

Structural control of biominerals by intracrystalline organic macromolecules

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Biominerals, which are inorganic materials formed thorough biological processes, often have strictly-controlled structures and superior properties to geological counterparts. These characteristics are ascribed to organic constituents or macromolecules contained inside the biominerals. Although the intracrystalline organic macromolecules (IOMs) are considered as one of the crucial parts in biomineralization, it is not clear how they interact with the biominerals and control their characters. We have used transmission electron microscopy (TEM) and scanning TEM (STEM) to visualize IOMs, and investigated the influence of the IOMs on the microstructures of biominerals. The goal of this study is to elucidate the interaction between inorganic materials and IOMs in biomineralization. In this paper, we present some of our recent results, to consider the possibility to apply our methodologies to other geoscience fields.

In this study, we compared the influence of IOMs in the prismatic structures of three mollusk shells; a pearl oyster (*Pinctada fucata*); a pen shell (*Atrina pectinata*); and an oyster (*Crassostrea nippona*). These prismatic structures are composed of calcite (CaCO₃) columnar crystals. Thermogravimetric analyses (TG) showed that every shell contains the IOMs of approximately 3 wt.%. TEM observations were conducted for thin specimens prepared using a focused ion beam system (FIB). In under-focused bright-field TEM images, spherular Fresnel contrasts appeared inside the crystals. Since the Fresnel contrasts in the shells are a few dozen nanometers, they were assumed to correspond to IOMs. This speculation was verified using electron energy-loss spectroscopy (EELS) equipped to STEM. The spectra obtained from the Fresnel contrasts exhibited a fingerprint of organic matter in the fine structure of carbon *K*-edge. Thus we can conclude that IOMs are visualized as Fresnel contrasts in defocused TEM images. Next three-dimensional distribution of IOMs was reconstructed using STEM tomography. In *Pinctada* and *Crassostrea* shells, the IOMs are distributed inhomogeneously to separate the crystals into sub-grains. On the contrary, *Atrina* shells show homogeneous distribution of the IOMs. Inhomogeneous distribution of the IOMs in *Pinctada* and *Crassostrea* not only induces small-angle grain boundaries and strain into the crystals but also influences mechanical properties such as suppression of cleavages in the calcite crystals.

Synthetic experiments were also conducted to understand the influence of IOMs on calcite crystals. Calcite crystals were synthesized *in vitro* in the presence of the IOMs extracted from the shells. The IOMs were incorporated into the crystals and observed as Fresnel contrasts in TEM images. The crystals synthesized with the IOMs extracted from *Pinctada* shells have defective microstructures similar to the original shells.

Keywords: intracrystalline organic macromolecules, biomineral, calcium carbonate, organic?inorganic interaction, electron microscopy, microstructure

Evidence of minimum aqueous alteration in rock-ice body recorded in ultracarbonaceous micrometeorite

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Introduction:

Ultracarbonaceous micrometeorites (UCMMs) are unique extraterrestrial materials that represent large sizes of high carbon contents [1]. In our recent study of an UCMM D05IB80 collected from near the Dome Fuji Station, Antarctica [2], it has been revealed that: (i) ten-micron-sized large organic material accounted for most part of the sample, (ii) the organic material was extremely rich in nitrogen functional groups such as nitrile, imine, and amide, (iii) sulfur is identified within the organic material surrounded by pyrrhotite rim, and (iv) there was no anomalies in hydrogen, carbon and nitrogen isotopic compositions. These features have not been observed from typical chondritic organic material, while they are partially similar to those from CR3 chondrite [3] and some particles from Comet Wild 2 [4]. In order to enhance our understanding of the origin and formation of UCMMs, we have carried out TEM observation of the focused ion beam (FIB) section of D05IB80.

Experimental:

Bulk mineralogy of an UCMM D05IB80 was investigated by using synchrotron radiation X-ray diffraction (SR-XRD) at the Photon Factory. D05IB80 was embedded in epoxy and ultramicrotomed into 70-nm-thick sections. After ultramicrotomy, the potted butt of the micrometeorite was analyzed by a Hokudai isotope microscope system at Hokkaido University. A thin section was prepared by the dual beam FIB-SEM JEOL JIB-4501 at Ibaraki University. Carbon-, Nitrogen-, and Oxygen-X-ray absorption near edge structure (XANES) spectra of the FIB section were acquired using a scanning transmission x-ray microscope (STXM) at the beamline 5.3.2.2., Advanced Light Source, Lawrence Berkeley National Laboratory. After STXM, the FIB section was observed by JEOL JEM-2100F field emission TEM at JEOL Corporation and by JEOL JEM-2100 at Ibaraki University.

Results and discussion:

Elemental mapping analysis and high resolution observation of the boundaries between the UCMM and the epoxy were performed. There are two types of boundaries between them, one is smooth and another is globular. Although morphologies are considerably different between these boundaries, high-resolution images revealed that there are very thin (< 5 nm) layers composed of less electron transparent material than carbonaceous material at the surfaces of both boundaries. Both of the surface areas containing less electron transparent material are enriched in C, O, Si, S, and Fe.

Minor crystalline phases identified are olivine and Ni-bearing pyrrhotite. Olivine occurs as a polycrystalline aggregate. On the other hand, Ni-bearing pyrrhotite occurs as fine-grained subhedral to rounded crystals embedded in amorphous silicate. The size and morphology of the amorphous silicate object containing Ni-bearing pyrrhotite are similar to GEMS (glass with embedded metal and sulfide) that are commonly observed in chondritic porous inter-planetary dust particles (CP IDPs) (e.g., [5]). However, no Fe-Ni alloy was identified from these GEMS-like objects. Observation of Ni-bearing pyrrhotite and GEMS-like objects without metals implies that the UCMM are very slightly aqueously altered. This condition could have been locally occurred at the early formation stage of the rock-ice bodies including comets and icy asteroids. The repetitive warming process of ice might have promoted the formation of ten micron-sized large, nitrogen-rich organic material observed from D05IB80. Association of organic material and sulfur supports the presence of fluid chemistry on the parent body. These features appear to be a very pristine signature of interaction of mineral, ice, and organics in the primitive small body.

