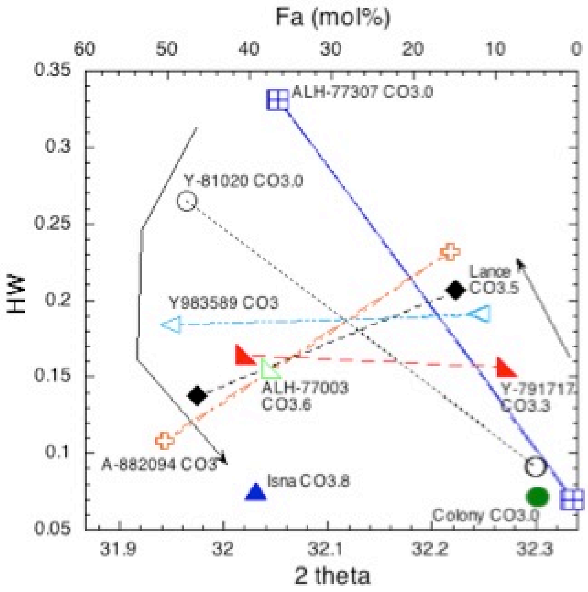

Fig. 1. The relationship between olivine (130) and half width of the diffraction for various subtypes of the CO3 chondrites.

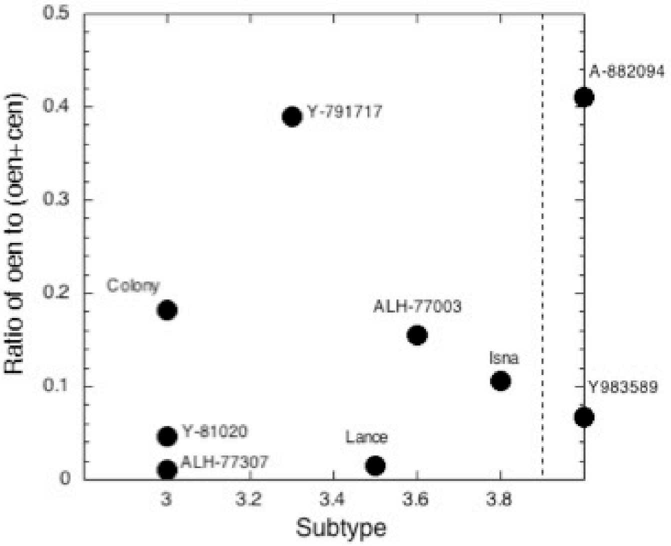

Fig. 2. The ratios of orthoenstatite (oen) to two phases of enstatites (opx+cpx) for various subtypes of the CO3 chondrites. Cen=clinoenstatite.

Formation process of nepheline in carbonaceous chondrites: Reproductive experimetal approach

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In CO/CV chondrites, nepheline is widely distributed in the Ca, Al-rich inclusions (CAIs), the chondrule mesostases and the matrices. Recent petrographic studies have shown abundant evidence suggesting that the nepheline is secondary phases altered from melilite and/or plagioclase by a chemical reaction with Na-rich fluids, and the reaction (Na-metasomatism) occurred in the chondrite parent bodies. Because of the high volatility and mobility, Na is potentially a powerful indicator reflecting aqueous environments of the parent bodies. While many petrographic studies of natural meteorites had made considerable progress on revealing behaviors of Na-metasomatism, quantitative uncertainty for the aqueous condition still remains. In the present study, we performed a number of hydrothermal experiments using melilite and plagioclase as starting materials, and made crystal identifications, micro-textural observations, chemical analyses and thermal analyses for run products. The purpose of this study is constraint of environment in carbonaceous chondrite parent bodies by revealing process of nephelinization.

