

## MINERALOGY OF STARDUST COMETARY GRAIN T112: SIMILARITY TO AMOEBOID OLIVINE AGGREGATES.

KOMATSU, Mutsumi<sup>1\*</sup>, MIKOUCHI, Takashi<sup>2</sup>, FAGAN, Timothy<sup>1</sup>, ZOLENSKY, Michael<sup>3</sup>

<sup>1</sup>Waseda University, <sup>2</sup>Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo, <sup>3</sup>NASA Johnson Space Center

### Introduction:

The successful analysis of comet 81P/Wild 2 particles returned by the Stardust mission has revealed that the Wild 2 dust contains abundant silicate grains that are much larger than interstellar grains and appear to have formed in the inner regions of the solar nebula [1]. Wild 2 particles include minerals which are isotopically and mineralogically similar to CAIs [e.g., 2], chondrules [e.g., 3], and amoeboid olivine aggregates (AOAs) [e.g., 4] in chondrites. In this study, we have examined the mineralogy of the Track 112 particle and compared the possible relationships between T112 and AOAs.

### Results and Discussion:

Our two TEM grids from T112 are dominated by 4 micron -sized forsteritic olivine. Submicron sized chromite is associated with the olivine. The olivine from T112 is near end-member forsterite, but shows a slight enrichment of Fe toward the grain rim. In the least metamorphosed chondrites, most AOAs consist of forsterite. Enrichment of olivine in fayalite component is correlated with petrologic subtype of a host meteorite [5]. In CV chondrites, Fe-enrichment is distinct in Allende (petrologic type >3.6). The Fe enrichment on the rim of T112 olivine may have been caused by a minor degree of thermal processing after the condensation of forsterite.

From EDS analyses, the chromite grains have high Cr<sub>2</sub>O<sub>3</sub> content (up to 65 wt. %), and yield Al-absent compositions with intermediate Mg# ; however, it is likely that some Mg detected by EDS is from neighboring olivine and that the grains are closer to pure chromite in composition. Chromite is a minor phase in Wild 2 particles. Cr-rich spinels have been identified in the chondrule-like particle Torajiro [3] and associated with Coki-B Kool fragments (T141 [6]); however, these spinels have significant Al<sub>2</sub>O<sub>3</sub>.

Three possibilities for the formation of chromite can be considered: (i) direct condensation from a gas; (ii) crystallization from chondrule melt; (iii) metamorphism/aqueous alteration. (i) Modeling by [7] predicts that Cr-rich spinel crystallizes in mixed vapor + silicate liquid + refractory solid reactions at high temperatures in dust enriched systems, but always with significant Al<sub>2</sub>O<sub>3</sub>. (ii) This modeling [7] also shows that chromite is stable with silicate liquid at high dust enrichment, but textures of T112 particle do not appear to be typical of chondrules. Furthermore, the 16O-rich composition of olivine in the potted butt sample from (T112) is more consistent with AOAs than chondrules. (iii) Tiny Cr-rich grains surrounding olivine in type 3 ordinary chondrites were identified by [8] as products of incipient metamorphism. The T112 chromite might have a similar origin.

The forsteritic, 16O-rich composition of T112 olivine suggests a condensation origin. Slight enrichment in Fa-content along the olivine rim suggests some metamorphism. At this point, we consider metamorphism the most likely origin of T112 chromite.

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Keywords: meteorites, carbonaceous chondrites, cometary dust

## Oxygen isotopic distribution of Fluffy Type A CAI from Efremovka

KAWASAKI, Noriyuki<sup>1\*</sup>, SAKAMOTO, Naoya<sup>2</sup>, YURIMOTO, Hisayoshi<sup>3</sup>

<sup>1</sup>Natural History Sci., Hokudai, <sup>2</sup>CRIS, Hokudai, <sup>3</sup>Natural History Sci., Hokudai

A formation process of planetesimals from dust grains is most uncertain part in the planetary formation theory. The dust grains in the micron-to-centimeter size range are preserved in chondrite. Especially, "fluffy" shaped Type A Ca-Al-rich inclusions (FTA CAIs) are aggregates of domains that contain micron-sized grains thought to be condensed from the nebular gas. In the CAI-forming region, distinct <sup>16</sup>O-rich and <sup>16</sup>O-poor gaseous reservoirs are considered to be co-existed (Yurimoto et al. 2008). In this paper, we study petrology and oxygen isotopic distribution of a FTA CAI from Efremovka CV3 chondrite in order to reveal the growth process and the environment of the grain size evolution.

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).

The CAI is 1 cm x 4 mm in size with "fluffy" shape and surrounded by the Wark-Lovering rim (WL rim). The CAI is divided into two domains that named as domain-1 and domain-2. The WL rim surrounds each domain.

In the domain-1, melilite crystals near the WL rim show reverse zoning and are observed as a layer of ~40 micron in width. The reverse zoning is typically ak30 in the center and ak15 at the grain boundary. Melilite crystals inside of the layer show oscillatory zoning, initially started as reverse zoning and changed to normal zoning. The compositions are ak35 in the center, ak30 at intermediate, and ak40 at the grain boundary. The oxygen isotopic compositions of the melilite crystals in the domain-1 are distributed homogeneously,  $\delta^{18}\text{O} = 5\text{-}10$  permil. In the domain-2, melilite crystals positioned shallower than ~150 micron in depth from the WL rim show reverse zoning that are typically ak15 in the center and ak5 at the grain boundary. The oxygen isotopic compositions of these crystals are distributed along CCAM line ranging between  $\delta^{18}\text{O} = -40$  and 0 permil and change from <sup>16</sup>O-rich to <sup>16</sup>O-poor with the distance from WL rim.

Reversely zoned melilite crystals in FTA CAIs are readily explained by the condensation from a solar nebular gas with falling pressure (MacPherson and Grossman 1984). The reversely zoned melilite crystals in the domain-1 and the domain-2 were also condensed from the nebular gas with decreasing pressure. The oscillatory zoned melilite crystals may be the result of overgrowth of normal zoning on the grain boundary of partially molten reversely zoned melilite crystals. The homogeneous oxygen isotopic composition in the domain-1 indicates melilite crystals were formed in a <sup>16</sup>O-poor nebular gas. On the other hand, the oxygen isotopic distributions observed in the domain-2 suggests that the gas was changed from <sup>16</sup>O-poor to <sup>16</sup>O-rich during the condensation of melilite.

Typical compositions of the reversely zoned melilite crystals in the domain-1 and the domain-2 are ak30-15 and ak15-5. They formed below the eutectic temperature of melilite and fassaite. According to Yoneda and Grossman (1995), these crystals condensed below 1570 K and lower pressure than  $10^{-2}$  atm. If the temperature is constant, the pressure of the gas surrounding the reversely zoned melilite crystals in the domain-2 is about 1.5-2 times lower than that of domain-1. For example if the temperature is 1400 K, the pressure was changed from  $3.2 \times 10^{-4}$  atm to  $2.2 \times 10^{-4}$  atm for domain-1, and from  $2.2 \times 10^{-4}$  atm to  $9.7 \times 10^{-5}$  atm for domain-2. However these conditions seem to be occurred continuously, the oxygen isotopic compositions of the melilite grains in each domain indicate that they were formed in the different nebular environment and incorporated into the FTA CAI.

