MACROMOLECULAR ORGANIC MATTER IN C-TYPE ASTEROID RYUGU.

H. Yabuta[1], G. D. Cody[2], C. Engrand[3], Y. Kebukawa[4], B. De Gregorio[5], L. Bonal[6], L. Remusat[7], R. Stroud[5], E. Quirico[6], L. R. Nittler[2], M. Hashiguchi[8], M. Komatsu[9], E. Dartois[10], J. Mathurin[11], J. Duprat[7], T. Okumura[12], Y. Takahashi[12], Y. Takeichi[13], D. Kilcoyne[14], S. Yamashita[13], A. Dazzi[11], A. Deniset-Besseau[11], S. Sandford[15], Z. Martins[16], Y. Tamenori[17], T. Ohigashi[18], H. Suga[17], D. Wakabayashi[13], M. Verdier-Paoletti[7], S. Mostefaoui[7], G. Montagnac[19], J. Barosch[2], K. Kamide[1], M. Shigenaka[1], L. Bejach[3], T. Noguchi[20], H. Yurimoto[21,] T. Nakamura[22], R. Okazaki[23], H. Naraoka[23], K. Sakamoto[24], S. Tachibana[12,24], S. Watanabe[8], and Y. Tsuda[24], [1]Hiroshima Univ., 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan. [2]Carnegie Institution of Washington, USA. [3]IJCLab, Univ. Paris-Saclay/CNRS, France. [4]Yokohama National Univ., Japan. [5]U.S. Naval Research Laboratory, USA, [6]Université Grenoble Alpes, France. [7]Muséum national d'Histoire naturelle, France. [8]Nagoya Univ., Japan. [9]The Graduate Univ. for Advanced Studies (Sokendai), Japan. [10]ISMO, Univ. Paris-Saclay/CNRS, France. [11]ICP, Univ. Paris-Saclay/CNRS, France. [12]Univ. of Tokyo, Japan, [13]High Energy Accelerator Research Organization, Japan. [14]Advanced Light Source, USA. [15]NASA Ames Research Center, USA. [16]Instituto Superior Técnico, Portugal. [17]SPring8, Japan. [18]UVSOR, IMS, Japan. [19]ENS Lyon, France, [20]Kyoto Univ., Japan. [21]Hokkaido Univ., Japan. [22]Tohoku Univ., Japan. [23]Kyushu Univ., Japan. [24]ISAS, JAXA Japan.

Introduction: Organic compounds in asteroids and comets record the chemical history from the protosolar molecular cloud to the early Solar System. They are thought to have been delivered to the early Earth as the building blocks of life. Therefore, it is important to reveal the chemical evolution of organic compounds in primitive small bodies for understanding the origins of planets and life. Macromolecular organic matter, that is often characterized as acid-insoluble organic matter (IOM), accounts for a major portion of total organic carbon in primitive carbonaceous chondrites [1]. Chemical variations of IOM from various types of small body materials have enabled our comprehensive understanding of the early Solar System history.

JAXA's Hayabusa2 mission aims to unveil the origin and evolution of organic compounds and water in the early Solar System as life's building blocks [2]. After the sample return on December 6, 2020, curatorial work at JAXA reported that the Ryugu samples contain high abundances of hydrous minerals and organics [3, 4]. Afterward, the initial sample analysis has started from June 2021 to classify and characterize the Ryugu samples in the context of the Solar System formation. The Organic Macromolecule Initial Analysis Team aims to unveil the elemental, isotopic, and functional group compositions, structures and morphologies of macromolecular organic matter from the Ryugu samples [5].

Samples and Methods: Chamber A aggregates (A0108) and Chamber C aggregates (C0109) collected at the first and second touchdown sites, respectively, have been analyzed. The individual intact grains from A0108 and C0109 range from 200 to 900 μm in size. Additional aggregates from Chamber A (A0106) and Chamber C (C0107) were transferred from the Soluble Organic Molecules team after their water and solvent extractions, and were treated with 6M HCl and 1M HCl/9M HF to yield IOM at Hiroshima University [5].

The analytical procedures included a combination of micro-Fourier transform infrared microspectroscopy (μ-FTIR), micro-Raman spectroscopy, synchrotron-based scanning transmission X-ray microscopy coupled with X-ray absorption near edge structure (STXM-XANES), scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS), atomic force microscope based infrared spectroscopy (AFM-IR), and nanometer-scale secondary ion mass spectrometry (NanoSIMS) [5].

