

Structural control of biominerals by intracrystalline organic macromolecules

Taiga Okumura^{1*}, Michio Suzuki², NAGASAWA, Hiromichi², BUSECK, Peter R.³, Toshihiro Kogure¹

¹Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, ²Dept. Applied Biological Chemistry, Grad. Sch. Agricultural and Life Sciences, The Univ. Tokyo, ³School of Earth & Space Exploration & Department of Chemistry/Biochemistry, Arizona State University

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

Hikaru Yabuta^{1*}, Takaaki Noguchi², Shoichi Itoh³, TSUJIMOTO, Shinichi², Naoya Sakamoto³, Minako Hashiguchi³, ABE, Ken-ichi³, KILCOYNE, David A. L.⁴, OKUBO, Aya⁵, Ryuji Okazaki⁶, Shogo Tachibana³, Kentaro Terada¹, Tomoki Nakamura⁷, Mitsuru Ebihara⁸, Hiroko Nagahara⁵

¹Osaka University, ²Ibaraki University, ³Hokkaido University, ⁴Advanced Light Source, ⁵Tokyo University, ⁶Kyusyu University, ⁷Tohoku University, ⁸Tokyo Metropolitan University

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.

References:

[1] Nakamura et al. (2005) MAPS 40, A110. [2] Yabuta et al. (2012) LPSXXXXIII, Abstract 2239. [3] Peeters et al. (2012) LPSXXXXIII, Abstract 2612. [4] De Gregorio et al. (2010) GCA, 74, 4454. [5] Bradley and Dai (2004) Ap. J. 617, 650. [6] Dworkin et al. (2001) PNAS 98, 815.

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

Minako Hashiguchi^{1*}, Sachio Kobayashi², Hisayoshi Yurimoto¹

¹Natural History Sci., Hokkaido Univ., ²CRIS, Hokkaido Univ.

[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

Yoko Kebukawa^{1*}, Michael Zolensky², A. L. David Kilcoyne³, Zia Rahman⁴, George D. Cody¹

¹Carnegie Institution of Washington, ²NASA Johnson Space Center, ³Advanced Light Source, Lawrence Berkeley National Laboratory, ⁴Jacobs-Sverdrup

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.

References: [1] Zolensky M. Z. et al. 2009. 40th Lunar & Planetary Science Conference, Abstract #2162. [2] Cody G. D. et al. 2008. Earth and Planetary Science Letters 272: 446-455. [3] Brearley A. J. 1990. Geochimica et Cosmochimica Acta 54: 831-850. [4] Zolensky M. E. et al. 1990. Cosmic dust catalog 11. NASA Johnson Space Center/Planetary Science Branch Publication 83: 170.

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

Hisayoshi Yurimoto^{1*}

¹Natural History Sciences, Hokkaido University

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

Noriyuki Kawasaki^{1*}, Naoya Sakamoto², Hisayoshi Yurimoto³

¹Natural History Sciences, Hokkaido University, ²CRIS, Hokkaido University, ³Natural History Sciences, Hokkaido University

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

Kohei Fukuda^{1*}, Hajime Hiyagon¹, Shogo Sasaki¹, Wataru Fujiya², Naoto Takahata³, Yuji Sano³, Yuichi Morishita⁴

¹Graduate School of Science, The Univ. of Tokyo, ²Max Planck Institute for Chemistry, ³AORI, The Univ. of Tokyo, ⁴Geological Survey of Japan, AIST

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.

Mutsumi Komatsu^{1*}, Timothy Fagan², Takashi Mikouchi³

¹Waseda Institute for Advanced Study, Waseda University, ²Department of Earth Sciences, Waseda University, ³Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo

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.

[1] Ebel D. S. et al., 2012. *MaPS* 47:585-593.

[2] Klock W. et al., 1989. *Nature* 339: 126-128.

[3] Ichikawa and Ikeda, 1995. *Proc. NIPR symp.* 8:63-78.

[4] Zolensky M. E. et al. 2006. *Science* 314: 1735-1753.

[5] Weisberg M. K. and Connolly Jr. H. C. 2008. *Lunar Planet. Sci. Conf.* 37, #1981.

[6] Sugiura N. et al. 2009. *MaPS* 44:559-572.

[7] Krot A. N. et al., 1998. *MaPS* 33:623-645.

[8] Chizmadia L. et al., 2002. *MaPS* 37:1781-1796.

Keywords: meteorites, carbonaceous chondrites, secondary alteration, AOA

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

Megumi Matsumoto^{1*}, Kazushige Tomeoka¹, Yusuke Seto¹, Akira Miyake², Daisuke Hamane³

¹Kobe Univ. Sci., ²Kyoto Univ. Sci., ³Univ. Tokyo, ISSP

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.

References:

- [1] Ikeda and Kimura (1995), Proc. NIPR Symp. Antarct. Meteorites, 8, 97-122.
- [2] Russell et al. (1998), Geochimica et Cosmochimica Acta, 62, 4, 689-714.
- [3] Kojima et al. (1995), Proc. NIPR Symp. Antarct. Meteorites, 8, 79-96.
- [4] Tomeoka and Itoh (2004), Meteoritics & Planetary Science, 39, 1359-1373.

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

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

Midori Sakai^{1*}, Kazushige Tomeoka¹, Yusuke Seto¹, Akira Miyake²

¹Kobe Univ. Sci., ²Kyoto Univ. Sci.

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.

[1]Kurat et al. (1989) Z.Naturforsch, 44a, 988-1004.

[2]Kojima et al. (1993) Meteoritics, 28, 649-658.

[3]Krot et al. (1995a) Meteoritics, 30, 748-775.

[4]Kojima and Tomeoka. (1996) GCA, 60, 2651-2666.

[5]Buchanan et al. (1997) GCA, 61, 1733-1743.

[6]Russell et al. (1998) GCA, 62, 698-714.

[7]Krot et al.(2000) Geochemistry International, 38, S351-S368.

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

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

Satoshi Moriya^{1*}, Kazushige Tomeoka¹, Yusuke Seto¹, Akira Miyake²

¹Kobe Univ. Sci., ²Kyoto Univ. Sci.

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.

[1]Rubin and Wasson (2005) *GCA* **69**, 211. [2]Scott et al. (1992) *GCA*, **56**, 4281.

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.

Shun Ichimura^{1*}, Yusuke Seto¹, Kazushige Tomeoka¹, Akira Miyake²

¹Kobe Univ. Sci., ²Kyoto Univ. Sci.

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 grossular ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$). 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

Takafumi Niihara^{1*}, BEARD, Sky P.², SWINDLE, Timothy D.², KRING, David A.¹

¹CLSE LPI-USRA, NASA Lunar Science Institute, ²University of Arizona, NASA Lunar Science Institute

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.

References: [1] Papanastassiou D.A. and Wasserburg G.J. 1971. EPSL 11. 37-62. [2] Turner G et al., 1973. Proc. LPSC 4, 1889-1914. [3] Tera F et al., 1974. EPSL 22, 1-21. [4] Norman M.D. et al., 2006 GCA. 70, 6032-6049. [5] Korotev R.L. 1994. GCA 58, 3931-3969. [6] Niihara T. et al., 2012.GCA submitted. [7] Niihara T. and Kring D.A. 2012 MAPS 47, Suppl. #5074. [8] Niihara et al., 2013 LPSC 44 submitted. [9] Liu et al., 2013 LPSC 44 submitted.

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

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

Hiroko Suzuki^{1*}, Takashi Mikouchi¹, Kazuhito Ozawa¹

¹Department of Earth and Planetary Science, The University of Tokyo

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

Satoki Okabayashi^{1*}, Shuhei Sakata¹, Takafumi Hirata¹

¹Department of Earth and Planetary Sciences, Kyoto University

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

Ken-ichi Bajo^{1*}, Itose Satoru², Matsuya Miyuki², Ishihara Morio³, Uchino Kiichiro⁴, Kudo Masato², Sakaguchi Isao⁵, Yurimoto Hisayoshi¹

¹Hokkaido University, ²JEOL Ltd., ³Osaka University, ⁴Kyushu University, ⁵NIMS

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 μm^2 and measurement area is 2.1×4.1 μm^2 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).

References: [1] Goswami J. N. et al. (1984) Space Sci. Rev., 37, 111-159. [2] Wieler R. et al. (2002) in Rev. Mineral. Geochem., 47, 21-70. [3] Ebata S. et al. (2012) Surf. Interface Anal., 44, 635-640. [4] Okumura D. et al. (2005) Eur. J. Mass Spectrom., 11, 261-266.