In this study, we revealed that the micron-sized dust grains that were condensed from gas experienced different nebular environment during the accumulation to millimeter-sized domains. These domains were accreted together to form the centimeter-sized FTA CAI.

Keywords: Fluffy Type A CAI, melilite, chemical zoning, dust coagulation, oxygen isotopes, solar nebula

## Oxygen isotopic distribution of a porous Type A CAI from Ningqiang chondrite

HAMADA, Leina<sup>1\*</sup>, SAKAMOTO, Naoya<sup>2</sup>, YURIMOTO, Hisayoshi<sup>3</sup>

<sup>1</sup>Natural History Sci., Hokudai, <sup>2</sup>CRIS, Hokudai, <sup>3</sup>Natural History Sci., Hokudai

Ca-Al-rich Inclusions (CAIs) have been reported oldest age in the solar system and large mass-independent fractionation for oxygen isotopic compositions. Fine grained CAIs, which are thought to be condensed from gas, often contain micron-sized voids (Lin and Kimura, 2003; Wasson et al., 2000). However, coarse-grained compact CAIs are usually unporous. We found a porous CAI having many micron-sized voids from Ningqiang C3-ungrouped chondrite. We studied petrology and oxygen isotopic distribution of the CAI in order to reveal the formation process of micron-sized voids.

Petrographic observation and chemical analysis were performed by FESEM-EDS (JEOL JSM-7000F + Oxford INCA Energy). Crystal orientation analysis was performed by EBSD (HKL Cannel 5). Oxygen isotopic composition was analyzed by SIMS (CAMECA, ims-1270).

A coarse grained CAI analyzed in this study has about 2x2 mm in size with rounded shape but with irregular portion in part. The CAI is mainly composed of melilite, diopside, spinel and perovskite. The CAI has a porous structure with voids occupying nearly 30% in volume. The CAI is rimmed by Wark-Lovering rim composed of melilite, spinel, anorthite and diopside layers. The CAI is classified into type A CAI with high perovskite abundance by the bulk composition and mineralogy.

Two types of void are observed in the CAI. We categorized small void and large void by their size and shapes. The small voids are three micrometers or smaller in size. The voids distributed in regions near the Wark-Lovering rim and in 50-100 micron sized regions consist of 5 micron sized melilite crystals with few micron sized perovskite crystals. Melilite crystals in the regions show reverse zoning, i.e., Mg-rich interior and Al-rich rim. The oxygen isotopic compositions of the melilite varies from  $\delta^{18}\text{O} = -40$  permil to  $\delta^{18}\text{O} = 0$  permil. Reversely zoned melilites in type A CAIs are believed to be condensed from gas (MacPherson and Grossman, 1984). Therefore, it is suggested that melilite in the regions did not experience melting, and small void was formed during the process of condensation and accumulation of melilite and perovskite.

The large voids have roundish irregular shape and distributed inside of 300 micron sized melilite crystals. In a single crystal of melilite crystals void-rich areas are gehlenitic (ak2-5) and void-free areas are akermanitic (ak15-24). Oxygen isotopic compositions of the melilite crystals at the void-rich areas were  $\delta^{18}\text{O} = -5$  permil and the void-free areas were  $\delta^{18}\text{O} = -20 \sim -10$  permil. Nepheline was sometimes observed at the area with voids. The mineral layer of diopside and anorthite exists at walls of some voids. Fine grained porous CAIs in Ningqiang are thought to be formed by an aqueous alteration on its parent body (Sugita et al., 2009). If the large voids in the CAI were formed by the aqueous alteration, it is required that voids were preferentially formed at gehlenitic area or that melilite compositions became gehlenitic during the void formation. We will study the relation between chemical zoning and crystals growth of melilite in order to clarify formation processes of the large voids in this CAI.

Keywords: void, CAI, oxygen isotopic composition, Ningqiang, melilite

## Rapid cooling of chondrule to reproduce olivine bars observed in barred olivine chondrules

MIURA, Hitoshi<sup>1\*</sup>, TSUKAMOTO, Katsuo<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Materials Science, Tohoku University

Chondrules are millimeter-sized and spherical-shaped crystalline grains consisting mainly of silicate material. Since chondrules occupy about 80 vol.% of chondritic meteorites in abundant cases, they must have great information about the early history of our solar system. They are considered to have formed from molten droplets about 4.6 billion years ago in the solar nebula; it is believed that they melted and cooled again to get solidified in a short period of time. They have various solidification textures that record the solidification process. Barred olivine (BO) chondrules show a unique texture characterized by parallel set(s) of olivine bars in a thin section. BO chondrule usually has an olivine crystal, which is termed as rim, which covers the chondrule surface. This olivine rim has the same crystallographic orientation as inner olivine bars, which connect to the rim. It is considered that the crystallographically continuous structure was formed by morphologic instability during olivine growth, like dendritic crystals. However, initial process of the morphologic instability that produces the olivine bars has not been investigated in details.

We investigated the initial process of formation of BO texture based on numerical simulation of solidification of chondrule melt. The thermodynamically consistent phase-field model for a binary alloy based on the entropy functional is adopted here. We adopted  $Mg_2SiO_4$ - $Fe_2SiO_4$  binary system in which only olivine is considered as a solid phase. We carried out a numerical simulation of a molten olivine droplet solidifying from a platy seed crystal at droplet surface. Under an extremely rapid cooling condition, in which the cooling rate is 5000 K/s, the platy seed crystal overgrew keeping its flat interface at the beginning of solidification, and then changed to cell-like pattern due to morphological instability. The initial stage before the instability can be considered as the formation of olivine rim, and the cell-like pattern as that of olivine bars. In this case, the average width of bars is about 5 micrometer in numerical result, which is comparable to that observed in natural BO chondrules ranging from 5 to 100 micrometer. If we consider that the bar width is proportional to a root of the cooling rate, the required cooling rate to reproduce 100 micrometer thickness is evaluated as  $12.5 \text{ K/s} = 45000 \text{ K/hr}$ , which is much faster than the canonical value of 1000 K/hr inferred from traditional experiments. We also found that the rim and olivine bars showed zoning profile in  $Fe/(Mg+Fe)$  value, which was similar to that of laboratory-synthesized BO chondrules.

Our numerical simulation of solidification of chondrule melt suggested that the cooling rate should be much faster than that inferred from traditional experiments to produce olivine bars of 5 ? 100 micrometer in width such as observed in natural BO chondrules.