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Keywords: ultracarbonaceous antarctic micrometeorite, organic compounds, organics-minerals-ice interaction, rock-ice body, aqueous alteration, STEM

Isotopic compositions and morphology of isotopically anomalous organic matters in carbonaceous chondrites

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[INTRODUCTION] Organic matters with D- and ¹⁵N-enrichment have been reported from carbonaceous chondrites. It has been considered that they have been produced in the cold molecular cloud and in outer solar nebula (e.g. Busemann et al., 2006, Hashiguchi et al., 2011), however, their origin and evolution are still unclear. Because insoluble organic matter (IOM) extracted from carbonaceous chondrites exhibited heterogeneous hydrogen (H) and nitrogen (N) isotopic composition (Busemann et al., 2006), the chondritic organic matters seem to have various origin or evolution. Therefore, characterization of the individual isotopically anomalous organic matters is important. Our previous study reported various morphologies of D-rich organic matters in a carbonaceous chondrite (Hashiguchi et al., 2011). The morphology may record the history of chondritic organic matters.

CR2 and CM2 chondrites have experienced some degree of aqueous alteration on the parent body (Brearley, 2006). Chemical or isotopic evolution of chondritic organic matters may record in the CM2 and CR2 chondrite. In this study, we report H and N isotopic compositions and morphology of isotopically anomalous organic matters in CR2 and CM2 chondrites found by in-situ analysis.

[EXPERIMENTAL] Polished thin sections of Murchison (CM2) and Northwest Africa (NWA) 801 (CR2) were used in this study. H and N isotopes were measured by in situ isotope ratio imaging (isotopography) using isotope microscope system (Cameca ims-1270 + SCAPS) (Yurimoto et al., 2003). Isotopically anomalous spots were located and observed by FE-SEM-EDS system (JEOL JSM- 7000F, Oxford INCA Energy).

[RESULTS] Total of 28 isotopically anomalous carbonaceous spots were found in isotopographs of 0.04 mm² and 0.08 mm² for Murchison and NWA 801, respectively. Maximum of the D- and ¹⁵N-enrichments were 7,920 permil in delta-D and 2,620 permil in delta-¹⁵N, respectively. Larger D-enrichments are not associated with larger ¹⁵N-enrichments in a carbonaceous spot. Most of the isotopically anomalous carbonaceous spots found in Murchison were enriched in ¹⁵N, whereas fraction of D-rich and ¹⁵N-rich carbonaceous spots in NWA 801 are comparable. These carbonaceous spots are single or aggregated globules. They showed no clear correlation between the morphology and the H and N isotopic compositions.

[DISCUSSIONS] D- and ¹⁵N-enrichment and association of H and N components suggest that the isotopically anomalous carbonaceous spots are corresponding to organic matters. The decoupled D- and ¹⁵N-enrichment suggests the isotopically anomalous organic matters are attributed to multiple isotopic fractionations in molecular cloud or in outer solar nebula including ion-molecule reaction (Millar et al., 1989; Rodgers and Charnley 2008), grain-surface reaction (Watanabe and Kouchi 2008), and self-shielding effects (Le Petit et al., 2002; Lyons et al., 2009).

It is suggested that aqueous alteration process decreases D/H ratio of organic matters in carbonaceous chondrites (Herd et al., 2011). Degree of aqueous alteration of typical CM2 chondrite would be larger relative to CR2 chondrite (Brearley, 2006). Therefore, less abundant D-rich organic matters in Murchison may be result from loss of isotopically heavy H by aqueous alteration.

Single or aggregated organic globules with D- and/or ¹⁵N-enrichments in carbonaceous chondrites also were observed by previous studies (Nakamura-Messenger et al., 2006; Hashiguchi et al., 2011), suggesting that they were ubiquitous in early solar nebula. Although H isotopic compositions seemed to be affected by aqueous alteration, no clear correlation with the isotopic compositions and morphology. This result may suggest that organic matters with various morphology and/or various isotopic compositions have been formed in molecular cloud and/or in outer solar nebula.

Keywords: Chondritic organic matters, Carbonaceous chondrites, Isotopic composition, Morphology, Isotope imaging

Characterization of Carbonaceous Xenolithic Clasts in Meteorites

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Primitive xenolithic clasts are found in many regolith-bearing meteorites [1]. They are most commonly similar to type 1-2 carbonaceous chondrites, but significant differences usually exist. Here we report organic analyses of these carbonaceous clasts in Sharps (H3.4), Zag (H5) and Kapoeta (Howardite) using C-, N-, and O- X-ray absorption near edge structure (XANES), and Fourier transform infrared micro-spectroscopy (microFTIR), with mineralogical observations using a transmission electron microscope (TEM).

Approximately 100 nm-thick sections were extracted with a focused ion beam (FIB) at JSC from the carbonaceous clasts. The sections were analyzed using the micro FTIR, and the scanning transmission X-ray microscope (STXM) on beamline 5.3.2.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory for XANES spectroscopy. After XANES analysis, some of the sections were observed by TEM.

C-XANES and FTIR spectra of clasts in Zag and Kapoeta show a mostly aromatic nature with minor aliphatic signatures. The carbonyl features obtained by C-XANES might have been caused by the focused ion beam (FIB) used in sample preparation. C-XANES spectra of clasts in Zag and Kapoeta do not show significant 1s-SIGMA* exciton features, suggesting that these clasts have not experienced high temperature, probably <200°C [2], although their parent meteorites have been subjected to strong thermal processing.

The clasts in Sharps have distinctive features from those in Zag and Kapoeta. Sharps (H3.4) meteorite contains unusual large carbonaceous clasts up to ~1 cm in diameter, which have been reported earlier as poorly graphitized carbon with Fe,Ni metal [3]. C-XANES spectra show two types of carbonaceous material in the Sharps clasts: (1) aggregates of graphite-like carbon, and (2) poorly graphitized carbon with O-bearing functional groups. Graphite-like carbon aggregates show significant 1s-SIGMA* exciton features which indicate they have been subjected to high temperatures (~700-1000°C) [2]. TEM observation indicates these aggregates are poorly-crystallized graphite with lattice fringes of 3.5-3.75 Angstroms. The other type of carbonaceous material is distributed throughout the clast. C-XANES of these areas shows carbonyl groups as well as aromatic C=C with a small amount of aliphatic C-H. Lower 1s-SIGMA* exciton intensities observed in the matrix area indicate that this phase did not experience heating temperatures as high as the graphite-like carbon. TEM observation of this area reveals mainly pyroxene and olivine, the former as laths as in anhydrous chondritic interplanetary dust particles (IDPs) [4].

These primitive xenolithic clasts in Sharps, Zag and Kapoeta have organic features that are distinct from their parent meteorites and preserve their history from before final accretion on single parent bodies. However, they may also have been affected by secondary processes on their parent bodies. In addition, clasts in Sharps contain graphite-like carbon which experienced higher temperatures compared to their surrounding materials. The origin of the graphite-like carbon is probably different from its surrounding material, which indicates a very complex history. Our results from these clasts support the idea of radial mixing in the early Solar System.