We used i) synthetic melilite ($Ca_2Al_2SiO_7$) + SiO_2, and ii) natural plagioclase ($Na_{0.5}Ca_{0.5}Al_{1.5}Si_{2.5}O_8$) as starting materials. The reaction solution of 1N (mol/l)-HCl (pH 0), H_2O (pH 7), 0.1N-NaOH (pH 13) and 1N-NaOH (pH 14) were prepared for the hydrothermal experiments with different water/rock ratios (4.67, 46.7 and 467 ml/g). Na^+ concentration in all solutions is maintained at 1 mol/l by addition of NaCl. Hydrothermal alteration experiments were performed with a PTFE reaction vessel loaded into steel autoclave at 200 °C and 1.5 MPa for run duration time of 168 hours. The recovered samples from the hydrothermal and thermal experiments were analyzed by XRD, SEM, TEM, and TG-DTA.

The experiments using melilite without SiO2 under the conditions of WR 46.7 and pH 7-14 showed that hydro-grossular ($Ca_3Al_2[SiO_4]_{1.5}[OH]_6$) forms as a secondary altered phase. Under the same WR and pH conditions, as the proportion of SiO2 in increases, various Na-rich zeolitic materials were observed in the run products including analcime (Anl, $NaAlSi_2O_6H_2O$), nepheline-hydrate (NephH, $NaAlSiO_4[H_2O]$) and hydroxy-cancrinite (Canc, $Na_8Al_6Si_6O_{24}[OH]_2[H_2O]_2$). At the high W/R (=467) condition, no secondary phase was observed, while Anl and Canc occur at the low W/R (=4.65) under pH 14. In the experiments using plagioclase with high W/R ratios and pH 0-7 solutions, no secondary phases formed. Anl and NephH formed under pH 13-14 conditions. At low W/R ratios, secondary phases were identified as Anl, and NephH.

The TG-DTA and XRD analyses for nepheline hydrate showed that NephH is transform to nepheline at 796-841 °C at the heating rate ranging of 1-14 °C/min. From the analyses of the reaction kinetics, we estimated that NephH alter to nepheline for ~10^5 years at 515 °C. Although we failed to analyze the reaction kinetics for Canc and Anl because of their complicated DTA curves, thermostatic experiments suggested that both material also change to nepheline at 760 °C (Canc) and 800 °C (Anl).

The present results suggest that melilite and plagioclase are easily altered into zeolitic materials in Na^+-rich high alkali solutions. The present experimental condition demonstrated in the present study seems to be comparable to actual carbonaceous chondrite parent body. Thus, we infer that nepheline in carbonaceous chondrite formed initially as zeolitic materials during aqueous alteration, and they were subsequently dehydrated to nepheline.

Keywords: nepheline, chondrite, aqueous alteration

Negative crystals of calcite and empty crystals in the shape of hexagonal plate in carbonaceous chondrites.

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CI, CM and CR chondrites have calcite formed by aqueous alteration. Aqueous fluid inclusions have been searched from these mineral grains using an X-ray micro-tomography technique combined with FIB micro-sampling [1]. During the course of this research, we found pores with facets (negative crystals) in the shape of hexagonal plate in calcite and hexagonal platelet cavities (empty crystals) in matrix. Calcite has a variety of crystal morphology, which reflects their formation conditions such as temperature and partial pressure of CO_2 [2]. In this study, the shapes of these negative and empty crystals, which might have their formation conditions during aqueous alteration, were investigated based on crystallographic consideration. The shapes of negative crystals in terrestrial calcite were also examined for comparison.

Samples used in this study are a calcite grain (about 30 mm) with negative crystals in the Sutter’s Mill meteorite (CM) and a grain of unknown phase (about 40 mm) with hexagonal platelet cavities in a matrix of the Ivuna meteorite (CI). Two single crystals with different morphologies, hexagonal plate and stud-like shape, which contain fluid inclusions, from Kamioka Mine were used as the terrestrial samples. Cubes or a cylinder 20 to 30 μm in size were sampled from thin sections using SEM/FIB and imaged by x-ray absorption imaging tomography with the effective spatial resolution of approximately 150 nm at BL47XU of SPring-8, Japan (e.g., [1]). The 3D shape of negative and empty crystals were extracted from CT images by binarization. The crystallographic orientations of the terrestrial calcite were determined with an FE-SEM/EBSD and the Miller indices of negative crystal facets were determined.