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

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

Tooru Matsumoto^{1*}, Akira Tsuchiyama², Aki Takigawa², Keisuke Yasuda³, Yoshinori Nakata³, Akira Miyake²

¹Osaka University, ²Kyoto University, ³The Wakasa wan energy research center

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

Akira Tsuchiyama^{1*}, Takashi Matsushima², Tooru Matsumoto³, Tsukasa Nakano⁴, Daiki Amemiya¹, Junya Matsuno¹, Takashi Nagano³, Akira Shimada³, Kentaro Uesugi⁵, Akihisa Takeuchi⁵, Yoshio Suzuki⁵, Makiko Ohtake⁶

¹Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University, ²Graduate School of Systems and Information Engineering, University of Tsukuba, ³Department of Earth and Space Science, Graduate School of Science, Osaka University, ⁴AIST, ⁵JAXA/SPring-8, ⁶ISAS/JAXA

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.

References: [1] Tsuchiyama A. et al. (2013) LPS XLIV, Abstract #2169. [2] Tsuchiyama A. et al. (2011) Science, 333, 1125-1128. [3] Nagao K. et al. (2011) Science, 333, 1128-1131. [4] Noguchi T. et al. (2011) Science, 333, 1121-1125. [5] Noguchi T. et al. (2012) Meteoritics & Planet. Sci., submitted. [6] Matsumoto T. et al. (2013) This volume. [7] Capaccioni F. et al. (1984) Nature, 308, 832-834. [8] Katagiri J. (2010) Proc. 12th Internat. Conf. Engin., Sci., Construct., Operat. in Challenging Environments, Am. Soc. Civil Engin., 254-259. [9] Heiken G. H. et al., Eds., Lunar Sourcebook (1991).

Keywords: Hayabusa mission, Apollo mission, space weathering, impact, x-ray tomography, SPring-8

Development of a new analytical scheme for micrometeorites and discovery of micrometeorites with intriguing mineralogy

Shinichi Tsujimoto¹, Takaaki Noguchi^{1*}, Ryuji Okazaki², Tomoki Nakamura³, Mitsuru Ebihara⁴, Shoichi Itoh⁵, Hiroko Nagahara⁶, Shogo Tachibana⁵, Kentaro Terada⁷, Hikaru Yabuta⁷

¹Ibaraki University, ²Kyushu University, ³Tohoku University, ⁴Tokyo Metropolitan University, ⁵Hokkaido University, ⁶University of Tokyo, ⁷Osaka University

Introduction: Combined mineralogical and isotopic studies of individual Wild 2 cometary particles revealed that the materials formed in the inner solar system had been transported to the outer solar system before the formation of the Wild 2 comet [e. g. 1,2,3,4]. We sought another analytical scheme for MM (micrometeorite) studies. In this new analytical scheme, we have two objectives: identification of nonchondritic MMs and identification of asteroidal MMs with mineralogy indistinguishable from CP IDPs, which are regarded as cometary grains [5].

Samples and methods: MMs used in this study were found in the surface snow collected near the Dome Fuji Station, Antarctica in 2003 and 2010. The surface snow was melted and filtered in a clear room. After identification of MMs, we performed SR-XRD, FIB section preparation, TEM, micro-Raman, SEM, EPMA, INAA, and/or noble gas mass spectroscopy for each MM.

Results and discussion: We investigated twelve MMs and could classify them into five types based on their mineralogy: refractory MMs, chondrule-like MMs, fine-grained polycrystalline MMs, coarse-grained crystalline MMs, and phyllosilicate-rich MMs. Here we show the mineralogical results of two MMs with intriguing mineralogy.

Refractory MM A MM is composed mainly of anorthite, diopside, and spinel. A BSE image of the cross section of the MM showed that it has an amoeboid structure, in which small (<5 micrometer) Al-rich and Ti-bearing diopside exists on its surface and its interior and anorthite fills the interstices of diopside. The major minerals are similar to those in type C CAIs [6]. Although its amoeboid structure suggests low degrees of melting during the formation event, the MM has a compact interior, in which diopside and anorthite have triple junctions with $\sim 120^\circ$ angles. Therefore, the refractory object was probably formed by low degrees of melting and subsequent prolonged cooling. It is different from meteoritic type C CAIs that experienced intense melting and crystallization from melt droplets. Fine-grained material attached on the refractory object is composed of GEMS (glass with embedded metal and sulfide)-like objects, olivine, pyrrhotite, and carbonaceous material. Because GEMS-like objects have not been identified among meteorites yet, this MM may have derived from a comet.

Fine-grained polycrystalline MM A MM is composed of small (<400 nm) crystals of Fe-bearing olivine, Fe-free low-Ca pyroxene, Fe-Ni metal, Fe sulfide, amorphous silicate, and interstitial carbonaceous material. Although these crystals have often triple junctions with $\sim 120^\circ$ angles suggestive of recrystallization, both olivine and low-Ca pyroxene show almost no compositional zoning. The low-Ca pyroxene crystals elongate near the a-axis direction and are composed of a unit cell-order mixture of ortho and clino low-Ca pyroxene with stacking disorders. Its microstructure indicates rapid cooling ($>20\text{-}30\text{ K hr}^{-1}$) from above 1275K [7]. Both olivine and low-Ca pyroxene in this MM contain abundant tracks with $\sim 5 \times 10^{10}\text{ cm}^{-2}$, which corresponds to $\sim 10^4$ -year exposure to the solar wind [8]. Tracks in olivine are erased by flash heating above $\sim 600^\circ\text{C}$ [9]. Because typical cometary IDPs are heated to $>720^\circ\text{C}$ [10], it is plausible that the MM was derived from an asteroid instead of a comet although any materials similar to this MM have not been found among meteorites.

References: [1] Zolensky et al. (2006) *Science* 314, 1735-1739. [2] McKeegan et al. (2006) *Science* 314, 1724-1728. [3] Nakamura et al. (2008) *Science* 321, 1664-1667. [4] Matzel et al. (2010) *Science* 328, 483-486. [5] Ishii et al. (2008) *Science* 319, 447-450. [6] Krot et al. (2008) *GCA72*, 2534-2555. [7] Brearley and Jones (1993) *LPS XXIV*, 185-186. [8] Bradley (2006) In: *Meteorites, Comets, and Planets*. [9] Fraundorf et al. (1982) *GCA* 45, 915-943. [10] Joswiak et al. (2005) Workshop on dust in planetary systems (abstract), #4106.

Keywords: micrometeorites, TEM, noble gas, FIB, INAA

Chemical compositions of cosmic dust samples recovered from Antarctic snow

Mitsuru Ebihara^{1*}, Shun Sekimoto², Naoki Shirai¹, Shinichi Tsujimoto³, Takaaki Noguchi³, Tomoki Nakamura⁴, Ryuji Okazaki⁵, Shoichi Itoh⁶, Shogo Tachibana⁶, Hikaru Yabuta⁷, Kentaro Terada⁷, Aya Okubo⁸, Hiroko Nagahara⁸

¹Department of Chemistry, Tokyo Metropolitan University, ²Kyoto University Research Reactor Institute, ³College of Science, Ibaraki University, ⁴Department of Earth and Planetary Materials Sciences, Tohoku University, ⁵Department of Earth and Planetary Sciences, Kyushu University, ⁶Department of Natural History Sciences, Hokkaido University, ⁷Department of Earth and Space Science, Osaka University, ⁸Department of Earth and Planetary Science, University of Tokyo

We investigated four micrometeorites (MMs) recovered from Antarctic ice: D10IB034, D10IB103, D10IB179, and D10IB187. Bulk mineralogy was investigated by SR-XRD, TEM, FE-EPMA, and INAA. Analytical procedure for INAA was essentially the same as used for Itokawa grains [1]. The MMs were irradiated with neutron (total neutron fluence: 6.1×10^{18} n/cm²) along with reference standards at Kyoto University Research Reactor Institute (KURRI). After cooling for a few days, the MMs were measured for gamma-ray activity by using germanium semiconductor detectors at KURRI.

A total of eight elements (Na, Sc, Cr, Fe, Co, Ni, Sm and Ir) were determined at least for one MM sample. Their abundances relative to CI chondrite and Fe contents of individual samples show that siderophiles (Co, Ni, Ir) are more variable and depleted compared with lithophiles (Na, Sc, (Sm)). Compared with literature data for bulk and matrix samples of CM and CR meteorites, an agreement is not good within the limited data set. Even in the comparison with MMs from Antarctic ice, the four dust MMs from Antarctic snow seem to have distinct chemical features.

The FeO/Sc ratio can be used for judging the origin of planetary materials. When these ratios for the four MMs of this study are compared with data for bulk chondrites, Earth, Moon, Mars, olivine and pyroxene separates from ordinary chondrites and the Itokawa grain samples [1], the four MM samples along with chondritic materials and Itokawa grains have higher FeO/Sc ratios than those for terrestrial samples. This suggests that the four MMs are extraterrestrial in origin although their compositions are not chondritic and are not similar to MMs from ice.

