

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

*Kouta Suzuki¹, Naoki Shoda¹, Shun Ichimura¹, Yusuke Seto¹

1. Graduate school of Sciences, Kobe University

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

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

Keywords: Chondrule, Gas levitation technique, Crystal growth

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

*Megumi MORI¹, Shogo TACHIBANA¹, Laurette PIANI¹

1.Hokkaido University

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

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

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

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

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Genesis of chemical zoning of asteroid belt and origin of Earth

*Shigenori Maruyama¹, Toshikazu Ebisuzaki²

1.Earth-Life Science Institute, Tokyo Institute of Technology, 2.RIKEN

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

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

Keywords: asteroid belt, chemical zoning, origin of Earth

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

*Noriyuki Kawasaki¹, Shoichi Itoh², Naoya Sakamoto³, Hisayoshi Yurimoto^{1,3}

1.Natural History Sciences, Hokkaido University, 2.Department of Earth and Planetary Sciences, Kyoto University, 3.Isotope Imaging Laboratory, Creative Research Institution, Hokkaido University

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

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

Petrography of a Type A CAI evolved by multiple heating.

*Shun Yoneyama¹, Shoichi Itoh²

1.Kyoto University, 2.Graduate school of Science, Kyoto University

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

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Keywords: CAIs, rare earth elements , petrography

Nucleosynthetic Neodymium Isotope Anomalies in Carbonaceous and Ordinary Chondrites.

*Ryota Fukai¹, Tetsuya Yokoyama¹

1. Department of Earth and Planetary Sciences, Tokyo Institute of Technology

We have performed high precision Nd isotope analysis of chondrites coupled with a new sample digestion technique that confirms complete dissolution of acid resistant presolar grains. We also developed an improved dynamic multicollection method using TIMS to improve the analytical reproducibilities. To test the analytical reproducibility in the dynamic method, we repeatedly analyzed a standard sample (JNdi-1) for eight months. The long-term reproducibilities obtained in the dynamic method were 4.2 ppm, 6.6 ppm and 9.7 ppm for $^{142}\text{Nd}/^{144}\text{Nd}$, $^{148}\text{Nd}/^{144}\text{Nd}$, $^{150}\text{Nd}/^{144}\text{Nd}$ ($n = 35$), which are 2-11 to times superior to the static and multistatic method.

We analyzed eight ordinary chondrites, showing uniform isotope anomalies for $\mu^{142}\text{Nd}$ (-12 ± 5 ppm), $\mu^{148}\text{Nd}$ (10 ± 8 ppm) and $\mu^{150}\text{Nd}$ (20 ± 12 ppm). Although the $\mu^{142}\text{Nd}$ values for ordinary chondrites obtained in this study are generally consistent with those of previous studies, positive anomalies in $\mu^{148}\text{Nd}$ and $\mu^{150}\text{Nd}$ were not recognized in previous studies. In contrast to ordinary chondrites, carbonaceous chondrites show variable Nd isotope anomalies exceeding analytical uncertainties. individual carbonaceous chondrites are categorized into three groups as a function of $\mu^{142}\text{Nd}$; NWA 2090 (-5 ppm), Tagish Lake (-20 ppm), and Allende, DaG 190/082, and Dhofar 1432 (-30 ppm).

The data points for ordinary chondrites are generally plotted on mixing line between the terrestrial composition and the putative *s*-process endmember. This means that the isotope anomalies in ordinary chondrites are induced by the heterogeneous distribution of *s*-process nuclides in early Solar System. By contrast, most of the carbonaceous chondrites deviate from the mixing line towards the direction with lower $\mu^{142}\text{Nd}$ values. We presume that the offset from the mixing line is caused by the heterogeneous distribution of *p*-nuclides in the early Solar System, because a part of ^{142}Nd was produced by the *p*-process nucleosynthesis and α decay of a pure *p*-nuclide ^{146}Sm . Although the Earth and parent bodies of chondrites do not share building blocks with a common Nd isotopic composition, the excess ^{142}Nd signature of the Earth would not necessarily require the existence of a hidden reservoir with a subchondritic Sm/Nd ratio deep in the Earth's mantle as proposed previously.