Two negative crystals about 2 mm are found in the Sutter’s Mill sample. One clearly has a hexagonal plate shape, while the other not. As the calcite grain is a single crystal based on X-ray diffraction, the Miller indices of negative crystal facets were estimated by assuming that the hexagonal face is parallel to (001) and secondary face corresponds to (101). Both of the negative crystals have almost common combination of crystal faces but are different from a popular hexagonal shape composed of {001} and {104}. A large number of small inclusions (<1mm) are distributed in the calcite grain as a band, which is almost parallel to (001) of the negative crystals. This suggests that calcite crystal grew with (001) surface.

Several cavities (about 3 mm) with hexagonal plate shape were observed in the Ivuna sample. Miller indexing by assuming the hexagonal face as (001) suggest that the cavity is an empty crystal of carbonate such as calcite with (001) and (100) facets, although we could not eliminate a possibility of different minerals such as pyrrhotite.

Negative crystals in both of the terrestrial calcite crystals are distributed along planes, suggesting that they are healed cracks. The hexagonal plate crystal with {001} and {104} has a negative crystal (5 mm) with common {104} facets but {001} facets are absent. The stud-like calcite with {018} has a negative crystal (5 mm) with different facets of {1-12}. These results can be explained by that negative crystals in healed cracks have, faces with low surface free energies by dissolution and recrystallization during the course of healed crack formation, and (001) facet with high free energy disappeared or was originally absent. In contrast, (001) in the Sutter’s Mill negative crystals corresponds to growing crystal surface. Thus, it is important to examine conditions for growth with (001) surface.

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Keywords: carbonaceous chondrite, calcite, negative crystal

In-situ obsevation of organic matter in the Allende meteorite matrix using X-ray microscopy

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Previous studies have reported that many kinds of carbon components are included in Allende CV3. The carbon components might be modified because they were extracted through acid treatments in the previous studies. Although the carbon components are mainly contained in the matrix of Allende CV3, their natures and occurrences have not been described in detail. *In-situ* sample extraction protocol without any chemical treatments should be applied for the characterization of the carbon components. In this study, we applied a scanning transmission X-ray microscopy (STXM) analysis combined with a focused ion beam (FIB) technique for functional group analysis and speciation.

First, Allende CV3 chip sample was cut by ISOMET under non-water and non-oil conditions. The cross section of the chip sample was coated with gold for a SEM observation. The matrix portion of the Allende CV3 was observed by a SEM. Several portions of interest selected through SEM observations were processed to ultra-thin foils using a FIB. The foils were attached to a Mo-grid. STXM analyses were conducted using STXMs at BL-13A, Photon Factory and BL-4U, UVSOR. After STXM observation, TEM observations were also conducted for textural observations.

The carbon components were found along with the grain-boundaries of fine-grained olivine crystals (diffusional). Several dense carbon components were also found in the diffusional carbon components (particulate). The constituent rates of particulate and diffusional carbons are approximately fifty-fifty. Based on C K-edge NEXAFS, the particulate carbon (aromatic-rich and carboxylic-poor) appears to be insoluble organic matter of Allende CV3 [1]. The diffusional carbon portion, on the other hand, mainly consists of aromatic-poor and carboxylic-rich carbon components. Fe L- and O K-edge NEXAFS spectra and TEM observations showed that spinel and chromite crystals are embedded in the particulate carbon. These minerals might be the fragments of CAIs, because such high temperature condensation minerals are not formed thorough thermal metamorphism occurred on the Allende parent-body. Our FIB-STXM analyses depict the existences of different two type carbon components in the Allende CV3. Based on the assumption that each carbon components had different origins, the following tow hypothesis is made. (i) The particulate carbon component might correspond to nano-globules included in carbonaceous chondrites. In some cases, silicate-minerals are surrounded by the nano-globules [2]. As same to this case, the particulate carbon component might had formed on the spinel and chromite crystals in the solar nebula, and accreted into the Allende parent-body. (ii) On the other hand, diffusional carbon component is similar to diffuse organic matter in the Orgueil and Murchison [3], except for the carbonate peak in the NEXAFS spectra. It is possible that the diffusional carbon component formed through aqueous alteration occurred on the Allende parent-body.