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Origin of H, N and O isotopic correlations between Earth and asteroids: Origin of water

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Present most plausible interpretation for origin of terrestrial water is that terrestrial water introduced by asteroids because of similarity of H isotopic composition between terrestrial water and asteroidal clay minerals. However, it is not trivial what the similarity occurred. In order to solve the origin of the similarity, it is necessary to add more independent analytical results of isotopic compositions of other elements. In this report, we discuss correlations isotopic compositions among H, N and O of inner planets and asteroids and try to specify the origin of water of the Earth.

Similarity of oxygen isotopic composition between inner planets and asteroids are established (Yurimoto et al, 2008). Nitrogen isotopic compositions seem to be similar among these asteroidal objects (Marty et al, 2011; Alexander et al, 2012). Hydrogen isotopic compositions show large variation among inner planets, but these variations are due to results of dissipation of planetary atmosphere after atmosphere formation. Therefore, it is considered that inner planets originally had the same isotopic composition for these elements corresponding to terrestrial values. Large D-enrichments have been shown in some chondrites, but most chondrites have similar D/H ratios to terrestrial value (Marty et al, 2011; Alexander et al, 2012). These results suggest that the isotopic compositions of these elements are originally essentially similar among inner planets including asteroids. The author suggest that isotopic variations of these elements in the whole solar system could be systematically interpreted by various degree of contribution of low temperature condensates (icy components) in the solar nebula (this conference). I discuss the origin of isotopic homogeneity of these elements in the inner planet region of the solar system by application of the same model. The results suggest that mixing between condensed icy components from inner solar nebular gas and icy components from outer solar nebular region is essential to determine the isotopic compositions of inner planets.

The mixing of the two icy components was demonstrated by the oxygen and hydrogen isotopic compositions of fluid inclusions on asteroidal bodies. These results show that isotopic analysis of icy components of asteroids, cometary objects and icy satellites by future planetary exploration must be needed. The new results must provide essential information to clarify the origin of water of our Earth.

Keywords: asteroid, Earth, isotope, water, H₂O

Oxygen isotopic and chemical zoning of melilite crystals in a Type A Ca-Al-rich inclusion of Efremovka CV3 chondrite

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CAIs (Ca-Al-rich inclusions) are composed of high-temperature minerals (Grossman, 1972) and formed in the innermost solar system (MacPherson et al., 2005; Yurimoto et al., 2008). From oxygen isotopic distributions of CAIs, the mixing of ¹⁶O-poor and ¹⁶O-rich gaseous reservoirs could frequently occur in the inner most solar system where is the CAI-forming region (e.g., Itoh and Yurimoto, 2003; Yurimoto et al., 2008). Reversely zoned melilite crystals in fluffy Type A CAIs are readily explained by direct condensation from a solar nebular gas (MacPherson and Grossman, 1984) so that these crystals are identical to the oxygen isotopic compositions of the surrounding solar nebular gas. In this study, we study the chemical compositions and oxygen isotopic distributions of melilite in a Type A CAI, HKE 01 from Efremovka CV3 chondrite to elucidate the formation processes and variations in oxygen isotopic composition of the solar nebular gas of Type A CAI-forming area.

FE-SEM-EDS-EBSD system (JEOL JSM-7000F; Oxford INCA Energy; HKL Channel 5) was used for petrologic study. Oxygen isotopic compositions have been measured by SIMS (Cameca ims-1270).

HKE 01 is constructed of two domains, each of which has a core-mantle structure. Reversely zoned melilite crystals were observed in the mantle part of both domains. Melilite crystals in one domain have a homogeneous ¹⁶O-poor composition on the carbonaceous chondrite anhydrous mineral (CCAM) line of $\delta^{18}\text{O} = 5\text{-}10$ permil, which suggests that the domain was formed in a ¹⁶O-poor oxygen isotope reservoir of the solar nebula. In contrast, melilite crystals in the other domain have continuous variations in oxygen isotopic composition from ¹⁶O-poor ($\delta^{18}\text{O} = 0$ permil) to ¹⁶O-rich ($\delta^{18}\text{O} = -40$ permil) along the CCAM line. The oxygen isotopic composition tends to be more ¹⁶O-rich toward the domain rim, which suggests that the domain was formed in a variable oxygen isotope reservoir of the solar nebula. Because reversely zoned melilite crystals are thought to be condensed with decreasing pressure (MacPherson and Grossman, 1984), the environment changed from ¹⁶O-poor to ¹⁶O-rich with decreasing pressure. This situation may correspond to the inner edge region of the solar nebula where ¹⁶O-rich solar and ¹⁶O-poor planetary gases are encountered and mixed (Yurimoto et al., 2008). The CAI recorded temporal variations of the mixing in the region and spatial variations by the radial transport (Itoh and Yurimoto, 2003; Ciesla, 2007). After the formation of each domain, the domains aggregated to form HKE 01.

Keywords: Type A CAI, melilite, SIMS, oxygen isotopes, solar nebula

An ion microprobe study of FUN-like hibonite-bearing inclusions from the Murchison (CM2) meteorite

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There is a minor group of refractory inclusions, so called FUN (Fractionation and Unknown Nuclear effects) inclusions, which exhibit distinct isotopic characteristics: (i) large mass-dependent fractionation in O, Mg and Si preferring heavy isotopes (F-signature), (ii) presence of unknown nuclear effects, esp., positive or negative anomalies in ⁴⁸Ca and ⁵⁰Ti (UN-signature), and (iii) little or no excess ²⁶Mg (and excess ⁴¹K) from the decay of ²⁶Al (⁴¹Ca). Absence of excess ²⁶Mg suggests either their late formation after the complete decay of ²⁶Al, or their early formation before injection of ²⁶Al into the solar system from (a) stellar source(s). The presence of Ca and Ti isotopic anomalies may suggest their earlier formation. The origin of FUN inclusions is still not well understood, but they may have important information about evolution and isotopic homogenization process(es) in the early solar system.

We found three FUN-like hibonite-bearing inclusions (MC037, 040, 003) from the Murchison (CM2) meteorite, which exhibit extremely large mass-dependent fractionation in Mg isotopes (up to ~50permil/amu) but almost no excess in ²⁶Mg. In order to better understand their isotopic characteristics, we further conducted ion microprobe analyses of Mg, Ca and Ti isotopes on these inclusions.