Two MMs (D10IB034 and D10IB179) yielded definite values for both Co and Ni. Their abundances and ratios give us reliable judgement for the origin of planetary materials. If their contents relative to Fe contents are compared with those for Itokawa grains [1] and some constituent minerals of L and LL chondrites, the two MM from Antarctic snow are on the line defined by the CI Co/Ni ratio, clearly indicating their extraterrestrial origin. This further suggests that these MMs contain tiny metal particles or primitive materials having high and unfractionated Co and Ni abundances. Crustal materials of differentiated planets like Earth and 4 Vesta (HED parent body) also plotted in lower left region off the CI line. One MM (D10IB103) seems to be also in such region.

Only one MM sample (D10IB034) was observed to have a distinct value of Ir. When its ratio relative Co and Ni is compared with data for chondrules from ordinary chondrites (mostly unequilibrated ordinary chondrites; [2]), bulk chondrites and chondritic metals in addition to the Itokawa grain [1], bulk chondrites and chondritic metals mostly converge around the cross defined by CI ratios for Ir/Ni and Ir/Co. These elements are typical siderophile elements and, hence, they are not largely fractionated in bulk chondrites, chondritic metals and even in iron meteorites. Instead, chondrules show a large spread in Ir/Ni and Ir/Co ratios [2]. CI-normalized Ir/Fe and Ir/Co ratios of chondrules are arrayed on the line having a slope of 1, implying that chondrules have unfractionated (chondritic) Co/Ni ratios with a large variation of Ir abundances. The Itokawa grains also fit on this line [1]. It is observed that the MM D10IB034 also stay on the same line. The difference between the Itokawa grain and the Antarctic dust sample is on the Ir content. We interpret that the MM D10IB034 contains an early condensate in which Ir condensed but Co and Ni scarcely did.

References: [1] Ebihara M. et al. (2011) *Science*, 333, 1119-1121. [2] Grossman J. N. and Wasson J. T. (1982) *GCA*, 46, 1081-1099.

Keywords: cosmic dust, micrometeorites, chemical composition

Noble gas isotopes of micrometeorites collected from Antarctic snow

Ryuji Okazaki^{1*}, Yu Tobimatsu¹, Takaaki Noguchi², TSUJIMOTO, Shinichi², Aya Okubo³, Tomoki Nakamura⁴, Mitsuru Ebihara⁵, Shoichi Itoh⁶, Hikaru Yabuta⁷, Shogo Tachibana⁶, Hiroko Nagahara³, Kentaro Terada⁷

¹Department of Earth and Planetary Sciences, Kyushu University, ²College of Science, Ibaraki University, ³Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, ⁴Department of Earth and Planetary Materials Sciences, Faculty of Science, Tohoku University, ⁵Graduate School of Science and Engineering, Tokyo Metropolitan University, ⁶Department of Natural History Sciences, Hokkaido University, ⁷Department of Earth and Space Science, Osaka University

As a comprehensive study [e.g., 1], we have been investigating micrometeorites (MMs) collected from Antarctic snow in 2003 and 2010 by JARE. MMs used in this study were recovered by filtering melted snow water at 20 °C in a clear room at Ibaragi Univ. Each MM was investigated by several analytical methods: identification using SED-EDS, followed by characterization by SR-XRD, TEM, micro-Raman, SEM, and EPMA analyses, and additionally by INAA, and/or noble gas mass spectroscopy. We classified the MMs investigated into five types based on their mineralogical features: 1) refractory, 2) chondrule-like, 3) fine-grained polycrystalline, 4) coarse-grained crystalline, and 5) phyllosilicate-rich MMs. Here, we report results of noble gas analyses for the MMs and show the relation between their noble-gas and mineralogical features.

Each of the samples mounted on Mo sheets was removed using acetone, and packed into an Al cup. The Al cups were set in a sample holder of a small furnace (designed for submicrogram to milligram samples) equipped with a purification line of the noble gas mass spectrometer at Kyushu Univ. The samples were heated *in vacuo* at 150 °C for 1 day to reduce adsorbed atmospheric gas contamination. Each sample was heated stepwise at 400, 650, and 1800 °C to extract noble gases. Absolute abundances and ratios of noble gas isotopes were calibrated by measuring known amounts of atmospheric gas and a He standard gas with ³He/⁴He of 1.71E-4. Blank levels of He and Ne at every extraction temperatures are reasonably low but those of the other elements are comparable to those released from MMs: e.g., ⁴He = 5E-12, ²⁰Ne = 5E-13, ³⁶Ar = 1E-12, ⁸⁴Kr = 1E-14, ¹³²Xe = 3E-15 cm³ STP for the 1800 °C blank run.

Samples studied are two chondrule-like MMs, one fine-grained MM, and three coarse-grained MMs, and are 30-60 micrometers in diameter. Isotopic ratios of He and Ne are indicative of solar wind (SW) origin, while elemental ratios of ⁴He/²⁰Ne are <90, lower than SW value (~650 [2]). Release profiles of SW noble gases are different among MMs: two out of seven begin to release noble gases at 400 °C, three at 650 °C, and two at 1800 °C. This indicates that they were heated to varying degrees during atmospheric entry. Plotting ⁴He concentrations against ⁴He/²⁰Ne ratios, a positive correlation is observed in the MMs, as is the case with Itokawa particles [3], IDPs [4], unmelted MMs [5, 6], and cosmic spherules [7]. The largest amounts of He and Ne among the MMs studied were obtained from a fine-grained MM (D03IB67), which consists mainly of sub-micron olivine and low-Ca pyroxene grains. This MM releases noble gases at 400-1800 °C, indicating that this MM was not heated above 400 °C during atmosphere entry. The TEM observation revealed that this MM contains abundant solar flare track with ~5E10 /cm² density, which corresponds to >1E4-years exposure [8] to solar wind and flare. The presence of the flare track is consistent with the noble gas release temperature, since the track can be erased by flash heating above ~600 °C [9].

A chondrule-like MM (D03IB057) and a single olivine MM (D10IB170) contain only small amounts of He and Ne with the lowest ⁴He/²⁰Ne ratios (1.4 and 0.4, respectively). They release detectable amounts of noble gases only at 1800 °C. Both of the MMs show signs of higher degrees of heating: the uppermost surface layer of D03IB057 is partly melted, while that of D10IB170 is decomposed into magnetite and glass.

References: [1] Yabuta et al. (2012) LPSC XXXXIII (Abs. #2239). [2] Heber et al. (2009) GCA 73, 7414-7432. [3] Nagao et al. (2011) Science 333, 1128-1131. [4] Nier and Schlutter (1990) Meteoritics 25, 263-267. [5] Osawa and Nagao (2002) Antarct. Meteorite Res., 15, 165-177. [6] Osawa et al. (2003a) Meteorit. Planet. Sci. 38, 1627-1640. [7] Osawa et al. (2003) Antarct. Meteorite Res. 16, 196-219. [8] Bradley (2006) In: Meteorites, Comets, and Planets. [9] Fraundorf et al. (1982) GCA 45, 915-943.

Keywords: micrometeorites, noble gas, solar wind

Mineralogical study of phyllosilicate-rich unmelted micrometeorites recovered from "Cape Tottuki" in Antarctica

Ken Tazawa^{1*}, Tomoki Nakamura¹, Yuki Kimura¹

¹Department of Earth and Planetary Materials Science, Faculty of Science, Tohoku University

In the present study, seventy six particles recovered from ice at "Cape Tottuki" in Antarctica were identified as Antarctic micrometeorites (AMMs) by SEM/EDS chemical analysis. Among them, twenty eight relatively less heated AMMs were analyzed by synchrotron X-ray diffraction (S-XRD) using Gandlfi camera, which reveals bulk mineralogy of individual AMMs. Based on the results of S-XRD, we have selected four primitive AMMs. They were embedded in resin and were sliced to be ultrathin sections by ultra microtomy. The ultrathin sections were analyzed by 200-KeV FE-TEM equipped with EDS, which is able to determine nano-scale mineralogy. Rest of the particles, which remained in the resin, were polished and analyzed by EPMA/WDS, which is able to determine the local and bulk chemical composition. We accomplished this multistage detailed analysis, and revealed the mineralogy and the physicochemical properties of each small cosmic dust particle.

The results of the multistage analysis indicated that KTP2H6 is a member of Tagish Lake type micrometeorites, which are believed to come from D-type asteroids in the outer main asteroid belt. HTP2H6 consists mainly of fine-grained saponite and magnetite. The survival of hydrous mineral saponite indicates that the particle almost escaped deceleration heating when it entered the Earth's atmosphere, because saponite is decomposed at 700 degrees Celsius during the brief heating. AMMs had been stayed deeper in the blue ice field in Antarctica for about 30 thousand years, however, the crystal structure was well preserved. Thus, KTP2H6 preserve material characteristics of D-type asteroids.