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Keywords: Allende meteorite, Carbon component, Scanning Transmission X-ray Microscopy (STXM), Focused Ion Beam (FIB), NEXAFS, Synchrotron radiation

Evaluation of gamma-ray effects for formation of amino acid precursors in the Solar System small bodies

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Delivery of amino acids from extraterrestrial materials such as meteorites could contribute to the emergence of life in the early Earth. Carbonaceous chondrites contain various organic matter, which mostly consists of insoluble organic matter (IOM), and also contain some soluble organic compounds including amino acids. Cody et al. [1] proposed IOM formation via formose reaction starting with formaldehyde and glycolaldehyde during aqueous activity in the small bodies. Additional hydrothermal experiments showed that ammonia enhanced the yields of IOM like organic matter [2]. The most effective heat source for melting water ice in small bodies is considered to the decay of ^{26}Al. We are focusing on the gamma-ray emission from ^{26}Al, and evaluate the effects of gamma-ray as an energy source for the formation of organic matter, specially amino acids.

Amino acids including glycine, alanine and beta-alanine were detected from the most of the irradiated and heated samples after acids hydrolysis, but little or no amino acids were detected from the solutions before acid hydrolysis. The yields of amino acids from the solutions after heating experiments were larger than these after gamma-ray irradiation with the presence of $Ca(OH)_2$, but the amino acid yields from heating were smaller than these of gamma-ray irradiation without the presence of $Ca(OH)_2$. These results indicate that $Ca(OH)_2$ was act as a catalyst to produce amino acid precursors in the heating experiments but was not in the case of gamma-ray irradiation. The solutions after heating had smaller alanine/glycine ratios than the solutions after irradiation, suggesting that heating and irradiation have different reaction mechanisms.

Insoluble fraction was only observed in the product from heating at 150 °C with ammonia. IR spectra of the insoluble fraction and soluble fraction (both dried on CaF_2 plates) revealed that soluble fraction contained amines and amides, but these bands were not significant in the IR spectra of the insoluble fraction. It suggest that the amino acids are produced from precursors containing amide bonds after braking these bonds by acid hydrolysis.

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Keywords: Meteorites, Asteroids, Organic matter, Gamma ray

Soluble organic molecules formed under hydrothermal conditions in small bodies

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Extraterrestrial organic materials found in chondrites, micrometeorites, and IDPs record the processes in the Sun’s parent molecular cloud, the protosolar disk, and parent bodies. Organic materials could be newly synthesized from simple molecules such as formaldehyde and ammonia (Cody et al., 2009) and/or altered by hydrothermal processes within parent bodies (Herd et al., 2011). The correlation between the L-enantiomeric excess of amino acids and the degree of alteration also indicates that organic materials evolved in parent bodies (Glavin and Dworkin., 2009). Recent studies on soluble organic matter in the Murchison meteorite (Schmitt-Kopplin et al., 2010; Yamashita and Naraoka, 2014) have shown that a large variety of soluble organic molecules are present in the aqueously altered Murchison, some of which could have been synthesized by parent body alteration processes.

In order to understand the formation of soluble organic molecules under hydrothermal conditions in Solar-System small bodies, we conducted hydrothermal experiments following the experimental procedure of Kebukawa et al. (2013). Paraformaldehyde, glycolaldehyde, calcium hydroxide, and ammonium water (8 wt%, NH_3) were put into pyrex glass tube with ultrapure water. The N/C atomic ratio of the starting material was set at 0.1. The glass tube enclosing the starting materials was sealed in the air, and the sealed glass tubes were heated at 90 degree C for 72 hours. We also made experiments without ammonia and only with ultrapure water for comparison.

The liquid phase changed its color from transparent to brownish after the heating, and solid organic components were found in the tube. The liquid phase was diluted by a factor of 100 with a water-methanol mixture (1:1), and was analyzed with Orbitrap Elite LC-MS (Thermo Fisher Scientific). A 10uL of the solution was first injected to a liquid chromatograph EASY-nLC 1000 (Thermo Fisher Scientific). The molecules separated through the LC depending on their polarities, were introduced to an electrospray ionization (ESI) source, and positively-charged ions were detected in the range of m/z=50-750 with a mass resolution of 240,000 at m/z=400.