Results -Mg isotope-: Data for MC040 and MC003 show rather homogeneous composition with Phi-²⁶Mg from ~97 permil to ~107 permil and ~29 permil to ~35 permil, respectively. However, MC037 data show highly heterogeneous composition with Phi-²⁶Mg from ~27 permil up to ~95 permil. Hibonite and spinel in MC037 probably crystallized at various stages of the evaporation event, while those in MC040 and MC003 only at the last stage of the evaporation event, suggesting slightly different heating conditions for these inclusions. All the data for these inclusions show no excess ²⁶Mg (Delta-²⁶Mg ~0) within uncertainties. Again MC037 data show large variations in the ²⁷Al/ ²⁴Mg ratio.

Results -Ca&Ti isotopes-: Both MC037 and MC040 do not show anomalies in ⁴⁸Ca within analytical errors, but have small (<10 permil) but resolvable anomalies in ⁵⁰Ti. MC003 show anomalies in ⁴⁸Ca (<15 permil) and ⁵⁰Ti (<6 permil).

Highly fractionated Mg isotopes, lack of resolvable excess in ²⁶Mg and existence of ⁴⁸Ca and ⁵⁰Ti anomalies suggest that they are newly found FUN inclusions. The present results and previous works show that there are variations in F, UN, and ²⁶Mg excess signatures among different types of FUN (F) inclusions. Further studies are required to better understand their relations and formation conditions.

Keywords: FUN inclusion, hibonite, ion microprobe, Mg isotope, Ca isotope, Ti isotope

Low-iron, manganese-enriched olivine in amoeboid olivine aggregates in carbonaceous chondrites.

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Introduction:

Low-iron, manganese-enriched (LIME) silicates (olivine and pyroxene) are important components found in some primitive materials formed in the early solar system. This type of silicate has wt % MnO/FeO >0.1, and usually <1.0 wt.% FeO, and is interpreted as a condensate that preserves the redox state of solar nebula gas [1]. LIME silicates were originally identified in IDPs and matrix in primitive chondrites [2], and subsequently found in chondrules in primitive chondrites [3], and in cometary particles from the Stardust samples [e.g., 4].

LIME olivine has been also described in amoeboid olivine aggregates (AOAs) from CR chondrites [5], and Y-81020 and Acfer 094 [6]. In this study, we have studied seven carbonaceous chondrites (Efremovka, Leoville, Vigarano, Y-86009, Allende, Y-81020, NWA 1152) with variable degree of alteration in order to examine the relationship between Mn content in olivines and their formation and alteration conditions.

Results and Discussion:

Low-Fe, Mn-rich olivine is observed in AOAs from Y-81020 (CO3.0) and Y-86009 (CVoxB). In the NWA 1152 (ungrouped C) AOAs, most olivines are forsteritic (Fo92-99), and several olivine analyses show enrichments in MnO (up to 0.4wt.%) and MnO/FeO ratio up to 0.7. Although the MnO/FeO ratio of Mn-rich olivine in NWA 1152 AOAs is not as high as in LIME olivine, it is likely that the formation of Mn-rich olivine is related to LIME olivine. Thermodynamic models show that LIME-like olivine in AOAs can form by gas-solid reactions as temperature declines to near 1100 K [e.g., 1]. The model of Ebel et al. [1] indicates that Mn-rich, Fe-poor olivine forms under relatively low oxygen fugacities (solar composition, no dust enrichment). Based on our observations, when the Mn-rich olivine is present in AOAs, it generally occurs at the edges of the inclusion. This is consistent with the condensation calculation that predicts Mn-enrichment with decreasing temperature [1].

The CV chondrites are subdivided into the reduced (CVred) and two oxidized subgroups. The CVoxB (e.g., Kaba, Bali) experienced hydrous alteration that resulted in formation of phyllosilicates, magnetite, fayalite, andradite, and salite-hedenbergite pyroxenes [7]. On the other hand, the CVoxA (e.g., Allende) experienced alteration under different conditions resulting in formation of nepheline, sodalite, andradite, salite-hedenbergite pyroxenes, fayalitic olivine, and zoning toward Fe-rich rims (Fo55) in primary olivines (Fo98). Compared to the oxidized subgroups, secondary minerals are rare in CVred.

Mn-rich olivine is observed in Y-86009 (CVoxB), however, it is not observed in reduced CV chondrites and Allende. Thermal alteration occurred in both reduced CVs (to a minor extent) and Allende (to a higher degree). The absence of Mn-rich olivine in the two types of meteorites may indicate the loss of Mn from olivine during the thermal alteration. Because Fe is introduced to AOA olivines during thermal alteration [e.g., 8], loss of Mn from olivine would occur with the Fe-enrichment in olivines.

It has been also shown that the rimmed AOAs which experienced annealing after aggregation tend to have lower Mn contents [6]. This is consistent with our prediction that Mn was lost by heating. It is likely that Mn-rich olivine was originally present in many AOAs as a primary phase, and then lost during the thermal processing. Therefore, Mn-rich olivine in AOAs can be a sensitive indicator for the thermal processes such as annealing in the solar nebula [1] and parent body thermal alteration.

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Keywords: meteorites, carbonaceous chondrites, secondary alteration, AOA

Sodium metasomatism of chondrules and Ca-Al-rich inclusions in the Ningqiang carbonaceous chondrite

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Chondrules and Ca-Al-rich inclusions (CAIs) in CV and CO chondrites contain various amounts of Na-rich nepheline and sodalite. Previous studies revealed that these minerals formed by replacing primary Ca-Al rich minerals (mesostasis glass, plagioclase, and melilite) in chondrules and CAIs [1, 2]. More recent studies showed that amounts of nepheline and sodalite in chondrules and CAIs in CO 3.0-3.7 chondrites increase with increasing degree of thermal metamorphism of the host meteorites [3, 4]. These results suggest that formation of nepheline and sodalite is related to alteration that occurred in the meteorite parent bodies. Na and Ca are highly mobile in aqueous activity, thus the alteration may have occurred in the presence of aqueous solutions. Our recent study revealed that the Ningqiang carbonaceous chondrite contains abundant nepheline and sodalite in matrix (Matsumoto et al., JpGU meeting 2012). Chondrules and CAIs in Ningqiang also contain nepheline and sodalite. However, detailed mineralogy and abundance of these minerals in chondrules and CAIs remain unknown. Here, we report the results of mineralogical and petrological study of nepheline and sodalite in Ningqiang chondrules and CAIs.

Although 97 % of the observed chondrules in Ningqiang contain mesostases, volume proportions of mesostases in individual chondrules are remarkably small (5.4 vol. % on average) compared to other CV chondrites. Our SEM, TEM and STEM observations show that plagioclase in mesostases has been extensively altered to fine grains (~10 micron) of mainly nepheline, sodalite, Fe-rich olivine, and minor hedenbergite. In relatively large chondrules (>1 mm in diameter), the alteration occurred preferentially along the outer margins, and plagioclase in the cores remains unaltered. However, in relatively small (<1 mm in diameter) chondrules, plagioclase was completely replaced.