Keywords: isotope anomaly, presolar grain

The initial abundance and distribution of ^{92}Nb in the Solar System*Tsuyoshi Iizuka¹, Yi-Jen Lai², Waheed Akram², Yuri Amelin³, Maria Schönbachler²

1.University of Tokyo, 2.ETH Zürich, 3.Australian National University

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

Here we present Nb-Zr data for mineral fractions from four unbrecciated meteorites, which originate from distinct parent bodies and whose U-Pb ages were precisely determined: the angrite NWA 4590, the eucrite Agoult and the ungrouped achondrites Ibitira. Our results show that the relative Nb-Zr isochron ages of the three meteorites are consistent with the time intervals obtained from the Pb-Pb chronometer for pyroxene and plagioclase, indicating that ^{92}Nb was homogeneously distributed among their source regions. The Nb-Zr and Pb-Pb data for NWA 4590 yield the most reliable and precise reference point for anchoring the Nb-Zr chronometer to the absolute timescale: an initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of $(1.4 \pm 0.5) \times 10^{-5}$ at 4557.93 ± 0.36 Ma, which corresponds to a $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of $(1.7 \pm 0.6) \times 10^{-5}$ at the time of the Solar System formation. On the basis of this new initial ratio, we demonstrate the capability of the Nb-Zr chronometer to date early Solar System objects including troilite and rutile, such as iron and stony-iron meteorites. Furthermore, we estimate a nucleosynthetic production ratio of ^{92}Nb to the p -nucleus ^{92}Mo between 0.0015 and 0.035. This production ratio, together with the solar abundances of other p -nuclei with similar masses, can be best explained if these light p -nuclei were primarily synthesized by photodisintegration reactions in Type Ia supernovae.

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Keywords: achondrite, early Solar System chronology, nucleosynthesis

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

*Nao Nakanishi¹, Tetsuya Yokoyama¹, Tomohiro Usui¹, Hikaru Iwamori^{1,2}

1.Department of Earth and Planetary Sciences Tokyo Institute of Technology, Japan, 2.Department of Solid Earth Geochemistry, Japan Agency for Marine-Earth Science and Technology, Japan

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

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

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

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

Mineralogy of C03.0-like clasts in the NWA 1232 C03 breccia: Evidence for aqueous alteration on the parent body

*Megumi Matsumoto¹, Kazushige Tomeoka², Yusuke Seto², Akira Miyake³

1.Center for Supports to Research and Education Activities, Kobe University, 2.Graduate School of Science, Kobe Univ., 3.Graduate School of Science, Kyoto Univ.

It is widely believed that C0 parent bodies have escaped significant degree of brecciation. However, NWA 1232 is a C03 breccia consisting of three distinct lithologies (A, B, and C) that have experienced different degrees of thermal metamorphism^[1]. Recently, we found that lithology A (whose petrologic type is estimated to be 3.5) contains numerous small (100-1800 μm) clasts^[1]. Most of the clasts show C03.0-like mineralogical characteristics. Type 3.0 chondrites are thought to preserve their primary states when their components were accreted into their parent bodies. Here, we present the results of a mineralogical investigation of the C03.0-like clasts in lithology A of NWA 1232.

C03.0-like clasts are widely distributed throughout lithology A. Each of the clasts typically consists of one chondrule surrounded by a fine-grained matrix material, exhibiting the appearance of a chondrule with a rim. Some clasts contain multiple chondrules and CAIs in fine-grained matrix. Most chondrules in the clasts are Mg-rich Type I, and their olivine phenocrysts have homogeneous compositions ($\sim\text{Fa}_1$), which correspond to type 3.0. It is known that type 3.0 can be subdivided into finer divisions using various mineralogical signatures indicative of metamorphism. Here, we investigated Fe-Ni metal nodules in chondrules to evaluate the metamorphic grade of the clasts using the criteria given by Kimura et al. (2008)^[2]. Kimura et al.^[2] reported that the textures of metal nodules changed from homogeneous martensite to plessitic intergrowths of kamacite and Ni-rich metal, and to coarser grained intergrowths in the early stage of thermal metamorphism. Our study showed that the metal nodules in the clasts consist of intergrowths of kamacite and Ni-rich metal. The Ni-rich metal grains are intermediate in size ($1.63\pm 3.91 \mu\text{m}^2$) between Semarkona LL3.01 and type 3.03-3.05 chondrites, whereas their distribution density ($0.060\pm 0.079 \text{ N}/\mu\text{m}^2$) is much lower than Semarkona and similar to type 3.03-3.05 chondrites. In addition, trace element (Si, P, Cr, Co) contents in kamacite and Ni-rich metal are comparable to type 3.03-3.05 chondrites. From these results, we suggest that the clasts correspond to type 3.02-3.05.