The solutions from the heated samples both with and without ammonia contained molecules showing a broad peak at the retention time of 15-25 min on chromatogram. The averaged mass spectra at the retention time of 19-20 min were averaged and analyzed with the “mMass”-software. Most of the molecules show a successive increase of CH_2O, suggesting that they were formed by the formose reaction (polymerization of formaldehyde). The solution with ammonia contained molecules with an odd number of molecular weights, while that without ammonia did not. These molecules with an odd number of molecular weights should contain an odd number of nitrogen.

Keywords: Extraterrestrial organic matter, Hydrothermal experiments, LC/MS

Evolution of three distinct water reservoirs through the history of Mars

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The surface geology and geomorphology of Mars indicate that it was once warm enough to maintain a large body of liquid water on its surface, though such a warm environment might have been transient. The transition to the present cold and dry Mars is closely linked to the history of surface water, yet the evolution of surficial water is poorly constrained. This study identifies three distinct Martian water reservoirs based on the analyses of Martian meteorites, telescopic observations, and Curiosity measurements. One is mantle-derived water that has a D/H ratio similar to those seen in planetary building blocks (i.e., chondrites) and in the Earth’s ocean water. The second reservoir is atmospheric water with a mean D/H ratio of ~6 times the terrestrial value. The third, subsurface-ice reservoir, has been recently detected based on analyses of Martian near-surface materials. This reservoir has a relatively restricted range of D/H ratios (2-3 times Earth’s ocean water), which is distinct from the low-D/H primordial and the high-D/H atmospheric water reservoirs. This subsurface-ice reservoir could have possibly acquired its intermediate-D/H composition from the ancient surface water before the rise of the atmospheric D/H ratio to the present level. During ancient times, the atmosphere and hydrosphere could have approached isotopic equilibrium due to the high water activity relative to the recent dry Mars.

Keywords: Mars, water, hydrogen isotope

Petrology and mineralogy of Northwest Africa 7397 lherzolitic shergottite

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Martian meteorites are important samples in order to understand geologic process on Mars. Shergottite, which is the largest group among Martian meteorites, is divided into three groups based on their petrologic and mineralogical features; i.e., basaltic shergottite, olivine-phyric shergottite, and lherzolitic shergottite. The petrologic and mineralogical features of lherzolitic shergottites are similar each other. In addition, their crystallization and exposure ages are also identical each other. Accordingly, it is widely accepted that lherzolitic shergottites share the same original source on Mars, and were probably ejected by the same impact event, and finally fell on the Earth as separate falls [1]. The major object of this study is to describing the detail petrographic and mineralogical characteristics of a newly found lherzolitic shergottite, Northwest Africa 7397 (NWA 7397).

A polished thin section of NWA 7397 was prepared for this study. A field-emission scanning electron microscope (FE-SEM) was employed for detailed textual observations. The chemical compositions of individual minerals were determined with an electron probe micro-analyzer (EPMA). Phase identification of the minerals was conducted using a laser micro-Raman spectrometer.