The abundance of CAIs in Ningqiang is very low (1 vol. %). All of the CAIs studied also exhibit abundant evidence of alteration. Melilite was replaced by fine grains (<5 micron in diameter) of nepheline, sodalite, hercynite and Fe-rich olivine. This alteration proceeded preferentially from the outer margins of CAIs. Our TEM and STEM observations revealed that some of the nepheline and Fe-rich olivine contain small (<100 nm in size) relicts of melilite.

The results of the present study showed that fine-grained Na-rich minerals (nepheline and sodalite) and Fe-rich minerals (Fe-rich olivine, Ca-Fe-pyroxenes, and hercynite) formed simultaneously by replacing mesostases in chondrules and melilite in CAIs. All of these secondary minerals also occur in the Ningqiang matrix (Matsumoto et al., JpGU meeting 2012). We infer that nepheline, sodalite, and the Fe-rich minerals in Ningqiang matrix were supplied from Na-metasomatized chondrules and CAIs, although we are yet uncertain of actual processes responsible for mixing the Na-metasomatized materials with matrix materials.

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Keywords: Ningqiang, nepheline, Na-metasomatism, chondrule, CAI, TEM

Microtextures of unusual dark clasts in the Allende chondrite: Implications for their precursor and alteration processes

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Dark clasts (also known as dark inclusions) commonly occur in CV and CO chondrites. They range in texture from chondritic one, with chondrules and Ca-Al-rich inclusions (CAIs) embedded in a matrix, to aggregates consisting almost exclusively of fine-grained Fe-rich olivine. In the past, dark clasts were considered to be primary aggregates of condensates from the solar nebula^[1]. However, more recent studies have shown that dark clasts exhibit evidence indicating parent-body alteration processes such as chondrule-pseudomorphs, fibrous and vesicular olivines^[2,4], and thus they suggested that dark clasts underwent aqueous alteration and subsequent thermal metamorphism in the meteorite parent body. We found two unusual dark clasts from the Allende CV chondrite that are mineralogically different from the dark clasts studied in the past in many respects. Here we present the results of mineralogical and petrological study of those two dark clasts using an SEM-EDS, an EPMA-WDS, and a TEM-EDS.

The two dark clasts (~86 mm² and ~5 mm²) were found in a polished thin section of the Allende meteorite (~1066 mm² in total area). Both clasts contain chondrule-pseudomorphs (~0.17 mm in average diameter), which are considerably smaller than chondrules (0.49 mm) in the host meteorite. The entire clasts, including pseudomorphs, mainly consist of fine grains (<10 micron in diameter) of Fe-rich olivine (~91 vol%) and Ca-rich pyroxene (6 vol%) and minor amounts of nepheline and opaque minerals (pentlandite and awaruite). From the criteria proposed by Krot et al. (1995a)^[3], they can be classified as type B. Type B dark clasts are considered to have experienced extensive aqueous alteration and subsequent dehydration in the parent body^[2,4]. Olivine grains in the dark clasts are very homogeneous in composition (~Fo₆₀) and most of them contain vesicles and Fe-Ni sulfide inclusions. Some of the pseudomorphs have abundant nepheline, spinel, and perovskite. Nepheline is known as a secondary mineral produced by Na-metasomatism of plagioclase and melilite in CAIs^[6]. Perovskite and spinel are typical primary minerals in CAIs. Therefore these pseudomorphs were probably formed from CAIs.

The dark clasts are surrounded and intersected by Ca-rich veins. These veins have three layered structure. The central layer consists of andradite and kirschsteinite and other layers consist of hedenbergite-diopside pyroxene. The boundary between veins and the clasts is clear, whereas that of veins and surrounding Allende matrix is irregular and gradational.

Previous studies on type B dark clasts in Allende reported that chondrule pseudomorphs in dark clasts and chondrules in their host are similar in size distribution, and thus concluded that the precursor of dark clasts have a lithology identical to the host^[4]. However pseudomorphs in the clasts we studied show much smaller sizes than chondrules in the Allende host. This suggests that the precursor lithology of the clasts was different from Allende. Other previous studies suggested that Ca-rich veins were formed by aqueous alteration that occurred after incorporation of the clasts into the host meteorite^[5,7]. However our observations show that such veins are absent in the host meteorite. These results suggest that the veins probably formed in the precursor lithology of the dark clast, before incorporation of the dark clasts into the host meteorite. The presence of the veins penetrating one of the clasts indicates that the veins were formed after the dark clast lithology was converted to fine-grained aggregates by extensive alteration.

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Keywords: dark clast, aqueous alteration, thermal metamorphism, Allende, carbonaceous chondrite

CI-like phyllosilicate-rich microclasts in the Yamato81020 (CO3.0) chondrite

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Yamato81020 (Y-81020) chondrite is classified as petrologic type CO3.0 and has been recognized as one of the most primitive CO chondrites, obviously unaltered by secondary parent body processes such as aqueous thermal metamorphism or aqueous alteration [1]. In addition, it has been reported that the meteorite shows no evidence of brecciation and no obvious shock effects [1-2]. Our thorough microscopic study of Y-81020, however, brought out the clear evidence of aqueous alteration from small clasts embedded in matrix. Here, we report detailed mineralogical and petrographic characteristics of aqueous altered texture in Y-81020 to unravel the early aqueous alteration history of the parent body.

A thin section of Y-81020 was studied using a scanning electron microscope (SEM), a transmission electron microscope (TEM), equipped with an energy dispersive X-ray spectrometer (EDS), and synchrotron radiation X-ray diffraction (SR-XRD) technique to identified crystal phase. Micro-sized sample were prepared with the focused ion beam (FIB) technique.

The studied Y-81020 contain well defined chondrules (52 vol.%) and CAI/AOA (3 vol.%) set in a fine-grained matrix (45 vol.%). In the matrix, we found a total of 20 clasts (30-300 micro-meters in size), those mineralogy is distinctly different from matrices. As SR-XRD analyses, the clasts consists mainly olivine and magnetite, with small (but significant) amount of smectite and serpentine. High resolution TEM observations indicated that the phyllosilicates show the periodicity of 1.1-1.3 nm, corresponding to (001) plane of smectite. The clasts often contain framboidal or platelet magnetite, which are typical morphology in CI chondrite. These results consistently suggest that the clasts had been altered by intensive aqueous alteration under a condition similar to CI chondrites. Moreover we found that matrix contain minor amount of serpentine. The presence of hydrated minerals in clasts and matrix suggests that the CO parent body was experienced various degree of aqueous alteration, and a brecciation process has subsequently occurred in the parent body.