KTP3I6 was also identified as Tagish Lake type micrometeorites, but it was slightly heated in the atmosphere. Although its phyllosilicate and carbonate phases were decomposed to amorphous phase and magnesiowustite, respectively, we could know the type of phyllosilicate from chemical composition. Si-rich compositions of phyllosilicates indicate that saponite is a major phyllosilicate before decomposition in the atmosphere. Magnesiowustite showed very Fe-rich composition, indicating that the particle had had Fe-rich carbonate. Fe/Mg ratios of the carbonates in KTP3I6 are the highest among carbonates found in Tagish lake meteorite and Tagish Lake-type micrometeorites. This means that the particle is identified as D-type asteroids material, but its formation process is different from the Tagish Lake meteorite. Therefore, we propose KTP3I6 is one of the varieties of D-type asteroids property. In addition, two anhydrous AMMs were also investigated in detail, however, they were highly decomposed during the atmospheric entry and also altered in the Antarctic ice layer.

Keywords: micrometeorites, Tagish Lake meteorite, D-type asteroids, carbonaceous chondrites

The search for Antarctic meteorites in the Nansen Ice Field by the joint team of JAPAN and BELARE

Naoya Imae^{1*}, Yukihiisa Akada¹, Christophe Berclaz⁵, Philippe Claeys³, Vinciane Debaille⁴, Steven Goderis³, Genevieve Hublet⁴, Hideyasu Kojima¹, Takashi Mikouchi², Nadia Van Roosbroek⁴, Wendy Debouge⁴, Akira Yamaguchi¹, Harry Zekollari³

¹National Institute of Polar Research, ²University of Tokyo, ³Vrije Universiteit Brussel, Belgium, ⁴Universite Libre de Bruxelles, Belgium, ⁵BELARE

So far, the meteorite search on the Nansen Ice Field spreading at the south of the Sor Rondane Mountains has been carried out only by the 29th Japanese Antarctic Research Expedition (JARE-29) and Belgian Antarctic Research (BELARE) 2010-2011. We carried out the meteorite search here by the joint team of JARE-54 summer members and BELARE2012-2013, consisting of ten members, that is, four (including one field assistant, FA) from JARE and six (including one FA) from BELARE. As a result, we collected about 420 Asuka meteorites with about 76 kg in total weight.

The total period was ~66 days, from the beginning of December 2012 to the middle of February 2013. The staying period in the Nansen Ice Field was 39 days, from the end of December 2012 to the beginning of February 2013. We used Dronning Maud Land Air Network (DROMLAN). Entering in Novo from Cape Town by Ilyushin D5 flight (5 Dec., 2012), in PE station from Novo by Basler Turbo (9 Dec., 2012). Leaving PE station to Novo by Basler Turbo (8 Feb., 2013) and Novo to Cape Town by Ilyushin D10 flight (8 Feb., 2013).

We accessed to the Nansen Ice Field from the Princess Elisabeth (PE) Station using ten snowmobiles (Ski-doo). The searched area was focused on the south-west part of the Nansen Ice Field for the first half period from the beginning until the middle of January, where we stayed at Base Camp 1 (BC1) located on 72 52 19.6 S and 24 20 28.0 E, 2909 m in elevation, and then the north-east part of the Nansen Ice Field for the latter half period since the middle of January, where we stayed at BC2 located on 72 42 04.3 S and 24 46 40.3 E, 2841 m in elevation. The camp system consists of two module containers for JARE and three containers for BELARE (among two BELARE containers are connected in line). The transportation of Japanese modules, BELARE containers, and a fuel sledge was carried out by the support from the PE station.

We formed the V-shaped system by ten snowmobiles for the method of the meteorite search, where a FA was at the top with the average moving speed of normally less than ~10 km/h. Mobile-typed small GPSs were used for the navigation of the planned route, for the recording of trajectories of the searched area, and for the positioning of found meteorites. This will be useful for the clarification of the meteorite distribution on the field. Although just after the moving camp from BC1 to BC2, we experienced the bad weather of the half period including the long-period bad weather of the continuing 12 days, the collected number of meteorites and the total weights were both larger than expected. Most meteorites appear to be ordinary chondrites, but carbonaceous chondrites and the largest meteorite of 18 kg at the present meteorite search are included among them. Possible achondrites such as eucrites and diogenites are also recognized. The detailed studies for classification and curation will be carried out in the laboratory at NIPR. In near future we are planning a detailed meteorite search of the south-east part where we could not carry out due to the restricted periods.

Acknowledgments: We are so grateful to the logistic support from the PE station, especially to the base head Mr. Alain Hubert.

Keywords: meteorite search, Asuka meteorites, JARE-54, BELARE2012-2013

Development of isotope analysis of fluid inclusions by secondary ion mass spectrometry I

Atsuko Ishibashi^{1*}, Naoya Sakamoto², Hisayoshi Yurimoto³

¹Natural history Sci., Hokudai, ²CRIS, Hokudai, ³Natural history Sci., Hokudai

Fluids play important role for element migration and circulation on the surface and interior of planets, and often control geological phenomena. The fluid caused geological phenomenon was indirectly assumed from the record of rock formed at the time. On the other hand, fluid inclusions trapped in minerals give the direct information of the fluid. Moreover, individual analysis for each fluid inclusion can reveal fluid evolution during a series of geological action because spatial position of fluid inclusions in the mineral corresponds to course of geological time. Especially, isotope analysis provides useful information for the origin of fluid.

In traditional mass spectrometry, analysis of fluid inclusions was conducted by extraction procedure method. The candidate for application of this method was limited because this method can measure fluid inclusions with a size of 1mm or larger. The fluid inclusions in rock have often several micrometers to several dozen micrometers in size. Therefore, development of mass spectrometry applicable to such minute fluid inclusions is important. In-situ analysis of fluid inclusions is expected to make significant progress for the study of evolution of fluid. Secondary ion mass spectrometry (SIMS) is an analysis method having such spatial resolution. However, SIMS can not analyze fluid because the sample should be exposed in high vacuum. In this study, we developed a sample preparation method in order to analyze fluid inclusions by SIMS.

The requirements for stable analysis of SIMS are (1) flat and smooth mirror surface, (2) fluid inclusions are exposed to polished surface, (3) conductive sample surface.

In order to satisfy (1) and (2), we developed freezing polishing instrument to polish the sample keeping fluid inclusions in a frozen state. The instrument has a lapping table including liquid nitrogen bath. The temperature of the table during polishing is controlled at -100 degree by automatic temperature controller. It takes approximately 14 minutes to cool the lapping table from room temperature to -100 degree. Freeze and dry polish of fluid inclusions is realized with alumina polish sheet on the lapping table.

In order to prevent condensation of water vapor in the atmosphere on the polished surface and make conductive surface (condition (3)), the polishing instrument and an ion coater (SANYU SC-701AT) are put in a glove box with nitrogen atmosphere. The sample stage of ion coater usable in cooling state satisfy condition (3) by making gold thin film on the polished surface keeping the temperature of sample below -100 degree during gold coating. A reflection microscope having a cold stage to observe surface condition is also put in the glove box. We are currently developing a simple observation method to check the exposed surface of frozen fluid inclusions.

Keywords: fluid inclusions, secondary ion mass spectrometry, freezing polish, isotope

Petrography, H₂O contents and hydrogen isotopic composition of phosphate minerals from LL5-6 ordinary chondrites

Kaori Yanai^{1*}, Shoichi Itoh¹, Hisayoshi Yurimoto¹, James Greenwood², Sara Russell³

¹Department of Natural History Sciences, Hokkaido University, ²Wesleian University, ³Natural History Museum, London

Ordinary chondrites of petrologic types 4 to 6 exhibit a sequence of progressive chemical and textural equilibration, and contain Cl-rich apatite grains (e.g., Jones et al., 2011).

Previous study reported that the water contents of chlorapatite are very low (<100ppm), even though apatite grains in ordinary chondrites seem to have a significant H₂O contents based on a deficit of anions (Jones et al., 2011). As results, they suggest that apatite grains were formed with a dry and halogen-bearing fluid that has been derived by degassing of chondritic melts.

In the preliminary study, we reported the petrography, H₂O contents and hydrogen isotopic compositions in chlorapatite from Mocs L5-6 and Ensisheim LL6 ordinary chondrites using secondary ion mass spectrometry (SIMS). The H₂O contents of apatite grains in Ensisheim (LL6) and Mocs (L5-6) are estimated to be ~60 ppm and ~35 ppm, respectively. These H₂O contents are similar to the previous reported values from LL chondrites (Jones et al., 2011). The hydrogen isotopic compositions of apatite grains from Ensisheim are extremely D-rich (dD= ~ +17000 permil). Remarkably, we found the reaction texture between apatite grain and olivine grain from Ensisheim LL6 chondrite, which reported that of texture from St. Severine LL6 chondrite (Jones et al., 2011). However, the origin of extremely D enrichment of those of Ensisheim LL6 is unclear whether this is resulting from LL6 general characteristics of thermal process of parent body or from unique results of late reaction by fluids only for Ensisheim LL6 chondrite, because of limited study of preliminary examination.