The clasts show abundant evidence of aqueous alteration. Phenocrysts and mesostasis in the chondrule peripheries were replaced by fine grains (10-20 nm) of phyllosilicates and an O-Fe-Si-Mg-Al-rich amorphous material. The phyllosilicates replacing phenocrysts are largely serpentine, and those replacing mesostasis are serpentine and smectite. The matrix mainly consists of a O-Si-Fe-Mg-Al-rich amorphous material and contains relatively coarse grains (1-2 μm) of magnetite, forsteritic olivine, enstatite, fine grains (100-500 nm) of olivine, troilite, and finer grains (10-20 nm) of serpentine. In addition, the matrix contains small amounts of C-rich amorphous spherules (100-200 nm in diameter), which have an appearance similar to organic globules that have commonly been found from CI and CM chondrites^[e.g. 3].

Our results suggest that the clasts in lithology A of NWA 1232 have experienced aqueous alteration in the least metamorphosed region in the meteorite parent body. The evidence of aqueous alteration has also been reported from other C03.0 chondrites^[4, 5]. These suggest that aqueous alteration occurred generally in the least metamorphosed regions in C0 parent bodies. In the NWA 1232 parent body, part (or whole) of the region was brecciated to form many small clasts, and subsequently those clasts were transported and incorporated into lithology A of NWA 1232.

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Keywords: CO chondrite, brecciation, aqueous alteration, thermal metamorphism, Fe-Ni metal, TEM

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

*Hiroshi Isobe¹, Misato Tokunaga¹, Koyo Horiguchi¹

1.Department of Earth and Environmental Sciences, Graduate School of Science and Technology, Kumamoto University

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

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

Redox conditions calculated by thermodynamic parameters show higher f_{O₂} in H₂O-rich fluid compositions in this study. This estimation is concordant with experimental results on reactivity of metal components and compositions of carbonate and phyllosilicate minerals. Water components strongly promote production of carbonate and phyllosilicates. It is quite distinctive that production of carbonate minerals is stimulated by H₂O rather than CO₂ compositions in aqueous alteration processes.

Keywords: Aqueous alteration, carbonate, phyllosilicate, oxygen fugacity

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

*Akira Tsuchiyama¹, Tsukasa Nakano², Akira Miyake¹, Takeuchi Akihisa³, Kentaro Uesugi¹, Yoshio Suzuki, Akira Kitayama¹, Junya Matsuno¹, Michael E. Zolensky⁴

1.Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University,
2.AIST/GSJ, 3.JASRI/SPring-8, 4.NASA/JSC

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

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

We used POM ($[\text{CH}_2\text{O}]_n$), silicon, quartz, forsterite, corundum, magnetite and nickel as standard materials for examining the δ and μ values. A fluid inclusion in terrestrial quartz and bivalve shell (*Atrina vexillum*), which are composed of calcite and organic layers with different thickness, were also used for examining the spatial resolution. The Ivuna (CI) and Sutter's Mill (CM) meteorites were used as carbonaceous chondrite samples. Rod- or cube-shaped samples 20-30 μm in size were extracted by using FIB from cross-sectional surfaces of the standard materials or polished thin sections of the chondrites, which was previously observed with SEM. Then, the sample was attached to a thin W-needle and imaged by SIXM system at beamline BL47XU, SPring-8, Japan. The slice thickness was 109.3 nm and the pixel size was mostly 100 nm.