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Keywords: CO3.0, Yamato81020, CI-like, clast, phyllosilicate, aqueous alteration

Constraints on water/rock ratio and solution pH of nepheline formation in chondrite parent bodies.

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Ca-Al-rich inclusions (CAIs) and chondrule mesostasis of carbonaceous chondrite contain secondary minerals such Nepheline (NaAlSiO_4) and sodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$). These minerals are considered to be secondary altered minerals replaced by melilite or plagioclase. Although recent studies reported that the nepheline formation is correlated with hydro-thermal process on their parent body, its detailed condition is not yet established.

We conducted hydrothermal alteration experiments to understand the formation process of nepheline in chondrite parent bodies. As starting material, we prepared synthetic pure melilite (gehlenite, formula), mixture of melilite and SiO_2 , plagioclase ($\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$). Hydrothermal alteration experiments were performed with a PTFE reaction vessel loaded into steel autoclave. The experiments were carried out at temperature of 200 °C for run duration of 168 hours, with different pH condition (0, 7, 13, 14) and different water/rock ratios. Na^+ concentration in all solution is maintained at 1 mol/l. We conducted also heating experiments. The experiments were performed at temperature of 500,600,700 and 800 °C for 24 hours with an electric furnace. We use run products of hydrothermal experiments as starting materials. After these experiments, run products were identified by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Under pH 14 conditions, products from gehlenite- SiO_2 and plagioclase were nepheline hydrate ($\text{Na}_3\text{Al}_3\text{Si}_3\text{O}_{12}\text{H}_2\text{O}$) and analcime ($\text{NaAlSi}_2\text{O}_6\text{H}_2\text{O}$), whereas at high water/rock ratios, these alteration didn't occurred. Under pH 14-7 conditions, Gehlenite alternated to hydro grossulor ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$). Under pH 13-7 conditions, analcime formed by replacing gehlenite or plagioclase. Under pH 0, no products formed from gehlenite and plagioclase, but gehlenite was dissolved. Under 500-700 °C conditions, we did not obtained from any products from analcime by heating experiments. Under 800 °C condition, analcime metamorphosed into amorphous material.

The results indicate that alteration of gehlenite and plagioclase dependent on the experimental conditions, pH and water/rock ratios. As far as we know, the results also indicate that concentration of ion in solution is related to form potassium rich hydrous mineral like nepheline hydrate and analcime. They suggest that in carbonaceous chondrite parent body aqueous alteration of gehlenite occurred under high pH and lower water/rock ration.

Keywords: nepheline, melilite, aqueous alteration, hydrothermal experiments, carbonaceous chondrite

Evidence for Late Stage Heavy Bombardment from Centimeter-sized Impact Melt Clasts in Apollo 16 Regolith Breccias

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Isotopic ages from lunar rocks cluster around 4.0-3.8 Ga [e.g., 1,2] and are interpreted to indicate terminal lunar cataclysm [3]. However, this age cluster can be also interpreted as the overprint of a single large impact event; the Imbrium basin forming event. To evaluate this issue, we are focusing on impact melt clasts in ancient regolith breccias that lithified ~3.8 Ga recovered at the Apollo 16 traverse site. Norman et al. [4] first addressed and reported that at this issue and report at least 4 distinct impact events are required based on petrological textures and Ar-Ar ages of large-sized Apollo 16 impact melt rocks. Among 25 samples, they found ages from 3.75 to 3.96 Ga. To further test this issue, we examined 11 impact melt clasts from 60016, 65095 and 61135 [6-8].

To clarify the origins of impact melt clasts, we focus on compositions of relict minerals and bulk compositions. Relict minerals could remain information about original target materials if the shock-metamorphic overprint is not severe. For 6 melt clasts from 60016, at least 4 different target regions are required; Clast 1 comes from a terrain with high bulk Al₂O₃ (26.4 wt. %) and bimodal compositions in mafic minerals (Mg-suite and ferroan anorthosite), Clasts 2, 3 and 4 come from a terrain with low Al₂O₃ (20.4-16.4 wt %) composition and relatively ferroan composition in mafic minerals (Mg-suite), Clast 5 comes from a terrain with high-bulk Al₂O₃ (23.9 wt. %) and high Mg# in mafic minerals (Mg-suite), and Clast 6 comes from a terrain with low bulk Al₂O₃ (18.6 wt. %) and high-Mg# in mafic minerals (Mg-suite). All clasts have high- K₂O (>0.3 wt. %) and - P₂O₅ (>0.3 wt. %), and require KREEPy material [6]. Three clasts from 65095 have similar relict mafic mineral (Mg# in olivine = ~79.5) and bulk (Al₂O₃ = 23.5 wt. %; K₂O = 0.16 wt. %; P₂O₅ = 0.22 wt. %) compositions among the clasts implying they have a same origin, however, different origin from clasts from 60016 [7]. Five regions in 2 clasts from 61135 might be generated by mixing of two end member melts; high-K (K₂O = 0.72 wt. %) and low-K (K₂O = 0.27 wt. %) and require at least one distinct impact site [8].

We obtained Ar-Ar shock retention ages for 6 impact melt clasts from 60016 and a clast from 65095 [6]. We find evidence for at least five different impact events clustered within short span of 4.0-3.7 Ga for 6 clasts from 60016. However, a recent thermal disturbance of the K-Ar system means that the formation age of the one clast in 65095 analyzed so far cannot be determined precisely enough to compare. Analyses of siderophile elements in some of these clasts also point to multiple impact events [9].

From the combined results from relict minerals and bulk compositions, 11 melt clasts require at least 6 individual target regions with KREEPy material. Ar-Ar ages confirm that clasts from 60016 originated from at least 5 distinct impact events. Thus, multiple impact events occurred in or near the PKT region and impact melt clasts were not produced by a single (i.e., Imbrium) impact event.

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Keywords: Apollo16, Impact melt, Late Stage Heavy Bombardment, KREEP

Origin of D'Orbigny glass: Towards the understanding of the angrite parent body

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D'Orbigny is an unusual angrite in its presence of abundant glasses (Kurat et al., 2001). So, it is very important to reveal the origin of the glasses for understanding of the formation process of D'Orbigny and internal properties of the angrite parent body. Varela et al. (2003) and Kurat et al. (2004) argued that the D'Orbigny glass is a nebular condensate that later suffered from alteration by a metasomatic event. However, this idea contradicts the more popular arguments of igneous origin for D'Orbigny (e.g. Mittlefehldt et al., 2002; McCoy et al., 2006) in that they also regard the constituent minerals as nebular condensates. We have investigated the origin of the glasses by observation with optical microscope and FE-SEM and by chemical analyses of glasses and minerals with EPMA and EDS to resolve the confusion about the origin of D'Orbigny and to extract more reliable information on the D'Orbigny parent body.