In this study, we will report the petrography of phosphate minerals with other thin sections, LL5-6 (Ensisheim LL6 and Tuxtuac LL5) to compare it with those of Ensisheim LL6 chondrite. Thin section (Tuxtuac) loaned from Natural History Museum, London (NHM) were used in this study. Phosphate grains were identified using elemental X-ray mapping using scanning electron microscope (FE-SEM JEOL JSM 7000-F) and energy dispersive X-ray spectrometry (EDS Oxford INCA Energy) at Hokkaido University.

Phosphate minerals (merrillite and apatite) from Tuxtuac show the reaction texture at the boundary of olivine and phosphate minerals. However, the chemical compositions (P, Cl and Ca) of olivine grain are homogeneously distributed using 5kV, even if those of distribution are enriched in the rim of olivine grain with 15kV X-ray mapping. This suggests that the reaction texture with BSE image might be resulting from the effect of edge crystal. On the other hand, the Cl-zonation in the reaction texture between olivine and apatite from Ensisheim LL6 chondrite with D-enrichment signature are identified with 5KV X-ray mapping.

In the future, we will further examine the petrography of phosphate minerals from other LL4-6 chondrites has already been loaned thin sections from NHM and compare with the petrography, hydrogen isotopic compositions of phosphate minerals to give an constraint for the origin of D-enrichment of phosphate minerals in the Ensisheim LL6 chondrite.

Keywords: apatite, Hydrogen isotope, LL ordinary chondrite, phosphate mineral

Oxygen isotopic composition of the solar nebula gas inferred from high-precision isotope imaging of melilite crystals

Changkun Park¹, Shigeyuki Wakaki¹, Naoya Sakamoto^{1*}, Sachio Kobayashi¹, Hisayoshi Yurimoto¹

¹Hokkaido University

High-precision isotope imaging analyses of reversely zoned melilite crystals in the gehlenitic mantle of Type A CAI ON01 of the Allende carbonaceous chondrite reveal that there are four types of oxygen isotopic distributions within melilite single crystals: (1) uniform depletion of ¹⁶O ($\delta^{18}\text{O} = -10$ permil), (2) uniform enrichment of ¹⁶O ($\delta^{18}\text{O} = -40$ permil), (3) variations in isotopic composition from ¹⁶O-poor core to ¹⁶O-rich rim ($\delta^{18}\text{O} = -10$ permil to -30 permil, -20 permil to -45 permil, and -10 permil to -35 permil) with decreasing akermanite content, and (4) ¹⁶O-poor composition ($\delta^{18}\text{O} > -10$ permil) along the crystal rim. Hibonite, spinel, and perovskite grains are ¹⁶O-rich ($\delta^{18}\text{O} = -45$ permil), and adjoin ¹⁶O-poor melilites. Gas-solid or gas-melt isotope exchange in the nebula is inconsistent with both the distinct oxygen isotopic compositions among the minerals and the reverse zoning of melilite. Fluid-rock interaction on the parent body resulted in ¹⁶O-poor compositions of limited areas near holes, cracks, or secondary phases, such as anorthite or grossular. We conclude that reversely zoned melilites mostly preserve the primary oxygen isotopic composition of either ¹⁶O-enriched or ¹⁶O-depleted gas from which they were condensed. The correlation between oxygen isotopic composition and akermanite content may indicate that oxygen isotopes of the solar nebula gas changed from ¹⁶O-poor to ¹⁶O-rich during melilite crystal growth. We suggest that the radial excursions of the inner edge of the protoplanetary disk gas simultaneously resulted in both the reverse zoning and oxygen isotopic variation of melilite, due to mixing of ¹⁶O-poor disk gas and ¹⁶O-rich coronal gas. Gas condensates aggregated to form the gehlenite mantle of the Type A CAI ON01.

Keywords: Chondrite, Melilite, CAI, SIMS, Oxygen isotope imaging, Solar nebula gas

Relationship between oxygen isotope zoning and crystal growth in melilite crystals from fluffy type A CAI

Juri Katayama¹, Shoichi Itoh^{1*}, Hisayoshi Yurimoto¹

¹Department of Natural History Sciences, Hokkaido University

The oxygen isotopic microdistributions within melilite measured using in situ secondary ion mass spectrometry correspond to the chemical zoning profiles in single melilite crystals of a fluffy Type A Ca-Al-rich inclusion (CAI) of reduced CV3 Vigarano meteorite. The melilite crystals show chemical reverse zoning within an individual single-crystal from the akermanite-rich core to the akermanite-poor rim. The composition changes continuously with the crystal growth. The zoning structures suggest that the melilite grew in a hot nebular gas by condensation with decreasing pressure. The oxygen isotopic composition of melilite also changes continuously from ¹⁶O-poor to ¹⁶O-rich with the crystal growth. These observations suggest that the melilite condensation proceeded with change consistent with an astrophysical setting around the inner edge of a protoplanetary disk where both ¹⁶O-rich solar coronal gas and ¹⁶O-poor dense protoplanetary disk gas could coexist. Fluffy Type A CAIs could have been formed around the inner edge of the protoplanetary disk surrounding the early sun.

Keywords: FTA, SIMS, oxygen isotope, CAI

Beryllium-beryllium measurement of a melilite-rich calcium-aluminium-rich inclusions in the NWA5958 CM chondrite

Masakuni Yamanobe^{1*}, Tomoki Nakamura¹, Yuki Kakazu², Hatsumi Ishida¹

¹Faculty of Tohoku University, ²CSNSM Univ. Paris Sud-CNRS/IN2P3

CAIs (Ca, Al-rich Inclusions) are the oldest object in the solar system. In CAIs, there are evidence of now-extinct isotopes like ²⁶Al and ¹⁰Be. They have a short-half-life (<100Ma) and because of short-half-life, they are expected to indicate an accurate relative age. In order to estimate a relative age using now-extinct isotopes, it is required that they were homogeneously distributed in the solar nebula. In terms of ²⁶Al, it has been almost already proven that they were homogeneously distributed in the solar nebula, while ¹⁰Be has not proven yet. ²⁶Al decays by electron capture to ²⁶Mg with a half-life of 0.71Ma. ¹⁰Be *B*-decays to ¹⁰B with a half-life of 1.5Ma. In terms of Al-Mg chronology, it is difficult to detect excess of ²⁶Mg in CAIs which experienced late-stage alteration (e.g reheating in the nebula or asteroids), because the Mg diffusion in anorthite where Al-Mg measurements were made is fast. The B diffusion, however, in melilite where Be-B measurements were made is slow. Therefore, it is suggested that Be-B chronology is effective way to measure a relative age of CAIs which experienced late-stage alteration. Hence, it is significant to confirm that ¹⁰B was distributed in solar nebula homogeneously or heterogeneously.

In this study, we have carried out Be-B measurements in one CAI (Type-A CAI) from CM chondrite NWA5958. This CAI consists mainly of a large melilite crystal and small spinel and perovskite are contained as inclusions in the melilite. Our SIMS measurements at Tohoku University showed that this CAI has ¹⁰B excesses in melilite. The initial ¹⁰Be/⁹Be ratio inferred 4.6×10^{-2} . This ratio is much higher than those obtained in other CAIs from CV chondrites (e.g. 9.5×10^{-4} ; MacPherson et al. 2003, 7.2×10^{-4} ; Sugiura et al. 2001). We have also analyzed rare earth elements (REEs) abundance and oxygen isotopes ratios of this CAI. Melilite shows nearly flat (unfractionated) CI-normalized REEs pattern with anomalies in Eu and ¹⁶O-rich composition, whereas melilites in CV chondrites usually have ¹⁶O-poor composition (e. g. Clayton et al. 1977). REE pattern indicates that the large melilite in this CAI formed from a melt, thus the CAI experienced melting by reheating in the nebula. ¹⁶O-rich oxygen isotope ratios suggest that this CAI stayed nearer the Sun, while CAIs in CV chondrite stayed away from the Sun because of ¹⁶O-poor composition of melilite. Our result implies that the nebula gas near the Sun contained much more ¹⁰Be than the gas far from the Sun. This suggests that ¹⁰B was distributed in solar nebula heterogeneously and Be-B system can't measure a relative age.