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

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

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

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

*Aiko Nakato¹, Tomoki Nakamura², Yoko Kebukawa³, Yasuo Takeichi⁴, Hiroki Suga⁵, Chihiro Miyamoto⁶, Kazuhiko Mase⁴, Yoshio Takahashi⁶

1.Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, 2.Tohoku University, 3.Yokohama National University, 4.High-Energy Accelerator Research Organization (KEK), 5.Hiroshima University, 6.The University of Tokyo

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

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

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

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

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

*Hiroshi Naraoka¹

1. Department of Earth and Planetary Sciences, Kyushu University

Many soluble organic compounds have been reported from carbonaceous meteorites in various solvent extracts ranging from non-polar hexane to polar water, in which amino acids and carboxylic acids have been targeted in the water-soluble fraction. The compositional and structural diversities of amino acids and carboxylic acids are well documented up to C8 observed with most structural isomers at each carbon number. The non-polar hexane extract contains non-polar components including aromatic hydrocarbons. To date, about a few thousands of soluble organic compounds have been identified in meteorites by GC and/or LC/MS. However, a high-resolution mass spectral study revealed ~160,000 ion peaks in various solvent extracts of the Murchison meteorite by electrospray ionization using Fourier transform-ion cyclotron resonance/mass spectrometry (FT-ICR/MS) to assign ~50,000 elemental compositions consisting of CHO, CHNO, CHOS and CHNOS (Schmitt-Kopplin et al., 2010). The methanol extracts of carbonaceous meteorites are enriched in organic content with more enriched in D and ¹⁵N relative to other fractions, implying more primitive organic compounds. The FT-ICR/MS study did not clarify the detailed chemical structures due to no chromatographic separation. In particular, the organic compounds with their elemental compositions of CH and CHN were not discussed. In the previous study (Yamashita and Naraoka, 2014), homologous series of alkylated pyridines ($C_nH_{2n-4}N^+$ and $C_nH_{2n-6}N^+$) were predominant peaks in the MeOH extract. In this study, we further examine the distribution of soluble organic compound using ultrahigh-resolution HPLC/MS in order to investigate reaction mechanisms for extraterrestrial molecular evolution. The exact mass between the observed mass and calculated values matched within 1 ppm. Using a hydrophilic interaction liquid chromatography (HILIC) mode, complex compound mixtures were observed with mass peaks between m/z 80 and 1400, where strong ion peaks are distinguished between m/z 90 and 400 with the maximum at m/z ~300. Most peaks have CHN in composition with minor CHO and CHNO compositions. More than ~600 peaks match with the calculated masses for $C_nH_mN^+$ and $C_nH_mN_2^+$ with the range of $5 < n < 33$. Extensive alkylated N-containing cyclic compounds are distinguished by every 14.0156 (-CH₂-) difference, which consisted of $C_nH_{2n-4}N^+$, $C_nH_{2n-6}N^+$, $C_nH_{2n-8}N^+$, $C_nH_{2n-10}N^+$ and $C_nH_{2n-12}N^+$ in the earlier retention time, and the $C_nH_{2n+4}N^+$, $C_nH_{2n+2}N^+$, $C_nH_{2n}N^+$, $C_nH_{2n-2}N^+$, $C_nH_{2n+3}N_2^+$, $C_nH_{2n+1}N_2^+$, $C_nH_{2n-1}N_2^+$ and $C_nH_{2n-3}N_2^+$ in the later retention time. In addition to the predominant $C_nH_{2n-4}N^+$ (saturate-alkylated pyridines, $C_nH_{2n-5}N$) and $C_nH_{2n-6}N^+$ (unsaturate-alkylated pyridines, $C_nH_{2n-7}N$), alkylated imidazole homologues were identified by MS/MS analysis. Both alkylpyridines and alkylimidazoles could be produced from aldehydes and ammonia through aldol condensation and imine formation under an alkaline environment. Further redox reactions could have proceeded during water-rock interaction to give alkylpiperidines and pyridine carboxylic acids. Aldehyde polymerization with ammonia is an important pathway to produce the relatively high-molecular alkylated N-containing cyclic compounds on the meteorite parent body.