Our FE-SEM observations and EPMA analyses reveal that the petrologic and mineralogical features of NWA 7397 are similar with other lherzolitic shergottites. NWA 7397 shows two areas with poikilitic and non-poikilitic. In the poikilitic area, coarse-grained pyroxene oikocrysts enclose olivine (< ~500 μm) and chromite (< ~150 μm) grains. In the non-poikilitic area, the major constituents are olivine, pyroxene, and plagioclase (now maskelynite), with minor chromite, ilmenite, alkali feldspar, Ca-phosphate, and Fe-sulfide. Pyroxenes in the poikilitic area are chemically zoned from core ($En_{71}Fs_{25}Wo_4$) to rim ($En_{65}Fs_{25}Wo_{10}$). Most pyroxenes in the non-poikilitic basaltic area are pigeonite with small amount of augite. Olivine in the non-poikilitic area (Fa_{38-40}) is more Fe-rich than that in the poikilitic area (Fa_{29-37}). NWA 7397 may have originally been located at a shallower level within the lherzolitic shergottite igneous block because Fe contents in the olivine are higher than those in other lherzolitic shergottites. Several melt-pockets were observed in the non-poikilitic area. The existences of maskelynite and melt-pockets are obvious evidences for an impact event occurred on Mars. Some plagioclase entrained in the melt-pockets dissociate into CAS + stishovite. This is the first report of CAS and stishovite from lherzolitic shergottites. Based on the phase diagram of basaltic composition [2], the pressure and temperature conditions recorded in the melt-pocket are estimated to be ~25 GPa and 2300-2500 °C. Olivine around the melt-pockets probably dissociated into bridgmanite + magnesiowüstite. The bridgmanite would have back-transformed to glass due to residual heat during adiabatic decompression.

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Keywords: lherzolitic shergottite, shock metamorphism, High-pressure polymorph

Petrography and formation process of Martian breccia meteorite NWA 7034

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NWA 7034 and its pairings were identified as Martian regolith breccia meteorites. Some minerals in these meteorites have chemical compositions similar to those in SNC meteorites and Martian soil. In this study we analyzed the textures and chemical compositions of this meteorite, and considered its formation process.

NWA 7034 meteorite is a polimict breccia composed of various clasts and fine-grained matrix. We divided the clasts into six groups, such as igneous clast, monomineralic clast, proto-breccia clast, Group X clast, Group Y clast and melt clast.

I) Igneous clast is composed of multiple minerals (plagioclase, pyroxene, magnetite, ilmenite and others), and have ophitic and glanular textures similar to those in Martian igneous rocks. The clast size is 40 μm~1 mm, and most mineral grains are 10-50 μm. Chemical composition of pyroxene resembles that in SNC meteorites. Based on the texture and chemical composition of minerals, we concluded the igneous clasts originated from Martian igneous activity.

II) Monominaralic clast is a fragment of feldspar, pyroxene, apatite, magnetite and ilmenite. The size of the fragments are mostly <100 μm. Plagioclase and pyroxene clasts have various chemical compositions, and some clasts have exsolution textures. This clast may be fragments of other clast groups such as an igneous clast based on the similarity of their chemical compositions.

III) Proto-breccia clast is composed of fine and elongated crystals (<1 μm), and subhedral crystals (<100 μm). Both crystals are mainly plagioclase, pyroxene and magnetite. The clast size is 340 μm~1.8 mm. We consider these are the breccia formed before NWA 7034 breccia formation, and it was partially melted and quenched by impact or other processes.

IV) Group X clast is composed of two or three crystals, but they don’t interlock like igneous clasts. The clast size is 40 μm~1 mm. Constituent minerals are plagioclase, pyroxene, apatite, magnetite and ilmenite. On the basis of the texture and constituent mineral assemblages, we considered these clasts are fragments of igneous clasts.

V) Group Y clast is fine-grained pyroxene (<10 μm) aggregate with plagioclase rim. These clasts are 70-580 μm in size, and have various forms (amoeboid, spherical and so on). Some clasts contain magnetite inside. This clast is also included in proto-breccia clasts.

VI) Melt clast has a spherical shape and its diameter is 3 mm. The clast contains olivine dendrites. The length of the olivine dendrites are 1 mm at the center, and 150-200 μm in the margin. As unique nature, it has three-layered rims. The innermost rim contains needle-like pyroxene crystals (50-150 μm long). Mg# of these pyroxene is higher than that of olivine in the main body. The middle rim contains Na-rich plagioclase crystals that have similar size and shape with pyroxene in the innermost rim. Some olivine, pyroxene and plagioclase crystals are partly joined and form a single acicular crystal aggregate. The outermost rim is composed of fine-grained (<1 μm) plagioclase, pyroxene and Fe-oxide. In terms of the spherical shape and the existence of olivine dendrite, this melt clast is formed by a similar process with that of chondrules (i.e., rapid quenching from a melt droplet). The two rims that contain needle-like pyroxene and plagioclase crystals might have formed at the time of secondary heating. The mineralogy of the rim is different from any of chondrules in meteorites.