Keywords: chondrule, solidification texture, crystal growth, zoning profile

## Artificial micrometeorites from powdered Allende meteorite

GONDO, Takaaki<sup>1\*</sup>, ISOBE, Hiroshi<sup>1</sup>

<sup>1</sup>Grad. Sch. Sci. Tech., Kumamoto Univ.

Micrometeorites (MMs) are extraterrestrial dust particles that have been captured by the Earth and are thought to be derived from asteroids and comets. Depending on their velocity, mass and entry angle, MMs have undergone various degrees of heating during their deceleration in the atmospheric entry within a few seconds. This heating may lead to significant textural, mineralogical and chemical modifications in MMs.

In this study, we carried out immediate heating and quenching experiments on fine particles to represent for atmospheric entry of MMs. The experimental system is reported by Isobe and Gondo (2012). We used powdered Allende meteorite (typical CV3 chondrite) with approximately 100 micron meters in diameter as the starting material.

The run products show analogues textures to MMs including scoriaceous, porphyritic olivine and dendritic magnetite. Fe sulfide occurs on melted particle surfaces. Immiscibility between sulfide melt and silicate melt may induce sulfide melt discharge from silicate melt. The surface distribution of iron sulfide in MMs has not been reported. Sulfide on MMs may be removed by abrasion in the upper atmosphere. This process may be constant source of sulfur species other than volcanic activity to the upper atmosphere. Maximum temperature and thermal history of particles were estimated from compositions of melt and minerals. Analogy of the run products to MMs are discussed on textural, mineralogical and chemical modifications during atmospheric entry.

Keywords: micrometeorite, heating / quenching experiment, Allende meteorite, atmospheric entry

## Correlations between D and $^{15}\text{N}$ -rich organic matters in a carbonaceous chondrite

HASHIGUCHI, Minako<sup>1</sup>, Kobayashi Sachio<sup>2</sup>, YURIMOTO, Hisayoshi<sup>1\*</sup>

<sup>1</sup>Natural History Sci., Hokkaido Univ., <sup>2</sup>CRIS, Hokkaido Univ.

Carbonaceous chondrites contain organic matters that are enriched in D and/or  $^{15}\text{N}$  [1-2]. The D and/or  $^{15}\text{N}$ -rich organic matters are believed to have formed in molecular cloud or outer protoplanetary disk in early solar system [1-2], however, relationship between the D and  $^{15}\text{N}$  enrichment is unclear. Previous study suggests that there are good correlation between D-rich and  $^{15}\text{N}$ -rich region in organic matters of carbonaceous chondrite [1], but other studies suggest that the D and  $^{15}\text{N}$  enrichment are not correlated [2].

In this study, we tried to analyze D and  $^{15}\text{N}$ -rich organic matters in carbonaceous chondrite by in-situ analysis. We determined spatial distribution of D and  $^{15}\text{N}$  enrichments of organic matters in NWA 801 CR2 chondrite by isotope imaging. Our previous study reported that the NWA 801 contains many D-rich organic matters [4]. The isotope imaging was performed using isotope microscope of Hokkaido university (Cameca ims-1270 + SCAPS [5]). The sample surface was homogeneously irradiated over a field area with a broad  $\text{Cs}^+$  primary beam of  $\sim 50$  micron in diameter. Secondary ion images of  $\text{H}^-$ ,  $\text{D}^-$ ,  $^{12}\text{C}^-$ ,  $^{12}\text{C}^{14}\text{N}^-$  and  $^{12}\text{C}^{15}\text{N}^-$  were obtained from a field. We obtained  $^{12}\text{C}^-$  images before and after the analysis for a field to check whether carbonaceous matter was disappeared during the isotope analysis. Total integration time for a field was  $\sim 10$  minutes. After the isotope analysis, morphological observations of isotopically anomalous materials were performed by FE-SEM-EDS (JEOL JSM-7000F, Oxford INCA Energy).

Seven D-rich materials and six  $^{15}\text{N}$ -rich materials were found in NWA 801 matrix of approximately  $0.2 \text{ mm}^2$ .  $^{12}\text{C}$  were detected from the five D-rich materials and six  $^{15}\text{N}$ -rich materials during measurements. The continuously D and  $^{15}\text{N}$  enrichments were observed from different spots. Hydrogen isotopic compositions of the D-rich carbonaceous matters are 2,300-7,900 permil in delta-D. Nitrogen isotopic compositions of the  $^{15}\text{N}$ -rich carbonaceous matters are 1,100-1,200 permil in delta- $^{15}\text{N}$ . The morphologies of D-rich or  $^{15}\text{N}$ -rich carbonaceous matters are determined by FE-SEM analysis. The D-rich and  $^{15}\text{N}$  rich matters have similar morphology, which are round or irregular shaped carbonaceous globules, or aggregate of some carbonaceous globules.

The carbonaceous matters with D or  $^{15}\text{N}$  enrichment might be organic matters that have formed in molecular cloud and/or outer protoplanetary disk in early solar system. Large D-rich and  $^{15}\text{N}$  enrichment believed to have occurred in extremely cold region [6, 7]. The D or  $^{15}\text{N}$  enrichments signatures suggest that they have survived through alteration on parent body of NWA 801. The lack of correlation between D and  $^{15}\text{N}$  anomalies may be due to different origin for D and  $^{15}\text{N}$ -rich carriers.

Other than these carbonaceous matters, two D-rich materials have not detected for  $^{12}\text{C}$  peak in isotopography. Possibility of the carbonaceous matters for the D-rich materials are ruled out, because carbon was not detected in  $^{12}\text{C}^-$  images obtained before and after the measurement. N related peaks were not detected at the D-rich spots. Hydrogen isotopic compositions of these D-rich materials are 3,400 and 3,800 permil. Si, O, Mg, Fe and Al were detected from these D-rich materials by the X-ray analysis. The results suggest that the D-rich materials are silicates and plausibly phyllosilicate because previous study revealed that phyllosilicates in Rennazo CR2 chondrite were enriched in deuterium [7].

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Keywords: D and  $^{15}\text{N}$ -rich organic matters, Carbonaceous chondrite, Correlation of D and  $^{15}\text{N}$  enrichment, Isotope imaging

## The observation of shock textures in fragments of Kilabo, LL6 ordinary chondrites

YAKAME, Shogo<sup>1\*</sup>, UESUGI, Masayuki<sup>2</sup>, KAROUJI, Yuzuru<sup>2</sup>, ISHIBASHI, Yukihiro<sup>2</sup>, YADA, Toru<sup>2</sup>, OKADA, Tatsuaki<sup>2</sup>, ABE, Masanao<sup>2</sup>, FUJIMURA, Akio<sup>2</sup>

<sup>1</sup>University of Tokyo Department of Science, <sup>2</sup>JAXA

The Hayabusa space-craft reached S-type asteroid 25143 Itokawa in 2005 [1]. As a result of observations of telescope and a series of remote sensing researches, it is estimated that Itokawa has compositions similar to L or LL5 to 6 ordinary chondrites [2,3,4]. Then Hayabusa could have retrieved samples of Itokawa back to the Earth from the asteroid surface called MUSES-Sea Regio in 2010. Initial analyses showed that those samples collected by Hayabusa correspond to LL4 to 6 ordinary chondrites because analyses data of mineralogy, chemical compositions and oxygen isotopic ratios are consistent with LL4 to 6 chondrites [5,6,7,8,9,10].