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

Chemistry of formaldehyde and ammonia in the Solar System small bodies

*Yoko Kebukawa¹, Shusuke Misawa¹, Jun Kawai¹, Hajime Mita², Keita Nanbu³, Takahito Ouchi³, Yasuji Muramatsu³, Shogo Tachibana⁴, Kensei Kobayashi¹

1.Yokohama National University, 2.Fukuoka Institute of Technology, 3.University of Hyogo,
4.Hokkaido University

Formaldehyde and ammonia is ubiquitous in the universe. Comets contain up to 4% H₂CO and up to 1.5% NH₃ relative to H₂O, and interstellar medium (ISM) contains up to 8% H₂CO and up to 80% NH₃ relative to H₂O [1]. Cody et al. [2] proposed the formation scenario of insoluble organic matter (IOM) in chondritic meteorites, in the presence of liquid water starting with formaldehyde and glycolaldehyde that is the simplest sugar produced by two H₂CO molecules. We have conducted further experimental studies and showed that the presence of ammonia enhanced the IOM like organic solid formation via formose reaction followed by carbonization [3]. These studies were focusing on the solid materials, and now we study the liquid phase of the products with various analytical methods including electrospray ionization mass spectrometry (ESI-MS), X-ray absorption near edge structure (XANES), infrared spectroscopy and amino acid analyses using high performance liquid chromatography (HPLC).

Each starting solution contained 1mL water with 2 mmol formaldehyde, 1 mmol glycolaldehyde, 0.4 mmol ammonia (equivalent to H₂O : C : N = 100 : 7.2 : 0.72) with catalytic amount of Ca(OH)₂, and was sealed in a glass tube, then isothermally heated at 90 degrees C up to 250 degrees C. XANES and FTIR analyses showed that aromatic or olefinic C=C bond abundance increased with temperature in the soluble fractions. This indicates that the insoluble residues precipitate as a result of increase in the hydrophobic moieties in the products as the reaction proceeds. This is consistent with the previous results that the amount of insoluble fractions (organic solids) increases with temperature [3]. Acid hydrolysis of the solutions produced various amino acids up to four carbons. Alanine abundance was larger than glycine, and may indicate high abundance of methyl (-CH₃) or methylene (-CH₂-) substitutions in the amino acid precursor molecules. ESI-MS results suggested that various carbohydrates (CHO molecules) and these with nitrogen containing substitutions. This is somewhat consistent with ultrahigh-resolution ESI-MS analysis of the Murchison meteorite extract that shows various CHO and CHNO molecules [4], although only formaldehyde and ammonia chemistry cannot explain all of the diverse molecules found in this meteorite.

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Keywords: Meteorites, Asteroids, Organic matter

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

*Minako Hashiguchi¹, Sachio Kobayashi², Hisayoshi Yurimoto²

1.Japan Aerospace Exploration Agency, 2.Hokkaido University

[Introduction]

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

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

[Experimental]

A polished thin section of NWA 801, covered with a 30 nm thick carbon film [3], was used in this study. In situ quantitative H isotope ratio imaging was performed on matrix regions of the thin section using HokuDai isotope microscope system. The selection criterion for distinguishing D-rich materials that one of their D/H ratios is 2 sigma away from the 3 sigma the distribution of the surrounding matrix. Elemental ratio of H/C for the organic materials were measured using secondary ion intensity of H⁻ and C⁻ by SIMS analysis, assuming that average H/C ratio of less D-rich organic materials is corresponding to that of bulk CR2 IOM reported from previous study [4]. Identification and observation of organic materials were performed using FE-SEM-EDS. Raman experiments were performed by Renishaw Invia Reflex Raman microscope at the Open facility of Hokkaido University. An excitation wavelength is 532 nm (Nd: YVO₄) with spot size of ~1 μm. The laser power on the sample was less than ~300 μW.

[Results and Discussion]

Less D-rich organic particles in NWA 801 occur as sub-micron-sized globules with various morphology that can be classified as follows: ring globule, globule aggregate, round globule, and irregular-shaped globule, that are similar to those of D-rich organic globules in NWA 801 [3].

Although molecular structure of IOM is modified and their H/C ratio is decreased by thermal metamorphism and aqueous alteration [e.g. 4], D-rich and less D-rich organic globules in NWA 801 showed similar H/C ratio, mostly <1.5. Our results imply that the less D-rich organic globules in NWA 801 are not attributed to release of D-enrichment from D-rich organic globules by metamorphism and/or alteration.

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

the early solar nebula.