The 0.1mm-thick black glossy glass in the sample covers D'Orbigny minerals. The glass surface is covered by numerous vesicles as Varela et al. (2003) called foamy glass. This glass is further covered by aggregates of terrestrial minerals with average grain size less than 10 microns, such as K-feldspar, quartz and orthopyroxene, which are not derived from the angrites. Along the contact between the D'Orbigny glass and the aggregate, a thin layer of silica-rich glass, different from the D'Orbigny glass in including K, is present. The internal parts of D'Orbigny show partial melting texture and decomposition texture of FeS only within 0.5 mm from the glass.

The average chemical composition of D'Orbigny glass is almost identical to that of the bulk rock, which is consistent with Varela et al. (2003). The chemical composition varies within the area defined by connecting main mineral compositions on the oxide plots. There exists flow structure exhibited by the compositional variation as reported by Varela et al. (2004). Olivine in contact with the glass is zoned and has an Mg-rich inner zone with thickness of max 5 micron and a Fe-rich outer zone with thickness of max 2 micron towards the contact. In addition, both Mg and Fe in glass decrease towards the olivine.

The average composition of D'Orbigny glass almost identical to that of the bulk rock excludes the idea that glass is a melt come from an external source (Varela et al., 2003). It is impossible to solidify glass with the bulk rock composition and the holocrystalline lithology with the max size of 1mm in one event, because they require very different cooling rate. We argue that the melting occurred on Earth because the terrestrial aggregate covers the D'Orbigny glass with the thin silica rich glass sandwiched inbetween. The chemical heterogeneity in contacting glass and olivine suggests that the olivine once melted and then grew rapidly. It is concluded that D'Orbigny melted during falling in the atmosphere by frictional heating, which produced abundant melt. The porous nature of D'Orbigny facilitates migration of frictional melt inside the meteorite through voids or druses. This idea is consistent with the noble gas analyses, which show that the D'Orbigny glass has the solar gas component, while the bulk rock has spallogenic component (Busemann et al., 2006).

The D'Orbigny glass represents quenched melt formed by frictional heating during falling though the atmosphere. The crystalline part of D'Orbigny is an igneous rock because of its texture and systematic sequence of minerals and chemical zoning toward interstices (Mittlefehldt et al., 2002; Suzuki et al., 2012). These results allow us to distinguish the information relevant to the parental body of D'Orbigny from that attributed to the frictional melting on the Earth. Internal processes of the angrite parental body can be examined based on the essential information from D'Orbigny by eliminating terrestrial phenomena.

Tungsten isotope analysis of meteorite samples using ETV-MC-ICPMS technique

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Hf-W chronometer is based on the decay of ^{182}Hf to ^{182}W with a half-life of 8.9 Myr. Hf is strongly lithophile elements, whereas W is moderately siderophile elements. Thus, the Hf-W age can provide critical information about the timing of metal-silicate differentiation (core formation) processes at the early stage of the planetary formation. Moreover, both the Hf and W is strongly refractory elements, the Hf-W age can reflect the timing of condensation or segregation of the metallic nuggets from chondritic reservoir at the early sequence of the solar system.

The thermal ionization mass spectrometry (TIMS) is widely used for W isotope analysis. However, a micro-gram amount of W is desired for Hf-W chronological studies in this technique. The ICP-MS technique coupled with the conventional nebulization technique is also used for W isotope measurement. With this technique, total amount of W required for the isotopic ratio measurements could be 50 - 100 ng. On the other hand, typical ion transmission efficiency from sample to ion collector would be <0.1% under the sample introduction using the nebulizer. This suggests that the sample introduction efficiency (i.e., high transmission efficiency) can be dramatically improved when the loss of sample mist could be minimized. To achieve this, we have developed a sample introduction technique using the electrothermal vaporization (ETV) technique for W isotope analysis.

In this study, W sample in 2% HNO_3 solution is loaded on the Re filament located in a small volume ETV chamber to achieve minimum loss of W vapor and also to reduce the memory of W within the chamber. Temperature of the Re filament is controlled by the incident current (0 - 4 A). The W evaporation is carried out under the two different ambient gasses, Ar or He. We found that W signal intensity profile obtained under the Ar carrier gas is spiky and unstable, and this is not suitable for the precise isotopic analysis. In strike contrast, the signal intensity profile obtained under the He carrier gas is very smooth and stable. Moreover, with the He carrier gas, total number of W atoms was about 1.7 times higher than that achieved by the Ar carrier gas. Taking these points into account, He carrier gas was used throughout the W isotope measurements.

The isotope analysis was carried out using various amount of W solution sample. As a result, we found that <25 ng of W can reveal the precise W isotope ratio. The W isotope ratios of some meteorite samples were also measured using the ETV-MC-ICPMS technique. The results will be discussed in this presentation.

Keywords: MC-ICP-MS, isotope, ETV, meteorite

Development of novel mass spectrometer to analyze solar wind noble gases

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Solar-gas-rich regolith breccia from asteroids has been studied [e.g., 1, 2], which were irradiated by solar wind (SW) on the parent body surface. Regolith breccia was lithified by compaction process from regolith soils. The compaction processes which were recorded in the breccias should reveal a migration, deposition, SW irradiation of the soil. To figure out the SW distribution in the breccia high spatial resolution is required because SW implanted layer is less than 100 nm [2].

LIMAS (Laser Ionization Mass nanoScope) [3] is a time-of-flight sputtered neutral mass spectrometer (TOF-SNMS) with non-resonant laser post-ionization system which can observe in-situ distributions of all elements in solid materials down to tens nm level. LIMAS is mainly composed of Ga focused ion beam (FIB) for sputtering, femtosecond laser for post-ionization of sputtered particles, and multi-turn mass spectrometer (MULTUM II [4]).

An n-type Si wafer, which was irradiated by 30 keV ⁴He of 2×10^{16} ions/cm² was used to evaluate and confirm sensitivity for He. The sputtering crater was 6.4×15.2 μ m² and measurement area is 2.1×4.1 μ m² of the center. The detection limit of ⁴He for the system is about 10^{18} ions/cm³ for ⁴He. The performance of LIMAS should be improved towards higher sensitivity and lower background noises because bulk concentrations of solar-He in gas-rich meteorite is 10^{-2} - 10^{-4} cm³STP/g [e.g., 1] which can be translated into 10^{16} - 10^{18} atoms/cm² for rocky material (density ~ 3 g/cm³).