The size of Itokawa samples analyzed by initial analysis is mainly as small as a few tens of micrometers. Sample size has problems because it is difficult for us to understand which processes and which parts of host rocks did micrometer sized samples come from on the surface of Itokawa. Therefore it is also difficult to extend their mineralogy and textures to those of larger scale.

On the other hand, many meteorites fallen to the Earth have been analyzed although their parent bodies are unknown other than the Moon and the Mars. But analyses of meteorites have not focused on micrometer sized samples so far. To study micrometer sized samples of meteorites in detail is important for extending their tiny samples to understanding of larger scale information about Itokawa samples. Furthermore, we may get new knowledge about meteorites from analyses of micrometer samples.

In this study, using the LL6 ordinary chondrite named Kilabo, we focused on shock textures in micrometer sized grains of Kilabo. Shock textures are generally observed in ordinary chondrites and caused by impact on the surface of asteroid [11]. As a result of initial analyses, Itokawa is supposed to be accumulated fragments of bigger parent body crushed by impact [5] and shapes of returned samples are also seems to be affected by impact [9]. This study observed shock textures in micrometer and millimeter samples of meteorites and compared both of them.

The results of the comparison showed that planar fractures, which typically observed in olivine and feldspar as shock textures, were found in real micrometer samples at 54% while they are found in millimeter samples at only 39%. In contrast, few micrometer samples have a melt texture caused by impact while Kilabo was reported that it has many shock veins by previous study [12].

These results suggest that micrometer grains broken from bigger chondritic materials are selective in specific textures in host materials. It is possible that these specific textures are also present in surface materials of Itokawa and also affect to brecciations on asteroid surface. Therefore micrometer samples made by brecciations may not be reflected mineralogy and textures of host rock because some shock textures occur in specific minerals.

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Keywords: Meteorite, Hayabusa, Itokawa, Shock metamorphism, Ordinary Chondrite

## H<sub>2</sub>O contents and hydrogen isotopic composition of apatite crystals in L, LL5-6 ordinary chondrites

YANAI, Kaori<sup>1\*</sup>, ITOH, Shoichi<sup>1</sup>

<sup>1</sup>Natural History Sci., Hokudai

**Introduction:** Ordinary chondrites of petrologic types 4 to 6 exhibit a sequence of progressive chemical and textural equilibration. However, the conditions and environment of metamorphism are not well constrained. The role of fluids is poorly understood, although there is evidence that fluids were present (Li et al., 2000; Dunn et al., 2010; Jones et al., 2011). The secondary phosphate minerals apatite and merrillite can be used to interpret the conditions of the metamorphic environment, since they can potentially preserve a record of interactions with parent body fluids (Jones et al., 2011). In this study, we report the petrography, H<sub>2</sub>O contents and hydrogen isotopes in chlorapatite from L, LL5-6 ordinary chondrites using secondary ion mass spectrometry (SIMS).

**Analytical methods:** 10 thin sections of Carnegie (L6) and thick section (Barwell (L5), Mocs (L5-6), Carnegie (L6), Ensisheim(LL6)) mounted one inch with San carlos Olivine were used in this study. Apatite 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. Quantitative analyses were also performed using FE-SEM-EDS system.

The Hokudai isotope microscope system (Cameca ims-1270 SIMS instrument at Hokkaido University) was applied to determine D/H ratio and H<sub>2</sub>O contents of apatite. The meteorite and standard sample were kept pumping about two months in the ultra-high vacuum chamber in order to reduce the surface adsorbed water on the samples. The Dorang apatite (0.0478wt%) and Linopolis apatite (1.28wt%) were used to estimate the H<sub>2</sub>O content using the calibration curve with H/18O ratio. In the same analytical session, the H/18O ratio of San carlos olivine crystals were also measured to compare with those of chlorapatite from ordinary chondrites. The hydrogen isotopic compositions was calculated using Dorango apatite (dDSMOW =-121permil). The overall analytical errors were about 20permil (2sigma). The detail analytical conditions are shown in Greenwood et al. (2011).

### Results and Discussion:

H<sub>2</sub>O content of apatite grain can only be estimated in Ensisheim (LL6) by SIMS because it is difficult to avoid cracks or metamorphic phases. H<sub>2</sub>O contents of apatite are estimated to be 18-35ppm. These results are much smaller than those based on a deficit. This difference is consists with that of Jones et al. (2011). In addition, the H/18O ratio of apatite grain from Ensisheim is about five times higher than those of San carlos olivine. In the future, H<sub>2</sub>O content of the apatite in chondrites will be estimated using a lower water content of standard.

The hydrogen isotopic compositions of apatite grains in the LL6 Ensisheim chondrite are likely to be D-rich. However, it is difficult to estimate these values quantitatively because of low water content. In the future, we will develop to measure the hydrogen isotopic compositions of such a low water content in apatite grains.

**Keywords:** ordinary chondrite, apatite crystal, H<sub>2</sub>O, hydrogen isotopic composition, SIMS



## Water Content of the 4.56Ga D'Orbigny Parent Body Estimated from Phosphate

SUZUKI, Hiroko<sup>1\*</sup>, OTA, Yoshihiro<sup>2</sup>, SANO, Yuji<sup>2</sup>, IIZUKA, Tsuyoshi<sup>1</sup>, MIKOUCHI, Takashi<sup>1</sup>, OZAWA, Kazuhito<sup>1</sup>, NAGAHARA, Hiroko<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo, <sup>2</sup>Division of Ocean and Earth Systems, Atmosphere and Ocean Research Institute, University of Tokyo

Behavior of water in the formation of planets is essential to understand the origin of the terrestrial water (Albarede, 2009) and evolution of planets. We estimated the water content of the parent body of D'Orbigny meteorite, a ~4.56Ga angrite, as 0.001~0.006wt% combining the water content of phosphate and petrological and mineralogical information on melting and crystallization history of D'Orbigny. This study shows that a planetesimal contains a minor but an appreciable amount of water in the very early stage of the solar system evolution.