[Acknowledgement] We thank Open facility of Hokkaido University for their support of this Raman analysis.

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

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

*Motoo Ito¹, Naotaka Tomioka¹, Naoya Imae²

1.Kochi Institute for Core Sample Research JAMSTEC, 2.Antarctic Meteorite Research Center, National Institute of Polar Research

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

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

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

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

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

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

*Ryuta Nakamura¹, Akira Tsuchiyama¹, Akira Miyake¹, Aki Takigawa^{1,2}, Yohei Igami¹, Shugo Ohi³, Tsukasa Nakano⁵, Kentaro Uesugi⁴, Akihisa Takeuchi⁴, Toru Matsumoto⁶

1.Division of Earth and Planetary Sciences, Kyoto University, 2.the Hakubi Center for Advanced Research, Kyoto University., 3.Faculty of Education, Shiga University, 4.Japan Synchrotron Radiation Research Institute, 5.Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, 6.Japan Aerospace Exploration Agency / Institute of Space and Astronautical Science

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

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

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

Lamellar Fe zoning in low-Ca pyroxene in ordinary chondrites

*Naotaka Tomioka¹, Takafumi Yamamoto², Jun-ichi Ando²

1.Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology,
2.Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University

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

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

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

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

Evolution of rheological structure of Mars

*Shintaro Azuma¹, Ikuo Katayama²

1.Earth-Life Science Institute, Tokyo Institute of Technology, 2.Hiroshima University

Change of the rheological structure significantly influences the Martian evolution, which might results in the different tectonics operated in between Mars and Earth. Here we show the evolution of rheological structure of Martian lowlands (North Pole) and highlands (Solis Planum) under wet and dry conditions. The thermal state of the past and present planetary interior can be calculated from surface heat flow and the present-day abundance of the radioactive isotopes ²³⁸U, ²³⁵U, ²³²Th, and ⁴⁰K [Turcotte and Schubert, 2002]. Rheological structure can be inferred from flow laws that indicate the strength of solids, which is dependent on strain rate, temperature, water content, and chemical composition [Frost and Ashby, 1982; Karato and Jung, 2003]. In plastic deformation region, power-law creep is generally used to infer the rheological structure and heat flow [Grott and Breuer, 2008; Ruiz et al., 2008; Grott and Breuer, 2010], and this type of flow law is commonly applied to high-temperature creep. However, the Peierls mechanism becomes dominant at low temperatures and high stresses [Tsenn and Carter, 1987]. In this mechanism, strain rate is exponentially proportional to applied stress. In this study, the Martian rheological structure is determined not only from Power-law creep but also from the Peierls mechanism and diffusion creep. In brittle deformation region, Byerlee's law ($m=0.6-0.85$) is generally used to calculate the rock strength. We took the low frictional coefficient such as clay mineral ($m=0.2-0.6$) into account [Morrow et al., 2000; Kubo and Katayama, 2015].

The rheological structure of Mars determined in this study indicates that shallow deformation on Mars is mostly controlled by the Peierls mechanism, and that application of power-law creep on its own leads to an overestimation of lithospheric strength. The effect of water is also significant. Our results show that the presence of water would have delayed increases in lithospheric strength on Mars. Moreover recent studies found from the hydrogen isotopes in Martian meteorite that the water loss during the pre-Noachian was most significant [Kurokawa et al., 2014]. Given the evolution of water reservoirs on Mars, the lithospheric strength on Mars may have significantly increased at 4 Ga, suggesting that Mars changed to severe environment in where development of plate boundaries, plate motion, and plate subduction were limited.

Keywords: Mars, Rheological structure, Evolution

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

*Minato Tobita¹, Tomohiro Usui¹, Tetsuya Yokoyama¹

1.Department of Earth and Planetary Sciences, Graduate School of Science and Engineering, Tokyo Institute of Technology

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

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

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

Keywords: Mars, Shergottite, Pb isotope

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

*Mizuho Koike¹, Tsuyoshi Iizuka¹, Naoto Takahata¹, Yuji Sano¹

1.the University of Tokyo

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

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

Analyses: Both U-Pb and hydrogen analyses were conducted using NanoSIMS 50 at AORI, UTokyo. The sample sections were first baked at ~100C in the NanoSIMS air-lock overnight and then kept in the vessel at $< 5E-9$ torr for 1 week, to remove the adsorbed water. The previously established NanoSIMS analytical methods of U-Pb were applied [8]. For hydrogen analyses, negative secondary ions of H, D, ¹²C and ¹⁸O were collected to calculate water contents and D/H ratios. The background level of hydrogen is ~56 ppm as H₂O.