Keywords: Be-B system, CAI, melilite

Internal structure of chondrules from Allende CV3 chondrite

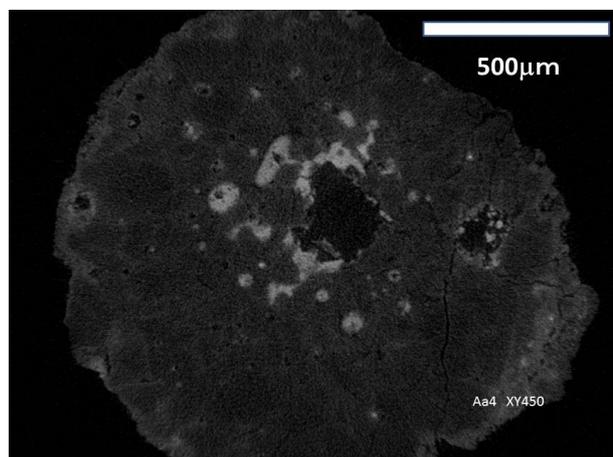
Eiichi Takahashi^{1*}, Ayaka Tsuda¹, Keisuke Nishida¹, Osamu Sasaki², Yasuhiro YANAGIDA³, Satoshi Okumura³, Michihiko Nakamura³, Taishi Nakamoto¹

¹Magma Factory, Earth and Planetary Sciences, Tokyo Institute of Technology, ²Museum of Natural History, Tohoku University, ³Department of Earth Science, Tohoku University

In order to clarify 3D shapes and internal structure of chondrules in Allende CV3 chondrite, we have separated 180 chondrules grains and investigated them with X-ray CT apparatuses (Scan Xmate-D180RSS270, Scan Xmate-D160TSS105/11000) recently installed at the Museum of Natural History, Tohoku University. We also developed an optical device to measure 3D shape of chondrules or other spherical objects (Nishida et al. JPGU 2013). Our results revealed that chondrules shapes show wide distribution consisting of true spheres, prolate-spheres (rugby-ball shape) and oblate-spheres (pancake shape) (Tsuda et al. JPGU 2013). Chondrules with porphyritic textures distribute in all three shape categories. Chondrules with granular texture (lower melting degree than porphyritic) also show nearly homogeneous distribution. Chondrules with barred olivine texture (quenched from super-heated melt) show a distribution between true sphere and oblate-shape. Implication of the 3D shapes and internal texture of chondrules will be discussed from the shock-wave heating model (e.g., Miura et al., 2008).

Melting textures of Fe-FeS and silicates were observed by high-resolution X-ray CT (Scan Xmate-D160TSS105/11000). Coagulation processes of molten Fe-FeS melt in chondrules were observed. An example of cross section of a porphyritic chondrule is shown in Fig. 1, which shows "the smallest core formation process" in the early solar system. Our observation shows that 1) there are group of "chondrules" which have undergone melting of Fe-FeS only (peak temperature:1000-1200 degreeC), 2) coagulation and separation process of Fe-FeS and silicate takes place during short heating duration, 3) degassing of sulfur would be the main source of bubbles.

Keywords: Allende, Chondrule, internal texture, metal-silicate separation



Formation mechanism of fine-grained rims surrounding chondrules, CAIs and forsterite aggregates in Tagish Lake

Akiko Takayama^{1*}, TOMEOKA, Kazushige¹

¹Graduate school of Science, Kobe University

Introduction: Tagish Lake carbonaceous chondrite consists of two major lithologies: carbonate-rich and carbonate-poor [1]. Most chondrules and coarse-grained aggregates in Tagish Lake are surrounded by fine-grained rims [1]. The origin of fine-grained chondrule rims has been controversial [e.g. 2-7]. Nakamura et al. [6] suggested that the rims in the carbonate-rich lithology were formed during brecciation on the parent body (or bodies). In contrast, by studying the carbonate-poor lithology, Greshake et al. [7] concluded that formation of the rims by dust accretion in the solar nebula most convincingly accounts for their observations. Here we present the results of our mineralogical and petrological study of fine-grained rims surrounding chondrules and coarse-grained aggregates in the carbonate-poor lithology of Tagish Lake.

Results and Discussion: We found 87 chondrules, 14 forsterite aggregates, and two CAIs in the two thin sections (~114 microns²). These coarse-grained components are embedded in the dominant matrix (84.1 vol.%) consisting mainly of phyllosilicates with minor amounts of Fe-Mg carbonate, magnetite, forsteritic olivine, Ca carbonate, and Fe-(Ni) sulfides. Most chondrules consist of irregularly shaped cores composed of forsterite and enstatite and phyllosilicate-rich outer zones (POZs) (5-100 microns in thickness). Also, characteristic round pseudomorphs of opaque nodules that consist largely of phyllosilicates were commonly found in both core and the POZs. The observation suggests that the POZs are altered zones which were formed by replacing the peripheries of chondrules.

96 % of the chondrules are surrounded by fine-grained rims which are significantly less porous than the matrix. The volume abundances of the minerals in the rims are significantly different from those of the matrix (e.g. Ca carbonate is totally absent). Most rims contain characteristic fractures that run radially from the core/altered zone boundaries, penetrate both altered zones and rims, and terminate at the rim/matrix boundaries. All of the CAIs and forsterite aggregates are also surrounded by fine-grained rims which are identical to those of the chondrules in texture, mineralogy and chemical compositions.

We found 55 clasts that consist of materials texturally and mineralogically identical to the fine-grained rims surrounding the coarse-grained components. We also found a large clast that contains three chondrules and three forsterite aggregates. The chondrules in this clast also have altered zones. The matrix of the clast exhibits fractures that run radially from the surfaces of the chondrules and forsterite aggregates and interconnect them. They always terminate at the clast/matrix boundary.

These observations suggest that the chondrules, CAIs, forsterite aggregates, and their rims and the clasts originated from a common precursor region in the meteorite parent body that was different from the location where the host meteorite was finally lithified. That is, the rims are remnants of matrix material of the precursor region. This model is essentially consistent with those previously proposed for the carbonate-rich lithology of Tagish Lake [6] and the hydrated clasts in the Vigarano and Mokoia CV3 chondrites [4, 8].

References:

[1] Zolensky et al. (2002) MAPS 37, 737-761. [2] Metzler et al. (1992) GCA 56, 2873-2897. [3] Sears et al. (1993) Meteoritics 28, 669-675. [4] Tomeoka and Tanimura (2000) GCA 64, 1971-1988. [5] Trigo-Rodriguez et al. (2006) GCA 70, 1271-1290. [6] Nakamura et al. (2003) EPSL 207, 83-101. [7] Greshake et al. (2005) MAPS 40, 1413-1431. [8] Tomeoka and Ohnishi (2010) GCA 74, 4438-4453.

Keywords: Tagish Lake carbonaceous chondrite, Chondrule rims, Aqueous alteration, Brecciation

Petrography of fine-grained rim surrounding chondrule in the Acfer331 CM2 chondrite

Jun Asakawa^{1*}, Shoichi Itoh², Hisayoshi Yurimoto²

¹Department of Natural History Sciences, Hokkaido University, ²Department of Natural History Sciences, Hokkaido University

Introduction

Chondrules in chondrites are commonly surrounded by fine-grained rim (FGR). It is widely believed that the rims were formed by accretion of dust in the solar nebula (Metzler et al. 1992) or in the parent body (Tomeoka and Tanimura, 2000). Because of changing in textures and chemical compositions by the physical processes in the parent body, such as aqueous alteration, in order to estimate the origin of FGR, it is important to estimate the changes of petrography for the FGR corresponding to the degree of aqueous alteration. In this study, we try to estimate the effect of aqueous alteration process to study about the petrography and chemical compositions of matrix and FGRs in the area for the different degree of aqueous alteration in the Acfer331 CM2 chondrite.

Analytical methods

The samples in this study were used in thin sections of Acfer331 CM2 chondrite. Since the major minerals in the matrix of Acfer331 chondrite are clay minerals consists of hydrous minerals, by polishing operation to make thin section using water, the expansion, deformation and fracture of matrix were occurred to destroy the original texture (Oohashi et al., 2008). Therefore, we made thin sections with and without water to estimate whether the original texture was destroyed or not. In order to estimate the original texture of matrix, cutting fragment of Acfer 331 CM2 chondrite with diamond blade are also compared with those of thin sections. As results, the petrography of matrix in a thin section with water indicates to be selectively destroyed a part of FeO-rich phyllosilicates and resulting from many voids in the matrix area relative to that of thin section without water and cutting fragments. A thin section without water were adopted. Petrographic observation, X-ray elemental mapping of thin sample (12 x 14 mm), and bulk quantitative analysis of the 30 x 30 micrometer were performed by FE-SEM-EDS system (JEOL JSM-7000F + Oxford INCA Energy) at Hokkaido University.

Results and Discussion

The major minerals in FGR and matrix consist of fine-grained phyllosilicates. From X-ray mapping of whole thin sections, there are different chemical distribution for vein of MgO-rich and CaSO₄ 2H₂O in the matrix. Previous study suggests that different MgO chemical compositions of matrix are corresponding to the degree of aqueous alteration (Howard et al., 2009). Using the distribution of MgO-rich and CaSO₄ 2H₂O, two different regions are divided. And the comparison of petrography of FGRs is corresponding to these two regions.

Region (1) are without vein of CaSO₄ 2H₂O and MgO-poor. FGRs in region (1) show layered structure with inner and outer rim. In the Fe?Si+Al?Mg ternary diagram, the quantitative analyses areas in the inner rim are plotted at MgO-rich area relative to that of outer rim and matrix surrounding FGR, which are plotted the same area.