At first, we have estimated the timing of phosphate crystallization to estimate the water content of D'Orbigny parent body from phosphate, an accessory mineral. D'Orbigny consists chiefly of plagioclase, clinopyroxene and olivine with ophitic texture accompanying many spherical voids and druses (Kurat et al., 2001; Mittlefehldt et al., 2002). Phosphate is always found in interstices of the major constituent minerals, and Fe and Ca in olivine and Fe, Al and Ti in clinopyroxene are extremely enriched to almost Mg-free composition toward the interstices, and intergrowth of olivine and kirschsteinite is developed. The interior of the intergrowth is systematically occupied by skeletal phosphate, ulvospinel, troilite, and rounded voids. This microstructure indicates that the phosphate crystallized from a residual melt before formation of troilite and voids (vesicles) in the waning stage of crystallization.

We analyzed 3 coarse grains of phosphate with a NanoSIMS to determine the hydrogen concentration and hydrogen isotopic composition. The average water content and isotopic composition is obtained to be 0.03wt% and D/H=2.9x10<sup>-4</sup>, respectively. This D/H ratio is near the lower limit of D/H of comets and Martian meteorites (Canup and Righter et al., 2000). This implies that the water in the D'Orbigny parent body had a similar origin as that of comets and that the D'Orbigny parent body could be a planetesimal that accreted to form Mars.

The water content of the D'Orbigny parent body is estimated from that of phosphate on the basis of the following petrologic evaluation. At first, D'Orbigny is inferred to have been liquid magma solidified in a closed system but not a cumulate, which is supported by ophitic texture and continuous Fe-increase and Mg-decrease in olivine and clinopyroxene towards the interstices. Then, the crystallinity at the phosphate crystallization is calculated to be 98 vol.% from the volume of troilite and voids, which further implies that the water content of the D'Orbigny melt is 0.003~0.012wt% on the basis of the water partition coefficient between apatite and melt (McCubbin et al., 2011). On the other hand, the meteorite contains much larger spherical voids and druses, which suggest that the melt was vesiculated at the early stage of crystallization. Assuming that water is the most dominant gaseous component and that the vesicles maintained equilibrium with the melt, the water held in the vesicles is calculated to correspond to 0.0005~0.0038 wt% in the melt by using the ideal gas equation and the volume fraction of spherical voids and druses. The sum of the two estimates is the initial water content of the melt. The water content of the parent body (mantle) is further estimated to be 0.001~0.006 wt% on the assumption that the melting degree was high enough (30~40 %) to consume pyroxenes, because the REE pattern of D'Orbigny is unfractionated. The estimate is comparable to 2~13 % of the water content of the Earth (0.046 wt%), if the Earth's interior has an equivalent amount of water to the amount of the seawater (Hirschmann, 2006). This study shows a planetesimal, which accreted to form solid planets, contained a little amount of water in the very early stage of planet formation. Application of this approach to various types of meteorites may pave the way for better understanding of the water origin and transporation in the planetary formation process.

## Na-metasomatism in the Ningqiang carbonaceous chondrite : A TEM and SR-XRD study

MATSUMOTO, Megumi<sup>1\*</sup>, SETO, Yusuke<sup>1</sup>, MIYAKE, Akira<sup>2</sup>, TOMEOKA, Kazushige<sup>1</sup>, SUGITA, Mitsuhiro<sup>1</sup>

<sup>1</sup>Graduate School of Science, Kobe Univ., <sup>2</sup>Graduate School of Science, Kyoto Univ.

Ca-Al-rich inclusions (CAIs) and chondrules in carbonaceous chondrites are known to be an initial condensate from the early solar nebula at high temperatures. However, they often include various amounts of nepheline ( $[\text{Na,K}]\text{AlSiO}_4$ ), which condenses under relatively low temperatures. The nepheline in CAIs and chondrules is, therefore, widely believed to be a secondary mineral which have formed by replacing the primary condensate phases through the process called Na-metasomatism. Recent studies [1,2] showed that a degree of Na-metasomatism is correlated with the petrologic subtype, and thus suggested that the Na-metasomatism occurred on the meteorite parent bodies. In the case, matrix, the major part of meteorite parent bodies, could not have escaped the process. Nonetheless, previous studies did not refer to the Na-metasomatism in the matrix. The Ningqiang carbonaceous chondrite is known to be rich in bulk Na content compared to typical CV chondrites [3], and its CAIs include large amount of nepheline [4]. Here, we will report detailed mineralogical characteristics of the chondrules and the matrix in the Ningqiang chondrite concerning its signature of the Na-metasomatism. The sample used in this study is one polished thin section of the Ningqiang chondrite ( $\sim 560 \text{ mm}^2$  total area). They were examined with a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS), a transmission electron microscope (TEM) equipped with an EDS, and a synchrotron radiation X-ray diffraction (SR-XRD).

The SEM and TEM observations revealed that more than 90 percent of the chondrules (39/41) include nepheline by replacement of plagioclase in their mesostasis. Small amounts of sodalite have been also observed. In many chondrules, plagioclase has been completely replaced by nepheline and sodalite, suggesting that the degrees of Na-metasomatism of the chondrules are probably high. The SR-XRD and X-ray mapping analyses revealed that about 10 vol.% of the matrix is composed of nepheline and sodalite. The abundance of nepheline and sodalite in the matrix is so large as not to be seen in other chondrites. These minerals are distributed throughout the matrix as fine grains ( $< 10$  micron). The estimated value of bulk Na content ( $\sim 4 \text{ mg/g}$ ) from the matrix volume ( $\sim 40 \text{ vol.}\%$ ) and the nepheline/sodalite abundance is consistent with the previous study ( $\sim 3.76 \text{ mg/g}$ ) [3]. These mean that nepheline and sodalite are the major host minerals of Na content of the Ningqiang chondrite.

In the Ningqiang chondrite, the most of CAIs and chondrules, and matrix include abundant nepheline and sodalite. These results indicate that Na-metasomatism on the Ningqiang parent body has extensively and ubiquitously taken place. Na-metasomatism might be an ordinary process which has occurred on many meteorite parent bodies. Although the most of previous studies had found the evidence of Na-metasomatism in CAIs and chondrules, further studies that focus on matrix may also give a new clue to solve the process of Na-metasomatism.

References: [1] Kojima et al. (1995) *Meteoritics & Planetary Science* 30, 1139-1146. [2] Tomeoka and Itoh (2004) *Meteoritics & Planetary Science* 39, 1359-1373. [3] Rubin et al. (1988) *Meteoritics* 23, 13-23. [4] Sugita et al. (2009) *Journal of Mineralogical and*

Keywords: carbonaceous chondrite, Ningqiang, nepheline, Na-metasomatism, TEM, SR-XRD

## On the location of the Yamato 00 meteorites

IMAE, Naoya<sup>1\*</sup>, Naoyoshi Iwata<sup>2</sup>, Yasuyoshi Shimoda<sup>3</sup>

<sup>1</sup>National Institute of Polar Research, <sup>2</sup>Yamagata University, <sup>3</sup>Ariake Junior High School

Search for meteorites on the bare icefield around Yamato Mountains were carried out by Japanese Antarctic Research Expedition (JARE-41), Nov. 2000 -Jan 2001, and collected ~3500 meteorites with the total weight of ~200 kg. Many large and unique meteorites are included in the Yamato 00 collection, such as the largest nakhlite (Yamato 000593), a large iron meteorite (Yamato 000378), a large diogenite (Yamato 002875), lherzolithic shergottites (Yamato 000027, Yamato 000047, and Yamato 000097), and so on.

