

**EARLY STAGE OF AQUEOUS ALTERATION AND INTERACTION BETWEEN INORGANIC AND ORGANIC MATERIALS IN COMETARY BODIES : INSIGHTS FROM ANTARCTIC MICROMETEORITES.** T. Noguchi<sup>1\*</sup>, H. Yabuta, S. Itoh, N. Sakamoto, T. Mitsunari, A. Okubo, R. Okazaki, T. Nakamura, S. Tachibana, K. Terada, M. Ebihara, N. Imae, M. Kimura, and H. Nagahara.  
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**Introduction:** The evolution and interaction of inorganic materials and organic materials (OMs) are one of the critical issues of planetary science, which is also a main target of current planetary missions including Rosetta by ESA, Hayabusa-2 by JAXA, and OSIRIS-REx by NASA. The theme is further related to future missions to outer planets and their moons with special interests to the origin and evolution of life in solar and extrasolar planets. Chondritic porous interplanetary dust particles (CP IDPs) have been known so far as most primitive materials, which consist mainly of sub-micrometer-sized anhydrous constituents including GEMS (glass with embedded metal and sulfide) and enstatite whisker/platelets [1]. Due to the presence of high abundance of presolar grains and carbon [2] and the presence of organic materials with high D/H and/or  $^{15}\text{N}/^{14}\text{N}$  ratios [e.g., 3], CP IDPs are thought to be derived from comets. In order to clarify the early stage of evolution of primitive materials in the solar system, we have carried out comprehensive study of micrometeorites (MMs), which are another primitive objects of the solar system.

**Micrometeorite samples:** MMs were sampled by melting and filtering in a clean room ~300 kg snow collected from the near Dome Fuji station of the Antarctica by a Japanese Antarctic Research Expedition team, and were observed with FIB-SEM. Eight fine-grained MMs with porous morphology (D10IB004, 009, 017, 064, 120, 163, 178, and 356) and one (D10IB087) for comparison were selected for detailed investigation. The samples were embedded in annealed Au sheet and coated by carbon, from which ~100 nm-thick FIB sections were prepared.

**Analytical Method:** Carbon-, N-, and O-XANES spectra of the FIB sections were acquired using STXM at Advanced Light Source, LBNL [4]. The peak assignment was followed to [5-6]. Then, TEM observations at Ibaraki and Kyushu Universities were carried out for identification of minerals and OM. The surface of the most primitive sample D10IB009 after FIB was investigated with SIMS equipped with SCAPS at the Hokkaido university. Isotope imaging of isotopographs of  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{12}\text{C}^{14}\text{N}$ , and  $^{12}\text{C}^{15}\text{N}$  was performed.

**Mineralogy:** The MMs are porous and loose aggregates of mainly sub- $\mu\text{m}$ -size constituents, and are divided into anhydrous and hydrous groups. The anhydrous MMs (D10IB004, 009, 064, and 356) consist mainly of sub- $\mu\text{m}$ -sized materials, such as olivine,

low-Ca pyroxene, pyrrhotite, and GEMS with lesser amounts of coarse-grained ( $>1 \mu\text{m}$  across) single crystals and polycrystalline aggregates of olivine, low- and high-Ca pyroxenes, and pyrrhotite. The hydrous MMs (D10IB017, 120, 163, and 178) consist mainly of Mg-saponite with Fe-hydroxide, minor amounts of serpentine, and Fe-rich saponite, and carbonate. Results are summarized in the table below.

D10IB009, 356, 064, and 004 have the same mineralogy; they contain GEMS where Fe-metal and Fe-sulfide are present, phyllosilicates are absent, there is no evidence for aqueous alteration of olivine and low-Ca pyroxene that are abundant in the matrix, Fe is either metal or sulfide without oxide and hydroxide, and carbonate is absent. All of them are porous in texture and have pyrrhotite.

D10IB178 does not have GEMS, but instead amorphous silicate is present. Fe metal in the amorphous silicate is absent, but sulfide is remained. It has Fe-rich saponite and minor serpentine. Although saponite is present, there is no evidence for aqueous alteration in fine-grained olivine and pyroxene. Fe-oxide, hydroxide and carbonate is absent.

D10IB163, 120, and 017 do not have GEMS, but the abundance of Fe-rich saponite increases and there are small amounts of serpentine and Mg-rich saponite. Small-grained olivine and low-Ca pyroxene show evidence for aqueous alteration and their abundance decreases. Fe-hydroxide is present.

DB10IB087 contains Mg-rich saponite alone as a silicate, and Fe-hydroxide is present. Mg-siderite is also present.