Results and discussion:

Intact Ryugu grains. In Raman spectra of the Ryugu intact grains [6, 7], the D- and G-bands, which are derived from polyaromatic structure, were detected. The spectral features were broad, reflecting disordered carbon, and showed a high fluorescence background. The Raman band parameters of the Ryugu samples are comparable to those derived from primitive CI and CM carbonaceous chondrites, while they are clearly distinct from petrologic type 3 chondrites and thermally metamorphosed CM chondrites. The results show that the Ryugu samples escaped significant heating events on the parent body.

The μ-FTIR spectra of the Ryugu grains showed bands due to organic aliphatic C-H, aromatic C=C, and carbonyl C=O, as well as bands due to mineral Si-O and structural OH of phyllosilicates, and carbonates [8, 9, 10]. These absorption bands are commonly observed in aqueously altered primitive carbonaceous chondrites.

STXM elemental maps showed the distributions of several hundred-nm sized organic grains as well as organic matter dispersed in matrix [11]. The Carbon-XANES spectra of Ryugu samples mainly included three peaks: aromatic C=C, aromatic ketone, and carboxyl groups. The peaks are typically seen in those of primitive carbonaceous chondrites. The C-XANES spectral patterns were classified into four types; Highly aromatic, aromatic, IOM-like, and diffuse carbon. The spectral shapes correlate with the morphologies of organic matter. Organic nanoglobules and nanoparticles are aromatic-rich, while organic matter in Ryugu matrix was IOM-like or diffuse carbon. The observed functional group diversity likely resulted from aqueous alteration on the asteroid parent body, while highly aromatic spectra could possibly have been derived from the solar nebula or protosolar molecular cloud [11].

The same samples analyzed by STXM were analyzed by STEM-EELS-EDS [12]. Many different morphologies of nano-sized organic matter from Ryugu samples include nanoglobules, diffuse carbon mixed into phyllosilicates, vesicles in carbonate grains, and dense irregular shaped nanoparticles. These organic microstructures were associated with Mg-rich phyllosilicates and carbonates, which could have been formed during aqueous alteration. Diffuse carbon may have been formed from the soluble molecules intercalated into clays [13] or may have been released by hydrolysis of macromolecular organic matter [14] during aqueous alteration.

Organic inclusions in Ryugu grains were also observed by AFM-IR with a spatial resolutions of several tens nm [15]. Mapping in specific vibrational modes, e.g., C=O, C=C, and Si-O, revealed the organic functional group diversity associated with surrounding phyllosilicate matrix.

NanoSIMS was used to measure hydrogen, carbon, and nitrogen isotopic compositions of the Ryugu grains [16, 17, 18]. The bulk δD and $\delta^{15}N$ of the Ryugu grains are between the bulk values of CI chondrites [19] and IOM in CI chondrites [20]. Most of the individual carbonaceous grains showed similar isotopic ratios to the bulk compositions, while some showed extreme D and/or ^{15}N enrichments or depletions, which are indicative of origin in a cold molecular cloud or nebula. A very small fraction of carbon-rich particles show anomalous carbon isotopes including presolar SiC grains [18].

IOM isolated from the Ryugu samples. The FTIR and XANES spectra of IOM isolated from Ryugu samples were broadly similar to those of the intact Ryugu grains [8-11]. An unique difference is that the peak intensity of the aliphatic C-H band from the Ryugu IOM was much higher than those of IOM from meteorites [9]. The CH_2/CH_3 ratios of the Ryugu IOM were also higher than those of meteoritic IOMs. This could reflect that the macromolecular organic matter in fresh asteroid samples contains long aliphatic chains compared to the meteoritic organics.

NanoSIMS elemental maps revealed that the bulk O/C of IOM from chamber A was roughly consistent with those of primitive carbonaceous chondrites [17], while the bulk O/C of IOM from chamber C was lower than those values. This difference may be due to local difference from the two touchdown sites or heterogeneity between the individual grains. The bulk N/C and S/C in chambers A and C were consistent with those of primitive carbonaceous chondrites.

The bulk δD of IOM from the Ryugu samples is lower than that in CI and CM chondrites [17]. On the other hand, the distributions of D-enrichments were within the range of CI, CM, and Tagish Lake C2 chondrites, respectively. The $\delta^{15}N$ of the IOM from Ryugu samples were similar to those in CI chondrites [17]. The distributions of ^{15}N-enrichments were also consistent with those of CI and CM chondrites.

Summary: Macromolecular organic matter is abundant and has complex structure in the asteroid Ryugu samples. The chemical, isotopic, and morphological diversities of organic matter from Ryugu record various degrees of parent body aqueous alteration and preserve the materials derived from nebula or molecular cloud.

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