Region (2) are with vein of CaSO₄ 2H₂O and MgO-rich. FGR in region (2) shows no layered structure with inner and outer rim. In the Fe?Si+Al?Mg ternary diagram, the FGR and matrix show the similar range of chemical compositions plotted for the total variation of FGR and matrix from region (1).

The degree of aqueous alteration from matrix at region (2) seems to be higher than that of region (1) because of MgO-rich and CaSO₄ 2H₂O vein. In addition, the inner rim of FGR from region (1) shows the MgO-rich variation compared with that of matrix surrounding FGR, but FGR from region (2) shows no obvious layered structure and no different chemical variation relative to that of matrix surrounding FGR. As results, this suggests that FGR from region (2) is subject to the aqueous alteration with mm-scale in the parent body.

Keywords: aqueous alteration, fine-grained rim, carbonaceous chondrite, matrix

Hydrothermal alteration experiments of amorphous silicates in the system of MgO-SiO₂ with different Mg/Si ratios

Ryohei Takahashi^{1*}, Akira Tsuchiyama¹, Junya Matsuno¹, Yusuke Seto²

¹Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University, ²Graduate School of Science, Kobe University

Meteorites have information on evolution process of materials in the early solar system. Carbonaceous chondrites are the most primitive meteorite class. Most of them, particularly CI, CM, CR chondrites, contain layer silicates, such as serpentine and saponite and have experienced aqueous alteration in their parent bodies. In order to understand evolution process of the early solar system, it is important to understand aqueous alteration process. Experimental studies to understand aqueous alteration have been performed so far. For example, aqueous alteration experiments using enstatite crystals were carried out, and conditions for serpentine and saponite formation were discussed [1]. On the other hand, it has been accepted that amorphous silicates are original building bricks of solid materials in the solar system, and thus it is important to understand aqueous alteration process of amorphous silicates.

Aqueous alteration experiments of an amorphous silicate with Fe, Ni and S free CI chondritic composition were performed [2]. In the experiments, serpentine and saponite formed easily from the amorphous silicate with pure water. However, some of layer silicates formation was not been well understood.

In the present study, aqueous alteration experiments of amorphous silicates were performed in the simple system MgO-SiO₂-H₂O to understand process of layer silicate formation. We focused serpentine (Mg₃Si₂O₅(OH)₄) and examine effect of the Mg/Si ratio of the starting material to formation of serpentine (Mg/Si=1.5).

The starting materials are nano particles of amorphous silicates (~10 nm in diameter), which were synthesized by induction thermal plasma method. Five types of starting materials with different Mg/Si ratios (1.15, 1.25, 1.50, 1.75, 2.02) were prepared. They were sealed in a Teflon vessel with pure water (water/rock ratio: 5.0) and heated at 150°C for 8, 24, 72, 168, 504 hours (pressure: 3.0 bar). Run products were examined by X-ray diffraction (XRD) for mineral identification. Some of run products were observed by field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM) and the chemical compositions were obtained by EDX equipped in FE-SEM and TEM.

Layer silicates formed in all run products. Brucite (Mg(OH)₂) and magnesite (MgCO₃) formed in runs with the Mg/Si ratio of more than 1.5 (carbon in magnesite was probably from Teflon). Basal reflections of the layer silicates are broad. Generally, with increasing the Mg/Si ratio, the layer spacing continuously decreases, and the peak intensity increases. In runs with Mg/Si=2.02, the layer spacing decreases with increasing time. Layer silicate in 504 hr run has the layer spacing mostly close to that of serpentine, and serpentine did not easily form from the amorphous silicate with Mg/Si=1.5.

FE-SEM observation showed that run products are composed of aggregates more than a few μm in size, and signature of the original 10 nm particles disappeared. The Mg/Si ratio of run products are always less than that of the starting material. These results indicate that Mg in the starting material selectively dissolved into water, and layer silicates and brucite (and magnesite) formed from the aqueous solution.

The relation between the Mg/Si ratios of run products with the layer spacing suggest that layer silicates might be randomly interstratified mineral with serpentine and stevensite (a kind of smectite with the talc composition). In TEM observation, layer structure seemed to be observed, but more detailed observation is required for further study to confirm the layer silicate structures.

[1] Ohnishi and Tomeoka (2007) Meteoritics & Planetary Science, 42, 49-61. [2] Noguchi (2010) JpGU Meeting, PPS009-10.

Keywords: aqueous alteration process, carbonaceous chondrite

Experimental study on serpentine and smectite formation on chondrite

Ayaka Utsuki¹, Yusuke Seto¹, Kazushige Tomeoka^{1*}, Daisuke Hamane²

¹Kobe Univ., Sci., ²Univ. Tokyo, ISSP

Aqueous alteration is one of the significant processes that occurred widely in the early solar system. Indeed, several groups of carbonaceous chondrites contain abundant hydrous phyllosilicates, most of which formed by aqueous alteration of anhydrous silicates such as olivine. Mineral species of the phyllosilicates is known to be unique for groups of carbonaceous chondrite; CM and CO groups contain serpentine, while CV contains mainly smectite. In CI and CR groups, both serpentine and smectite are found. These differences should be reflected from chemical conditions on their parent body, and yet are still unknown. In the present study, we conducted the hydrothermal alteration experiments using olivines (Fo100, 80, 50, 20, 0) with various pH solutions (pH 0, 7, 10, 14) as starting materials. They were sealed into gold capsules, loaded into a test-tube-type hydrothermal apparatus, and heated at 300°C under 500 bar. Run durations are 1 week and 1 month. All recovered products were analyzed by powder X-ray diffraction (XRD), scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS) and transmission electron microscope (TEM). As the results, serpentine was formed in various proportions by replacing Mg-rich olivine (Fo100, 80, 50) irrespective of pH conditions. On the other hand, smectite was formed replacing Fe-rich olivine (Fo20, 0) under alkaline condition (pH 14). Under the present conditions, we did not observe paragenesis of both serpentine and smectite, which might occur replacing Fo20~50 under alkaline conditions. EDS analyses showed that molar ratio of Fe/(Fe+Mg) in those phyllosilicates is significantly lower than that of olivine used as starting material. These results are basically consistent with previous studies [Ohnishi and Tomeoka (2007), MAPS; Zolensky et al. (1989), Icarus] where it has been suggested that aqueous alteration in the parent bodies occurred under high pH condition. The present study would provide more constraints on the aqueous-alteration conditions of the meteorites.

Keywords: carbonaceous chondrite, aqueous alteration, hydrothermal experiments, serpentine, smectite

Investigation of iron-nanoparticles in Martian meteorite olivine using electron microscopy

Atsushi Takenouchi^{1*}, Toshihiro Kogure¹, Sayako Inoue¹, Takashi Mikouchi¹

¹Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo

1. Introduction

Olivine crystals in Martian meteorites are often dark-brown colored because they were heavily altered probably by a shock event to escape the planet. It is suggested that this change results from iron metal and magnetite nanoparticles segregated in olivine [1-3]. Mikouchi et al. [4] performed shock experiments and proposed that either iron metal or magnetite by the temperature difference during the shock event. However, the relation between the morphologies of them and shock condition is still unclear. The purpose of this study is to obtain new insights into the formation of the iron nanoparticles, through a detailed investigation of Northwest Africa 1950 shergottite which potentially includes both iron metal and magnetite nanoparticles, using advanced electron microscopic techniques.

2. Sample and Experimental methods

NWA1950 is a Iherzolitic shergottite and its dominant phases are olivine (~55wt%), pyroxenes (~35wt%) and maskelynite (~8wt%) [5].

Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were mainly used for the observation. In the SEM observation, identification of the crystallographic orientation using electron back-scatter diffraction (EBSD) was performed. The mineral species of nanoparticles observed in crushed olivine fragments and thin film specimens prepared by a focused ion beam (FIB) instrument were identified by nano-beam electron diffraction (NBED) and the measurement of lattice spacing in high-resolution TEM images. In the STEM observation, Z contrast images and composition images were acquired by the high-angle annular dark-field (HAADF) detector and STEM-EDS, respectively.

3. Results

During the observation of the crushed olivine fragments using TEM, relatively large (more than 100 nm) iron metal particles were frequently found, as well as spherical iron metal nanoparticles of a few tens of nanometers reported in the previous works. In addition, iron metal nanoparticles surrounded with magnetite-shell were discovered, although they were very rare. According to these findings, the distribution of such large iron particles was investigated by SEM. As a result, platy domains of olivine with a more iron content than the surrounding olivine matrix and Fe-abundant bright particles arranged inside the plates were observed. EBSD analysis in SEM revealed that these platy domains are parallel to several fundamental lattice planes.

Thin film specimens were prepared by FIB to investigate these domains and bright particles in detail. According to TEM/STEM observations, the bright particles observed in SEM-BSE images have a film-like form of a few tens of nanometers thick, obliquely formed in the platy olivine domains (Fig. 1). They were confirmed as iron metals by using NBED. Furthermore, very thin, thread-like iron metal particles as well as the fine spherical particles were found only outside the domains in the Z contrast images by HAADF-STEM (Fig. 1). Silica-abundant area was not found around metal iron by the composition STEM image either.