Recovery position of each Antarctic meteorite is one of the basic field data and indispensable for the study of the meteorite concentration mechanism in Antarctica. However, the study is not enough. Although Global Positioning System (GPS) is useful for the recording the location, the member on snowmobile recorded collected time. Locations were recently recovered based on the trajectory of GPS on board in a large snow vehicle used for navigation during the meteorite search. The recovered locations show that large insufficiently searched area in icefields is remained around the Yamato Mountains.

Keywords: Yamato 00 meteorites, search for meteorites, Antarctica, bare icefield, Japanese Antarctic Research Expedition, Yamato mountains

## Ultra-sensitive noble gas analysis system for return samples from the solar system

OKAZAKI, Ryuji<sup>1\*</sup>

<sup>1</sup>Kyushu University

Isotopic compositions of terrestrial and extraterrestrial materials are important to understand the formation and evolution of the solar system materials and bodies, since they are contributed by some processes such as radioactive decay, mass fractionation, and isotope exchange. Noble gases are most sensitive to such isotopic effects because of the extreme depletion in solid materials. In extraterrestrial materials, He and Ne are dominated by isotopes that originate from solar wind implantation, spallation/n-capture reactions, and radioactive decay ( $^{235}$ ,  $^{238}$ U and  $^{232}$ Th). Heavy noble gases, Ar, Kr, and Xe are mixtures of products from stellar nucleosynthesis (s-, r-, and p-processes), radioactive decay ( $^{40}$ K,  $^{128}$ ,  $^{130}$ Te,  $^{238}$ U,  $^{232}$ Th,  $^{244}$ Pu, and  $^{129}$ I), and spallation/n-capture reactions, in addition to primordial (planetary) gas. Hence, the noble gas isotopes reflect many processes and should be a useful tool for cosmochemistry and geochemistry.

Because of their low abundances in solid planetary materials, extremely high sensitivity is necessary for a noble-gas analyzer. In order to measure microgram- or sub-microgram samples returned by space explorations, I have been constructing a new ultra-sensitive mass spectrometry system at Kyushu Univ. The system is a combination of a conventional mass spectrometer that consists of a magnetic sector-type MS with a Neir-type ion source), and a resonance ionization mass spectrometer (RIMS) that consists of a resonance ionization ion source and a time-of-flight (TOF) MS.

The conventional MS is useful to measure all noble gases (He, Ne, Ar, Kr, and Xe) with a detection limit of around 5000 atoms. Helium and Ne in Antarctic micrometeorites (around 0.5 microgram in weight) have been measured using a small resistant furnace (called Pot-pie furnace). Return samples from asteroid and lunar regolith should contain amounts of solar-wind He and Ne of which isotopic ratios and concentrations would reflect the regolith history.

The RIMS is designed to measure extremely small amounts of Kr and Xe (>100 atoms), referring to RELAX (Refrigerator Enhanced Laser Analyzer for Xenon) developed by Dr. J. D. Gilmour and his colleagues. The RIMS at Kyushu Univ. is equipped with a dye laser system (TII Tokyo Instruments Inc.) that generates 3.5 mJ per pulse (8 nsec of pulse width) at 216 and 256 nm of wavelengths applied for ionization of Kr and Xe, respectively. The power densities of the UV lights are probably high enough to ionize Kr and Xe with almost unit probability when focused to be <0.01 cm in diameter in the ion source. Ionization efficiencies and ion transmissions will be investigated. The RIMS enables to apply many radiometric dating (such as I-Xe, Te-Xe, and Pu-Xe) and Kr-Kr dating that will be very interesting for samples experienced cosmic-ray exposure.

For gas extraction from samples, the analysis system is equipped with a pulse Nd:YAG laser in addition to the furnace (Pot-pie). The Nd:YAG laser produces 200 mJ per pulse (10 nsec) at 1064 nm. The focused beam has a diameter of 50 micrometer and will create the plasma plume. The plasma lights have wavelengths that depend on the chemical composition of fused area of the sample, and are measured using a LIBS (Laser-induced Breakdown Spectroscopy) system. Using the LIBS system, the fused mass can be calculated by measuring the major element abundances. Also, potassium contents will be determined for micro-area K-Ar dating.

The RIMS and LIBS systems are now under construction, and the progress will be reported.

Keywords: return sample, noble gas

## The JAMSTEC NanoSIMS 50L: Imaging mass spectrometry at the sub-micron scale for meteorite and biology samples

ITO, Motoo<sup>1\*</sup>

<sup>1</sup>Kochi Institute for Core Sample Research, JAMSTEC

On November 4, 2011 the Cameca NanoSIMS 50L ion microprobe was delivered to Kochi Institute for Core Sample Research. The NanoSIMS is *the-state-of-the-art* instrument for microanalysis by a secondary ion mass spectrometry. The strong ability is to analyze extremely small *regions-of-interest* (achieving lateral resolutions down to 50 nm and small sputtering depth) while keeping very high sensitivity at high mass resolution. This derives from the new coaxial optical design of the primary ion sources and secondary ion extraction system, and from a new design of the magnetic sector mass analyzer. The capability of simultaneously measurement up to 7 masses, achieving more precise isotopic ratios from the same small volume, or better ion image superimposition in a imaging mode. This allows the comparison of images of the distribution of different measured isotopes or elements. This ability for imaging with sub-micro meter spatial resolution is very unique to the NanoSIMS and provides a new approach to the analysis of the isotope and/or element distributions in variety of samples. Faraday cups are also installed into the NanoSIMS, enabling to achieve the precision and external reproducibility of isotopic measurements down to the sub-permil level. Therefore, the JAMSTEC NanoSIMS will be the centerpiece of the ion imaging and geomicrobiology laboratories at the Kochi Institute for Core Sample Research and will be used to investigate extraterrestrial, terrestrial and biology samples (e.g., meteorites, oceanic crusts, deep life) explored by a scientific ocean drilling and sample-return missions from extraterrestrial locations opportunities.

The NanoSIMS instrument is in a clean room with class 10,000. Temperature (+- 0.3°C around a magnet) and humidity level (+-2% in the room) are well controlled. Currently the specifications of beam size (Cs+: ~30 nm, O-: 180 nm) and beam stability in 10 min (Cs+: 0.2 %, O-: 0.7 %) were achieved. We have done with Si and O isotopic measurements using electron multipliers and Faradays cups for Si wafer and quartz, respectively (Table 1).