VII) Matrix fills the space between the clasts, and is composed of mineral fragments (several to 10

µm in diameter) and fine-grained minerals (<1 µm). Constituent minerals are plagioclase, pyroxene, apatite and magnetite.
As summarized above, NWA 7034 breccia meteorite contains various clasts that formed by fracturing, brecciation and melting of Martian igneous rocks. The formation age and formation environment of each clast would be different, and some clasts experienced brecciation at least twice.

Keywords: Martian meteorite, regolith breccia, melt spherule

Characterization of LUNA 24 regolith for deciphering the magmatism history on Mare Crisium

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Lunar regolith is the mixture of fine grains/powders found on the surface of the Moon, and is considered to be the result of mechanical disintegration of basaltic and anorthositic rocks, caused by continuous meteoric bombardment over billions of years. Since LUNA 24 samples classified into Very-Low-Ti (VLT) basalt were dated as the youngest lunar rocks/soils of 2.9 Ga [1], it has been generally considered that VLT basalt magmatism is the most prolonged magmatism on the Moon (about 1.4 billion years from the oldest age of 4.35 Ga of monomict breccia, Kalahari 009 [2], to the youngest age of 2.9 Ga). However, in the chronology of regolith, it should be taken into account that individual grains have a different origin. Moreover, late impact events might have disturbed the radiometric age, making the age younger apparently. Therefore, comprehensive studies on both elaborating mineralogical description and the high-spacial resolution dating are required to decipher the precise history of VLT magmatism. Here, we report the characterization of LUNA 24 regolith collected from Mare Crisium at the depth of 130-132 cm and the future-plan of in-situ U-Pb dating.

Keywords: Lunar regolith

A high-pressure polymorph inventory in shocked L type ordinary chondrites

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Planetary collision phenomenon is one of fundamental process for planet evolution. So, shock metamorphism is recorded in many meteorites. The existence of high-pressure polymorphs is one of distinct evidences for the planetary collision phenomenon. Many colleagues have worked on high-pressure polymorphs in shocked ordinary chondrites. We could constrain shock pressure conditions, impact velocities and their parent-body sizes using the high-pressure polymorph assemblages in the shocked ordinary chondrites and their kinetics, which will give clues for how the ordinary chondrite parent-bodies were destroyed. Radio-isotope measurements along with such high-pressure mineralogical investigations could date when the parent-body destroys occur in the solar nebula. Ordinary chondrite is classified into H, L and LL based on metallic iron content. Individual ordinary chondrite is further divided into petrologic type 3, 4, 5 and 6 (and 7) based on the differences on thermal metamorphism degree. Most previous investigations working on high-pressure polymorphs have just focused on type 6, especially L6 ordinary chondrite. Few systematic investigations about a high-pressure polymorph in other type ordinary chondrites have not been conducted up to now. A parent-body of an ordinary chondrite is expected to have an onion shell-like structure. The inventories of high-pressure polymorphs included in all type ordinary chondrites are required to depict the destroy process of an ordinary chondrite parent-body. Accordingly, in this study, we described high-pressure polymorphs included in L3, L4 and L5 type ordinary chondrite through a fine textural observation by a FEG-SEM and mineral identification by a laser micro-Raman spectroscopy. Twenty-one Antarctica and one non-Antarctica L-type ordinary chondrite thin sections were used for this study.