**Organic materials:** C-XANES spectra of all the MMs exhibit the peaks of aromatic C=C, aromatic ketone, and carboxyl-carbonyl C=O, where the relative ratios of C=C to C=O is higher for D10IB004, 163 and 017 than 009 and 356. The spectral pattern of the former is similar to chondritic insoluble organic matter (IOM). D10IB009 shows a prominent peak that is assigned to be nitrile (C $\equiv$ N) and/or nitrogen heterocycles (C-N=C). Among the MMs investigated, D10IB009 contained the most abundant organic nanoglobules that were extremely enriched in C=O and C $\equiv$ N and/or C=N-C, and it has D and  $^{15}\text{N}$  enrichments ( $\delta\text{D} = +5000$  to  $+10000\%$ ;  $\delta^{15}\text{N} = +500$  to  $+1000\%$ ). OMs were hardly detected with XANES and TEM in 087, 120, and 178.

**Discussion:** On the basis of observation described above, we can estimate the primary materials and the sequence of aqueous reaction in the inorganic and organic materials in MMs. The most primitive assemblages are GEMS including Fe-metal and Fe-sulfide, tiny olivine and low-Ca pyroxene, and pyrrhotite, which are embedded in organic materials. The OMs are macromolecules enriched in C=O groups with C≡N and/or C=N-C groups, which accompany D and <sup>15</sup>N enrichments. Due to the heavy hydrogen and nitrogen, the organics are thought to be originated at very low temperature of the molecular cloud or prestellar environments and to have highly variable molecules.

The very early stage of alteration is recorded in organic materials; the loss of N-heterocycle, δ D, and δ <sup>15</sup>N, and enrichment of aromatic groups. Obvious first stage of aqueous reaction is seen in GEMS, where amorphous silicate and Fe-rich saponite are formed by consuming Fe metal in GEMS (Stage I). Aromaticity of the OMs becomes higher, and the organics becomes similar to IOM in primitive chondrites. Then, sulfide, small-grained olivine and low-Ca pyroxene, and Fe-rich saponite reacted with water to form Mg-rich saponite and Fe-hydroxide (Stage II). It is not clear whether sulfur from the sulfide was incorporated into phyllosilicate and/or organics or lost somehow. Finally, heterogeneous phyllosilicates changed into homogeneous Mg-rich saponite, carbonate is formed, and organics are depleted (Stage III). The final products are Mg-saponite, magnetite, and carbonates. The typical mineral assemblage and chemical composition of Mg-saponite are quite similar to that of primitive carbonaceous chondrites.

The physical conditions for the Stages I and II would be roughly at 0°C and the duration should be very short, in the order of days, which is suggested by the alteration experiments on GEMS [7]. Stage III may be at a little higher temperature in order to homogenize heterogeneous phyllosilicates into homogeneous one. The condition suggests that the aqueous alteration in Stages I and II might be caused by transient heating by an impact, but can be either by shock or approaching of cometary bodies to the Sun for Stage III, which lasted for weeks to months if temperature did not increase significantly. However, extremely porous nature of comets [8] suggests that the temperature and duration estimation should be evaluated carefully.

In summary, the present study revealed a series of aqueous reactions in cometary bodies probably at ~ 0°C, which took place heterogeneously in the highly porous parent bodies. The aqueous alteration in chondrite parent bodies took place more homogeneously due to pervasive liquid water distribution in more compact bodies.

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**References** [1] Bradley J. P. (2014) in *Treatise on Geochemistry* **1**, 287. [2] Thomas K. et al. (1994) in *Analysis of Interplanetary Dust* 165. [3] Messenger S. et al. (2003) *Science* **300**, 105. [4] Kilcoyne et al. (2003) *J. Synch Rad.* **10**, 125. [5] Leinweber et al. (2007) *J. Synch Rad.* **14**, 500. [6] Cody G. D. et al. (2008) *MAPS* **43**, 353. [7] Nakamura-Messenger K. et al. (2011) *MAPS* **46**, 843.

Sample	D101B 009	356	064	004	178	163	120	017	087	typical hydrated MM
Texture	porous								compact	compact
Mineralogy	GEMS or amorph silicate	GEMS			amorph sili	absent				absent
	metal and/or sulfide in GEMS or amorph silicate	metal + sulfide			sulfide	absent				absent
	phyllosilicates	absent			Fe-rich sap + minor serp	Fe-rich sap + minor serp + minor Mg-rich sap	Mg-rich sap	Mg-rich sap		
	aqueous alteration in ol and LPx	absent				present				
	sub-um ol and LPx	abundant				rare				absent
	Fe oxide or hydroxide	absent				Fe-hydroxide				magnetite
	carbonate	absent							Mg-siderite	Mg-siderite, dolomite
	isolated pyrrhotite	present								present
Organic material	N-heterocycle	present	absent	-	absent	-	absent	-	absent	-
	aromatic C	poor		-	abundant	-	abundant	-	abundant	-
	globule	abundant	-	present	-	-	present	-	-	present
	δ D (‰)	+5000 to +10000	-	-	0	-	-	-	-	-
	δ <sup>15</sup> N (‰)	+500 to +1000	-	-	+300	-	-	-	-	-