Some initial results for O and Mg isotopes in meteorites and terrestrial mineral standards, and isotope images of microbiology sample will be shown at the meeting.

Acknowledgements: Funding for the JAMSTEC NanoSIMS ion imaging laboratory was provided by the Leading-edge Research Infrastructure Program of the Ministry of Education, Culture, Sports, Science and Technology and Japan Society for the Promotion Science.

Keywords: NanoSIMS, Ion imaging, sub-micron spatial resolution

Table 1. Reproducibilities of Si and O isotopic measurements.

EMs		16 points (within 1 inch sample)	10 points (5 sample locations)	FCs		10 points (within 1 inch sample)	10 points (5 samples locations)
<sup>29</sup> Si/ <sup>28</sup> Si	Si wafer	+ - 0.7 permil	+ - 0.9 permil	<sup>29</sup> Si/ <sup>28</sup> Si	Si wafer	+ - 0.07 permil	+ - 0.13 permil
<sup>30</sup> Si/ <sup>28</sup> Si	Si wafer	+ - 0.7 permil	+ - 1.1 permil	<sup>30</sup> Si/ <sup>28</sup> Si	Si wafer	+ - 0.17 permil	+ - 0.26 permil
				<sup>18</sup> O/ <sup>16</sup> O	Quartz	+ - 0.6 permil	+ - 0.5 permil

## Ion microprobe analyses of Mg isotopes in hibonite inclusions from Murchison meteorite

SASAKI, Shogo<sup>1</sup>, HIYAGON, Hajime<sup>1\*</sup>, FUJIYA, Wataru<sup>1</sup>, TAKAHATA, Naoto<sup>2</sup>, SANNO, Yuji<sup>2</sup>, MORISHITA, Yuichi<sup>3</sup>

<sup>1</sup>Graduate School of Science, The University of Tokyo, <sup>2</sup>Atmosphere and Ocean Research Institute, The University of Tokyo,

<sup>3</sup>Geological Survey of Japan, AIST

Hibonite (CaAl<sub>12</sub>O<sub>19</sub>) is one of the most refractory minerals, which condense from the solar nebula at highest temperatures, and hence, hibonite-bearing refractory inclusions may have important information in the earliest history of the solar system. In fact, PLACs (PLATy hibonite Crystals) and BAGs (Blue AGgregates) (Ireland, 1988) show large isotopic anomalies in Ca and Ti, and low inferred initial <sup>26</sup>Al/<sup>27</sup>Al ratios. It is suggested that they might form BEFORE injection of <sup>26</sup>Al into the solar system (Liu et al., 2009). In order to better understand earliest evolution of the solar system materials, we recovered about ~30 of hibonite-bearing inclusions from the Murchison (CM2) meteorite and Mg isotopic compositions were analyzed for 5 SHIBs, 5 PLACs, 1 Blue Spinel (Ireland et al., 1986), and 2 F-inclusions (see below) using two Secondary Ion Mass Spectrometers, NanoSIMS 50 (at AORI, University of Tokyo) and ims-1270 (at AIST, Tsukuba).

Results: Inferred initial <sup>26</sup>Al/<sup>27</sup>Al ratios for SHIBs are (4.7 ± 1.0) × 10<sup>-5</sup>, consistent with the canonical ratio for normal CAIs (MacPherson et al., 1995; Jacobsen et al., 2008). On the other hand, PLACs and a Blue Spinel show no resolvable excesses in <sup>26</sup>Mg so that their initial <sup>26</sup>Al/<sup>27</sup>Al ratios are zero within errors. Among them, Δ<sup>26</sup>Mg for all the data of 5 PLACs are slightly negative (i.e., apparent deficits in <sup>26</sup>Mg), suggesting possible isotopic anomalies in Mg isotopes. These results are consistent with previous works (e.g., Liu et al., 2009). In addition to these inclusions, we found two inclusions with heavily fractionated Mg isotopes (up to >50 permil/amu), and here we call them as F-inclusions (F means Fractionation). They also show initial <sup>26</sup>Al/<sup>27</sup>Al ratios of ~0 within errors, indicating some relations to so called FUN inclusions (Lee, 1988). In order to produce such large isotopic mass fractionation of Mg, evaporation must occur from the molten state, and in the condition without back reactions (e.g., evaporation under vacuum). Large mass fractionation of Mg in spinel suggests that spinel was not present as a solid phase at least during the early stages of evaporation, so that the temperature must be ~1600C or higher (Stolper, 1982) during the evaporation event, which resulted in extensive loss (>95%) of Mg (Richter et al., 2007).

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Keywords: hibonite, refractory inclusion, ion microprobe, Mg isotopes, isotopic fractionation, Murchison meteorite

## Two types of orthopyroxene in a micrometeorite

MIYAKE, Akira<sup>1\*</sup>, IMAE, Naoya<sup>2</sup>

<sup>1</sup>Kyoto Univ., <sup>2</sup>National Institute of Polar Research

### [Introduction]

Four stable pyroxene polymorphs have been identified: Ca-rich clinopyroxene (Ca-rich Cpx, space group: C2/c), Ca-poor clinopyroxene (pigeonite) (Ca-poor Cpx, C2/c or P2<sub>1</sub>/c), protoenstatite (Pen; Pbcn), and low-temperature orthopyroxene (LT-Opx, Pbcn). Moreover, Ohi et al. (2008, 2010) established the stability field of high-temperature orthopyroxene (HT-Opx, Pbcn) in enstatite (Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>) - diopside (CaMgSi<sub>2</sub>O<sub>6</sub>) system. However, LT- and HT-Opx have never been reported in natural sample. Micrometeorite which has about 100 μm in size is collected from the ice in Antarctica. The most of them is like to be chondritic meteorite and consistent with olivine, pyroxene and so on. Two types of Opx which have the different chemical composition although the same space group (Pbcn) are found in a micrometeorite, TT001c5-48.

### [Methods]

Major elements in the micrometeorite were analyzed using an electron probe microanalyzer (EPMA) and the phase of pyroxene was investigated using a Raman spectroscope. Thereafter, the specimen for transmission electron microscope (TEM) was made using a focused ion beam (FIB) and microtextures and electron diffraction patterns were obtained using a TEM.

### [Result and Discussion]

Two types of pyroxene, which have a little different Wo content, were observed from EPMA and both of pyroxenes have the Ca-poor rim. Moreover, these pyroxenes have more Mn component than other micrometeorite. Raman spectra from these pyroxenes have almost same and indicate Opx with Pbcn symmetry according to Wang et al. (2001). Electron diffraction patterns show that both phases have Pbcn and no microtextures are observed in both cores of these pyroxene. On the other hand, both rims have the micro twin. These results suggest that two types of Opx with a little different Wo content are LT- and HT-Opx.

