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 $n\ t = 0.1\ \mathrm{cm}^{-3}$ 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 °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 (δ^{13}C values) start decreasing from the temperature of 600°C. Decomposition of carbonate, which has δ^{13}C value of ~+67‰ (Grady et al., 2002), is responsible for the decrease of carbon content and δ^{13}C value up to 600°C. Meanwhile, from 600 to 900°C, carbon content and δ^{13}C value decreased due to gasification of organic carbons (δ^{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

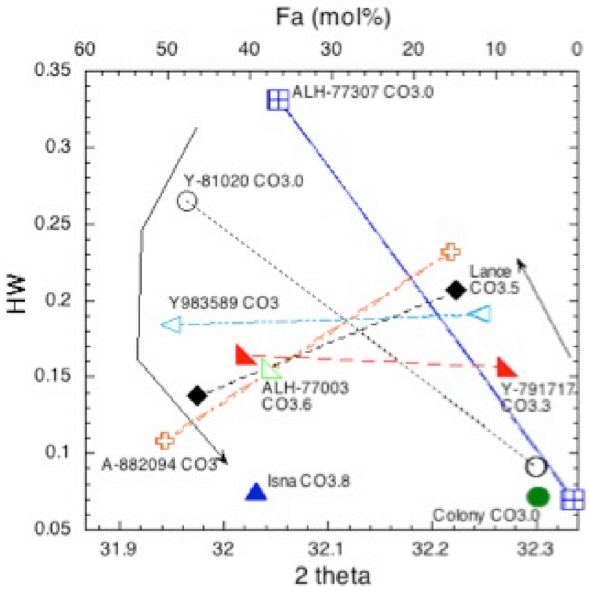

Fig. 1. The relationship between olivine (130) and half width of the diffraction for various subtypes of the CO3 chondrites.

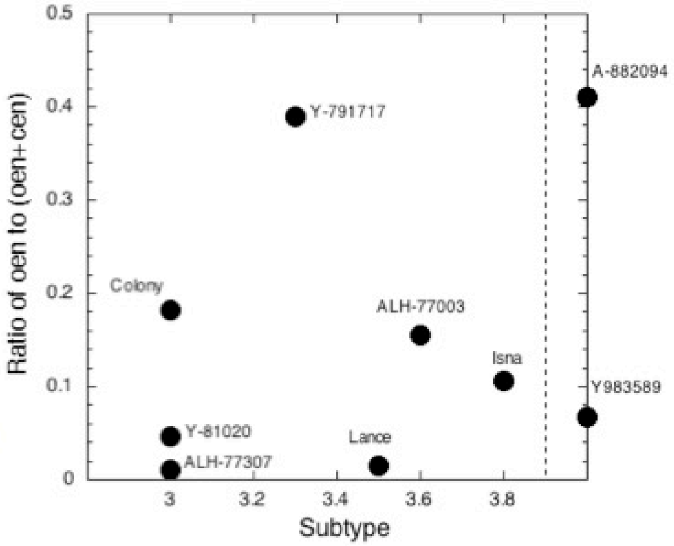

Fig. 2. The ratios of orthoenstatite (oen) to two phases of enstatites (opx+cpx) for various subtypes of the CO3 chondrites. Cen=clinoenstatite.

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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