Four L3 type ordinary chondrites including shock-induced melting textures were selected through optical microscopic observations. Most chondrules are slightly flattened. The boundaries between the flattened chondrules and surrounding matrices are distinct. Several isolated melting textures (hereafter, a melt-pocket) are observed around the boundaries. High-pressure polymorphs were not identified in and around the melt-pockets although several plagioclase grains become maskelynite. In case of L4 type ordinary chondrites (ten specimens), the boundaries between chondrules and matrices are not so clear compared with L3. The grain-sizes of constituents in the matrices are coarser than L3. Melt-pockets occur around the boundaries like L3. A shock-melt vein occurs only in one specimen. Jadeite was identified in plagioclase grains entrained in and around the melt-pockets or shock-melt veins. Maskelynite was also identified. In case of L5 type ordinary chondrites (five specimens), the boundaries between chondrules and matrices are indistinct. All melting textures occur as a shock-melt vein. Jadeite occurs in plagioclase grains entrained in or around the shock-melt veins. Maskelynite also occurs. The olivine grain entrained in the shock-melt vein partly transforms into wadsleyite.

Our investigations reveal that shock-induced melting occur in L3, L4 and L5 besides L6 ordinary chondrites. Most shock-induced melting occur as a melt-vein in L6 and L5, whereas as a melt-pocket in L3 and L4. Ringwoodite, wadsleyite, akimotoite, majorite, bridgmanite, jadeite, lingunite and tuite occur in and around the shock-melt veins of L6. Only jadeite occurs ubiquitously in and around the shock-melt veins and melt-pockets of L4 and L5. The shock pressure condition can be estimated based on a high-pressure polymorph phase equilibrium diagram deduced from static high-pressure synthetic experiments. The estimated shock pressure conditions are as follows; about

from 13 to 24 GPa for L6, about from 2.5 to 12 GPa for L4 and L5, and less than about 2.5 GPa for L3.

Keywords: High-pressure polymorph, Ordinary chondrite, Shock-induced melting

Development of Laser Post-Ionization Secondary Neutral Mass Spectrometer for in-situ U-Pb chronology

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In space and planetary sciences, Secondary Ion Mass Spectrometers (SIMS) with an ion micro-beam has been widely used for in-situ isotopic analyses of micron scale samples [1]. In the SIMS analysis, the surface of the sample is irradiated by a primary ion beam, and among the sputtered materials, secondary ions are introduced into the mass spectrometer. One of the disadvantage of the SIMS is that the secondary ion yield is low (less than a few %), and a large fraction of the sputtered samples are lost as neutrals without being analyzed, which makes it difficult to carry out trace element analyses with a sub-micron spatial resolution due to the severely low ion counting statistics.

In order to improve this disadvantage, we have carried out the post-ionization of the secondary neutrals with a femtosecond laser [2]. By irradiating the high power laser above 10^{15} W/cm^2, 100% of the sputtered atoms and molecules can be ionized. In addition, in the high electromagnetic fields, all kinds of species are ionized, regardless of ionization potential, through the non-resonant ionization regime and can be analyzed simultaneously by using the time of flight (ToF) mass spectrometer.

The multi-turn time of flight secondary neutral mass spectrometer (MULTUM-SNMS) has been developed in Osaka University [3]. This instrument consists of a focused ion beam with a liquid metal gallium ion source, a femtosecond laser and multi-turn ToF mass spectrometer. The sample is sputtered with a 30 keV Ga^+ ion beam which can be focused to a spot diameter of 40 nm and maximum current density is 30 A/cm^2. The ejected neutrals are irradiated with the femtosecond laser, and the post-ionized ions are introduced into the multi-turn ToF analyzer (MULTUM), the ion optical system of which achieves an ultra high mass resolving power of 250000 [4].

The performance evaluation of MULTUM-SNMS has conducted with a lead plate sample. It was demonstrated that the post-ionization with the femtosecond laser can make the Pb+ secondary yield about 10000 times higher. In addition, a mass resolution greater than 12000 is achieved utilizing MULTUM ion optics. Toward the application to U-Pb chronology, 91500 zircons which contain around 100 ppm uranium and used as a standard specimen of zircon U-Pb chronology was measured using MULTUM-SNMS. From a sputtered area of around 1 um in diameter, U^+, UO^+ and UO_2^+ signal peaks were detected. In this presentation, we will also report the lead isotope ratio of the same specimen and discuss the feasibility of sub-micron scale in-situ U-Pb chronology with MULTUM-SNMS.

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Keywords: U-Pb dating, SIMS, SNMS