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Keywords: Noble gas, Solar wind, Microscopic analysis, Mass spectrometry

Estimation of space weathering morphologies of Itokawa regolith particles by comparison with ion irradiation experiments

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Itokawa regolith particles recovered by the Hayabusa missions have important information about surface processes on a small asteroid without atmosphere. Analysis on the three-dimensional micro-morphology of the Itokawa particles by micro-tomography (CT) revealed that some particles (~25 %) have rounded edges [1]. Transmission electron microscope (STEM) analysis found space weathering rims caused by solar wind irradiation [2,3]. Comparison between the CT and TEM analyses showed that there was no correlation between the edge roundness and the thickness of the space-weathering rim [4], indicating that the surfaces with rounded edges can have formed by mechanical abrasion due to micrometeoroid impacts on Itokawa. On the other hand, a possibility of solar wind sputtering cannot be excluded [1,4]. The comparison between the surface structures observed by TEM with nm-scale resolution and by CT with several um-scale resolution is not enough for detailed discussion. In this study, the surface morphologies of Itokawa particles and experimentally ion irradiated olivine particles were compared using FE-SEM, which can identify structures of several tens nm to few um, and TEM. Experiments simulating solar wind irradiation to mineral grains were performed at the Wakasa Wan Energy Research Center. An olivine sample of 100 um in size from Sri Lanka with the composition of Fa₃₀, which is almost the same as the composition of olivine in Itokawa regolith, was chosen as an analog of Itokawa regolith. The olivine fragments were irradiated with H⁺, and ⁴He⁺ ions accelerated at 10 to 50 keV with fluences of 1 x 10¹⁶ to 1 x 10¹⁸ ions/cm². The olivine surfaces were observed using field-emission secondary electron microscope (JSM7001F) before and after the irradiation. TEM samples were prepared by focused ion beam (FEI Quanta 200 3DS) and observed by transmission electron microscope (H8000k) at Kyoto University. Samples irradiated with H⁺ and He⁺ ions at fluence of 1 x 10¹⁸ ions/cm² show numerous blister structures of several hundreds nm to 3 um in size on their surfaces. Observation by TEM showed that appearance of abundant vesicles beneath the surfaces. Blisters have vesicles structures in similar sizes as the blisters beneath the surface. The vesicles were suggested to be filled with H of He gas. In the previous study, vesicles were observed in thick space weathering rims [3] and blisters were observed by FE-SEM [5]. They were probably formed by solar wind He implantation because their depth (~50 nm) is consistent with implantation depth by solar wind He with typical energy of 4 keV. The fluence of 3 x 10¹⁸ ions/cm² correspond to the solar wind He irradiation duration of 1540 years. The blisters on the Itokawa particles should be formed between approximately in the order of 1000 years. The results indicate that the space weathering rim should be produced in a very short duration compared with the estimated residence time of regolith on the smooth terrain of Itokawa (<~3 Myr [6]). Mechanical abrasion by seismic vibration might occur for a long duration (<~3 Myr [5]) during the particles had been staying in the regolith. [1] Tsuchiyama A. et al. (2011) Science, 333, 1125-1128. [2] Noguchi T. et al. (2011) Science, 333, 1121-1125. [3] Noguchi T. et al. (2012) Met. Planet. Sci. submitted. [4] Tsuchiyama A. et al. (2013) LPSC XLIV,2169. [5] Matsumoto T. et al. (2013) LPSC XLIV, 11441. [6] Nagao K. et al. (2011) Science, 333, 1128-1131.

Keywords: Itokawa, regolith, space weathering

Abrasion of regolith particles on airless bodies: comparison between Itokawa and lunar regolith

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Preliminary examination of Hayabusa samples suggests that Itokawa regolith have experienced following processes on the airless body [1]. (1) Formation of fine particles (~100 um) by impact of small objects onto Itokawa [2]. (2) Irradiation and implantation of solar wind to particles on Itokawa's uppermost surface [3]. (3) Formation of space weathering rims (thin amorphous layers (<100 nm) with Fe-rich nano-blobs and sometimes blisters) on the particle surfaces mainly due to implantation of solar wind He with the time scale of ~10³ yr [4,5]. (4) Abrasion of the particles, called "space erosion", probably due to grain motion by impact-induced seismic waves in a regolith layer with time scale of sufficiently longer duration than 10³ yr [1,2,6]. Processes (3) and (4) should be repeated [3]. (5) Final escape of particles from the asteroid by impact within the residence time of < 8 Myr [3].

Evidence for the abrasion is mainly based on their 3D shapes and surface micro-morphologies obtained by x-ray micro-tomography [2]. The shape distribution of Itokawa particles cannot be distinguished from that of fragments formed by high-speed impact experiments [7], indicating that the particles are consistent with fragments mechanically crushed by impact. About 3/4 of the particles examined have sharp edges while rest of them have rounded edges at least on a part of the particle surface, suggesting that the fragments have been abraded. The shape distribution of lunar regolith particles (Apollo 16 highland samples: 60501) [8] was also compared. It was suggested that they are more spherical than the Itokawa and impact particles [2]. However, the lunar regolith samples were not imaged grain-by-grain by tomography [8], and imperfect separation of grains might affect the shape distribution data.

In the present study, 3D shapes of lunar regolith particles were obtained by the same method as the Itokawa particles. Particles (~50-100 um) picked up from 60501 and 10084 (Apollo 11 mare sample) were imaged grain-by-grain at BL47XU of SPring-8 using imaging tomography system with the effective spatial resolution of 200 or 500 nm. The longest, middle and shortest axis lengths (a, b and c) were obtained by ovoid approximation of solid portion extracted from CT images. The 3D shape distributions in b/a vs. c/b diagram were compared using Kolmogorov-Smirnov (K-S) test.

The shape distribution of 60501 particles (number of particles: N=21) can be clearly distinguished from those of the Itokawa particles (N=59) and impact fragments (N=6201) with P=0 (P: probability in the K-S test) while this cannot be distinguished from the previous 60501 data (N=55) with P=0.80. The rest of the lunar particles (N~90) will be analyzed. It has been reported that the mean b/a and c/b ratios of mare lunar regolith (0.72-0.78 and 0.73-0.86, respectively [9]) is larger than those of impact fragments (0.71 [8]). The present results and the previous data show that lunar regolith is more spherical than the impact fragments although lunar regolith is clearly the product of impact on the lunar surface. This strongly suggests that the regolith was abraded. The cause of the abrasion may be grain motion during gardening by impacts. The degree of abrasion is larger than the Itokawa particles due to larger scale of impacts and longer regolith residence time.

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