4. Conclusions

In this study, various forms of iron metal particles and their characteristic distribution in the parent olivine crystals were found by the combined observation using SEM, TEM and STEM. Moreover, an interesting structure, iron particles surrounded with magnetite-shells, was also discovered. These findings combined with further observation and analysis may be able to be applied to better understand remote sensing results and elucidation of temperature-pressure history by strong shock metamorphism.

References

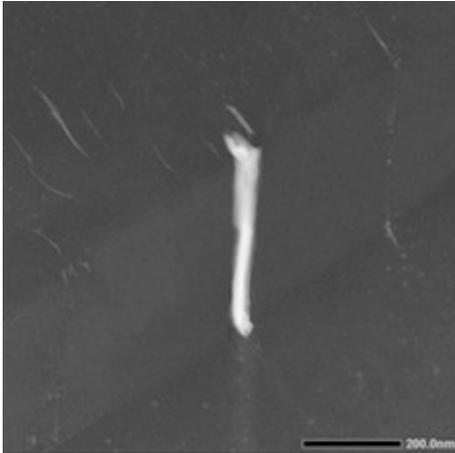
[1] Treiman A. et al., 2007, *J. Geophys. Res.* 112, E04002, doi:10.1029/2006JE002777.2007. [2] Van de Moortele B. et al., 2007, *Earth Planet. Sci. Lett.* 262, 37-49. [3] Kurihara T. et al., 2009, 40th LPSC, #1049. [4] Mikouchi T. et al., 2011, *Jour. for Japanese Soc. Planet. Sci.*, 20, 61-68 (in Japanese). [5] Mikouchi T., 2005, *Meteorit. Planet. Sci.*, 40, 1621-1634.

Keywords: Martian meteorites, olivine, electron microscope, shock, nanoparticle

PPS24-P16

Room:Convention Hall

Time:May 23 18:15-19:30



Nondestructive identification of a single primitive-grain using the translational motion induced by field gradient

Keiji Hisayoshi^{1*}, Keisei Sawano¹, Kento Kuwada¹, Chiaki Uyeda¹

¹Institute of Earth and Space Science, Graduate School of Science, Osaka University

Primitive chondrites are aggregates of small particles composed of different materials, and their origins are considered to be heterogeneous. It is desirable to identify the materials of individual grain before performing refined micro-probe analysis on isotopic, chemical or optical properties. The above method of identification should be non-destructive and easily performed. Moreover the method should be based on an established principle. We previously reported that a translation caused by field gradient force is induced on diamagnetic solid in common, in a condition that effect of gravity and viscous drag are negligible. A material possesses intrinsic diamagnetic susceptibility per unit mass. Therefore it is possible to identify the material of the translating particle by comparing the observed susceptibility with a list of published values. According to a Newton's equation of motional equation considered for a field gradient force, acceleration of particle was expected to be independent to mass of the particle; it is uniquely determined by the intrinsic susceptibility of material in a given field distribution. Accordingly, detection of susceptibility is possible for limitlessly small samples, and so as material identification.

It is noted that most of the particles that compose the chondrites are paramagnetic or ferro- (ferri-)magnetic materials; their size range from mm to sub-micron in diameter. In the present study field-induced ejections were newly observed for particles of diamagnetic, paramagnetic and ferri-magnetic materials; namely graphite, diamond, pyroxene and magnetite. Sample size was reduced to a level below 100 microns for the diamagnetic samples.

The field-induced motion is observable by the chamber-type drop box; the system was realized by introducing small Nd-Fe-B plates as a field generator. Using the above-mentioned box, material identification of a single grain that composes primitive materials becomes possible by a routine process that can be performed in an ordinary laboratory. The setup for observing the magnetic motion was attached inside a rectangular volume of 35x30x20 cm of a drop box. The setup was enclosed in a vacuum chamber; the sample motion was observable from the outside of the Pyrex wall of the chamber, using a high-vision video camera that had time resolutions of 0.033 s. Its spatial resolution was 0.004 cm. The pressure of the medium inside the chamber was P ? 100 Pa. Duration of microgravity inside the box was about 0.5 s, with residual gravity of 0.01G. .

Compared to the conventional methods to measure magnetic susceptibility in terrestrial gravity, the proposed principle based on the magnetic translation is free of a back ground signal of a sample holder; it is does not require a mass measurement of the sample. Hence susceptibility is obtainable for samples with a limitlessly small size, provided that translation of sample is detected. The lower limit of sample size may reach several microns by introducing an optical microscope in the compact drop box.

Keywords: magnetic ejection, nondestructive identification, microgravity, translational motion, magnetization measurement, body force

A Cleaning Method for Extraterrestrial Sample Holder

Yukihiro Ishibashi^{1*}, Yuzuru Karouji¹, Toru Yada², Masayuki Uesugi¹, Shogo Yakame³, Akio Fujimura², Tatsuaki Okada², Masanao Abe²

¹Lunar and Planetary Program Group, JAXA, ²Inst. of Space and Astronautical Sci., JAXA, ³Grad. School of Sci., Univ. of Tokyo

The Hayabusa spacecraft captured particles at the surface of a near-Earth asteroid (25143)Itokawa [1]. The samples were stored in the reentry capsule of Hayabusa, and successfully brought to the Planetary Material Sample Curation Facility (PMSCF) of JAXA in 2010 [2,3,4]. They were extracted from the capsule and have been preserved in PMSCF[3,4]. Typical size of the sample is less than 100 micron, so handling of them is performed with a micro-manipulation system in the clean chamber filled with purified nitrogen [4]. Picked up samples are identified by FESEM-EDS observation, then each of them is placed on the gridded quartz glass plate in the sample holder for preservation.

Contamination control of extraterrestrial samples is essential matter, and it is important to handle and preserve samples without terrestrial contamination and alteration as possible. We hereby report the cleaning of quartz glass plates which contacts with samples directly.

The cleaning processes are performed in the clean room of PMSCF. A series of ultra sonic cleanings is a typical procedure for all materials such as metals and glasses. The first step of ultra sonic cleaning is to remove mainly organic impurities. Its solvent is typically 2-propanol. The cleaning in the solvent is repeated more than twice with 40 kHz frequency band for 20min, changing the solvent each time. The next step is to remove particles and ions. Its solvent is ultrapure water, overflowing from the ultrasonic bath to keep providing fresh water. The frequencies for the cleaning are 40, 100, and 1000 kHz bands. The cleaning is repeated twice at each frequency for 20 to 30 min. After the series of ultrasonic cleanings, water on the cleaned parts are removed by the purified nitrogen gas blow or air in clean booth.

For quartz glass, an additional acid and alkali treatment is performed after the series of ultra sonic cleanings. They are washed by heated alkali and acid solutions to remove organics, ions, and particles again. The washing method is a batch cleaning, and its procedure is our modified RCA method, originally for washing semiconductor wafer. The alkali and acid solutions are used twice respectively with ultrapure water rinse. After the cleaning and drying, the quartz glass plates is assembled to the cleaned holder or case with a cover, and stored in a desiccator filled with purified nitrogen.

The cleanness of washed quartz glass plate was evaluated with 4 methods. After our previous study [5], the detection limit was improved for metals and ions, and the analysis method was changed for organics.

1. Contaminant metals remained on the plate were extracted with 3 ml of HCl (0.35%) with H₂O₂ (0.3%), then 32 elements (B, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Ni, Co, Cu, Zn, Ga, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Ba, La, Hf, Ta, W, Pt, Au, and Pb) were examined with inductively coupled plasma mass spectrometry. They were 1x10⁷ to 1x10¹⁴ atoms/cm² on the plate. Some contaminated elements are detected, but the amount of most of the elements does not affect the scientific analysis such as ion-probe measurement.

2. Contaminant ions were extracted with 60 ml of purified water, then 8 of ions (F⁻, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, SO₄²⁻, PO₄³⁻ and NH₄⁺), lactic acid, acetic acid, formic acid and a few amines are examined with ion chromatography. They were less than 1x10⁻⁹ g/cm² on the plate.

3. Organics released by thermal desorption from the surface of the plate was collected to Tenax^(R) adsorbent resin. The collected organics are measured with gas chromatography mass spectrometer. Total amount of the organic carbon was less than 1x10⁻⁸ g/cm² on the plate.

4. Contaminant particles, larger than a few micron, were not observed by microscopes.

References

[1] Fujiwara, A. *et al.* (2006) *Science* **312**, 1330. [2] Abe, M. *et al.* (2011) *LPS* **42**, #1638. [3] Fujimura, A. *et al.* (2011) *LPS* **42**, #1829. [4] Yada, T. *et al.* (2012) *MAPS* in press. [5] Ishibashi, Y. *et al.* (2012) *LPS* **43**, #2887.

Keywords: extraterrestrial sample, contamination control, cleaning, Hayabusa, Itokawa