Keywords: orthopyroxene, micrometeorites, FIB-TEM

## Estimation of space weathering rates based on reflectance spectra of a regolith-breccia meteorite

MISU, Takaaki<sup>1\*</sup>, NAKAMURA, Tomoki<sup>1</sup>, SASAKI, Sho<sup>2</sup>, HIROI Takahiro<sup>3</sup>

<sup>1</sup>Graduate School of Science, Tohoku University, <sup>2</sup>RISE Project, National Astronomical Observatory of Japan, <sup>3</sup>Department of Geological Sciences, Brown University

Space weathering is the term used for color alternation of asteroid surfaces from light to dark. This results from micrometeorite bombardment and cosmic-ray exposure, which generates metallic Fe nano-particles in the outermost layer of mineral particles at the asteroid surfaces. Because of space weathering, reflectance spectra of ordinary chondrites slightly differ from those of S-type asteroids that are parent bodies of ordinary chondrites. Therefore, when we establish the asteroid-meteorite connection based on the reflectance spectra, we must consider the effect of space weathering. Regolith breccia Tsukuba H chondrite is affected by space weathering on the asteroid surface of its parent body and shows characteristic dark-light structure. The dark portion is heavily weathered because of exposure to solar winds on the asteroid surface, while the light portion is not weathered because it was buried inside of the asteroid. Therefore the dark portion contains large amounts of cosmogenic and solar-wind derived noble gases, but the light portion is depleted in such noble gases.

In this study I compared dark portions and light portions of the Tsukuba meteorite in terms of mineralogy and reflectance spectra and investigated space weathering effects on this meteorite. Electron probe micro-analyzer (EPMA) analysis revealed that mineral chemistry of the dark portions and the light portions are the same. I applied the reflectance spectrometer for obtaining diffuse reflectance spectra of both dark and light portions. For comparison of the reflectance spectra, MGM (Modified Gaussian Model) is used. The results indicate that the band strength and areas of spectra derived from the dark portions are much lower than those of spectra from the light portions. Using the band strength and areas as parameters, we evaluate space weathering rates of S-type asteroids based on changes in reflectance spectra and cosmic-ray exposure ages of the Tsukuba meteorite. We use calculated results of cosmic-ray exposure age of the Tsukuba meteorite reported in a previous work. Applying the space weathering rates determined in this study to the reflectance spectra of S-type asteroids, we may be able to obtain surface ages of the asteroids only from reflectance spectra, which will greatly contribute to decipher the origin and evolution of asteroid belt in the solar system.



## Hydrothermal experiment of melilite and plagioclase: Implication for formation of nepheline in meteorite parent bodies

ICHIMURA, Shun<sup>1\*</sup>, SETO, Yusuke<sup>1</sup>, TOMEOKA, Kazushige<sup>1</sup>

<sup>1</sup>Kobe Univ. Sci

Nepheline ( $\text{NaAlSiO}_4$ ) in Ca-Al-rich inclusions (CAIs) and chondrule mesostasis of carbonaceous chondrite is believed to be a secondary altered mineral replacing melilite or plagioclase. Recent studies reported that the nepheline formation is correlated with hydro-thermal process on their parent body, but its detailed condition is not yet established.

To understand the formation process of nepheline in chondrite parent bodies, we conducted hydrothermal alteration experiments. As starting material, we prepared synthetic pure Ca-rich melilite (gehlenite,  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ), mixture of gehlenite and  $\text{SiO}_2$ , Mg-contained melilite ( $\text{Ca}_2\text{AlMg}_{0.5}\text{Si}_{1.5}\text{O}_7$ ), and 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 teflon reaction cell. 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.  $\text{Na}^+$  concentration in all solution is maintained at 1 mol/l. Run products were identified by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Under pH 14 condition, nepheline hydrate ( $\text{NaAlSiO}_4\text{H}_2\text{O}$ ) and analcime ( $\text{NaAlSi}_2\text{O}_6\text{H}_2\text{O}$ ) were observed in gehlenite- $\text{SiO}_2$  system. Under pH 13-7 conditions, analcime formed by replacing gehlenite or plagioclase. Under pH 0 condition, no crystalline phase was formed from gehlenite and plagioclase. In addition, these alterations proceeded under relatively low water/rock ratio condition.

The results indicate that the alteration process of gehlenite and plagioclase strongly depends on pH and water/rock ratio, suggesting that in carbonaceous chondrite parent body aqueous alteration of gehlenite and plagioclase occurred under high pH and lower water/rock ratio.

Keywords: nepheline, aqueous alteration, hydrothermal experiments, carbonaceous chondrites

## Stability of Amino Acids and Their Precursors (Hydantoins) against UV Light and Its Relevance to Origins of Life

Palash Kumar Sarker<sup>1\*</sup>, Jun-ichi Takahashi<sup>2</sup>, Yumiko Obayashi<sup>1</sup>, Takeo Kaneko<sup>1</sup>, Hajime Mita<sup>3</sup>, Kensei Kobayashi<sup>1</sup>

<sup>1</sup>Yokohama National University, <sup>2</sup>NTT Microsystem Integration Laboratories, <sup>3</sup>Fukuoka Institute of Technology

It is suggested that life on Earth could have been seeded by the delivery of organics from outer space during the intense bombardment period of primitive Earth. A large number of amino acids and their precursors have been detected in the extracts of carbonaceous chondrites, but their origins and original structure in the chondrites still remain controversial. Numerous simulation experiments have also suggested that these bioorganic compounds were formed from possible interstellar media by irradiation with high-energy particles or ultraviolet (UV) light. Furthermore, organics including amino acids and their precursors in inner part of comet and meteorites are safe from UV light, but organics in interplanetary dust particles (IDPs) are fully irradiated with strong solar UV as well as high-energy particles near Earth orbit. Thus, it is of interest to investigate how these organic compounds alter or survive against UV radiation. In this study, we examined the stability and photolysis products of hydantoin (Hyd) and its 5-substituted molecules, such as 5-methylhydantoin (M-Hyd), 5,5-dimethylhydantoin (DM-Hyd), 5-ethylhydantoin (E-Hyd), 5-ethyl-5-methylhydantoin (EM-Hyd). When 5-substituted hydantoins (EM-Hyd, E-Hyd, DM-Hyd and M-Hyd) were irradiated with UV light, Hyd (a precursor of glycine) was formed as major photolysis products. Therefore, it is assumed that 5-substituted hydantoins in extraterrestrial bodies were possible glycine precursors. Considering the photostability factor, EM-Hyd (precursor of isovaline) was less stable than isovaline against UV, though EM-Hyd is generally more stable than isovaline against radiation. It is due to the fact that isovaline has larger absorption coefficient in UV region than EM-Hyd. The present experimental results may point out the potential importance of the photochemistry of isovaline, glycine and their precursor molecules (i.e., hydantoin and 5-substituted hydantoins) in Solar System bodies.

Keywords: Hydantoins, Radiation, Ultraviolet, Photolysis, Isovaline, Glycine