Results & Discussion: The Agoult apatite has concordant ²³⁸U-²⁰⁶Pb and ²⁰⁷Pb-²⁰⁶Pb ages at 4476 ± 160 Ma and 4486 ± 61 Ma, respectively. The total Pb/U age is 4523 ± 13 Ma, significantly younger than Agoult zircon but consistent with the plagioclase and Camel Donga zircon. It is suggested that these younger minerals may have recorded the same reheating event at ~4523 Ma or the slow cooling in the Vesta's crust. The Camel Donga apatite has U-Pb and Pb-Pb ages at 4478 ± 86 Ma and 4474 ± 83 Ma, indicating it may have the same thermal records to that of Agoult apatite. The H₂O contents of them are < 100 ppm for Agoult and $< 1,000$ ppm for Camel Donga. Though their D/H ratios cannot be determined due to the low water contents, such dry apatite is consistent with the reductive conditions, previously estimated from the Agoult zircon [4] and Camel Donga metal [6]. Our results suggest that Vesta's crust, at least locally, was depleted in water at ~4523 Ma.

Refs: [1] McSween et al. (2013) MaPS 48, 2090-2104. [2] Srinivasan et al. (1999) Sci. 284, 1348-1350. [3] Yamaguchi et al. (2009) GCA 73, 7162-7182. [4] Iizuka et al. (2015) EPSL 409, 182-192. [5] Iizuka et al. (2013) LPSC abst. 1907. [6] Palme et al. (1988) Meteoritics 23, 49-57. [7] Zhou et al. (2013) GCA 110, 152-175. [8] Koike et al. (2014) GJ 48, 423-431.

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

Mineralogical study of quartz and tridymite in cumulate eucrites

*Haruka Oono¹, Atsushi Takenouchi¹, Takashi Mikouchi¹

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

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

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

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

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

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

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

*Yuki Hibiya¹, Tsuyoshi Iizuka¹, Kazuhito Ozawa¹, Akira Yamaguchi²

1. Graduate School of Science, The University of Tokyo, 2. National Institute of Polar Research

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

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

Cr and Ti are successfully extracted with a new five-stage column chromatographic procedure. The Ti isotope analyses yielded $\epsilon^{50}\text{Ti} = 2.28 \pm 0.23$, which is distinct from differentiated meteorites and ordinary and enstatite chondrites but within the range of carbonaceous chondrites (Warren et al., 2011). Given that the oxygen isotope composition of NWA 6704 is plotted near the fractionation line of CR chondrite (Irving et al., 2011), its carbonaceous chondritic $\epsilon^{54}\text{Cr}$ (Sanborn et al., 2013) and $\epsilon^{50}\text{Ti}$ even more likely support its genetic link with carbonaceous chondrites. Our results have indicated that the presence of carbonaceous chondrite-like asteroid at about ≤ 3.55 Ma (after CAI formation; U-Pb age). This is consistent with preservation of ^{26}Al in the undifferentiated parent asteroid at about $T=2-3.5$ Ma (Sahijpal et al., 2007). This and the inferred thermal history suggest high internal temperature of the parent body owing to ^{26}Al decay was augmented by impact to have achieved abrupt heating up to above liquidus, followed by rapid cooling and later slower cooling owing to blanketing effect of impact ejectas piled up on the parental body.

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

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

*Masahiro YASUTAKE^{1,2}, Akira Yamaguchi^{1,2}

1.SOKENDAI, 2.National Institute of Polar Research

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

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

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

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

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

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

References [1] C. Floss (2000) Meteorit. and Planet. Sci., 35, 1073-1085 [2] Yamaguchi et al., (2012) Meteorite Newsletter, vol. 21

Keywords: Primitive Achondrites, Acapulcoite-Lodranite Meteorites, Planetesimals