Spatial relationship between macromolecular organic matter and organic-bearing phyllosilicates in Ryugu grain.

Toru Matsumoto¹, Takaaki Noguchi², Tohru Araki³, Takuji Ohigashi⁴, Yohei Igami², and Akira Miyake²

¹The Hakubi center for Advanced Research, Kyoto University.²Division of Earth and Planetary Sciences, Kyoto University, ³Institute for Molecular Science, ⁴High Energy Accelerator Research Organization.

Introduction: Regolith samples recovered from the C-type asteroid Ryugu show chemical and petrological characteristics similar to those of CI carbonaceous chondrites [e.g., 1-3]. They consist of primitive components of the early solar system, including water and organic matter, but are highly modified in the parent body by aqueous alteration. Insoluble organic macromolecules (IOM) in Ryugu grains are the dominant components of organic matter in Ryugu's materials [3]. The chemical structures, distributions, and morphologies of the macromolecular organic matter can be tracers of the evolution of organic materials in the interstellar medium, the protosolar disk, and the aqueous environment in the parent body of Ryugu [3]. Recent analysis of the interlayer spaces of phyllosilicate minerals in Ryugu grains suggested the presence of organic molecules in clay structures [4, 5]. The infrared absorption band at around 3 µm obtained from Ryugu grains may come from N-H bearing molecules trapped in the interlayers of phyllosilicates [6]. These results suggest that phyllosilicates have been affected by organic matter during the aqueous alteration. Detailed investigation of the interlayer spaces of phyllosilicates and their spatial association with macromolecular organic matter will provide insight into the interaction between minerals, water, and organic matter in the parent body of Ryugu. In this study, we focused on carbon-rich regions in a Ryugu grain and examined the spatial relationship between organic materials and phyllosilicates, together with their chemical features.

Methods: A Ryugu grain from the chamber A (grain No. A0142) was distributed by JAXA as a sample for the international announcement of opportunity and was used in this study. The surface features of the grain was observed using a field-emission (FE)-scanning electron microscope (SEM) (JSM-7001F). Electron-transparent sections were extracted from the regions of interest using a focused ion beam system (FIB Helios NanoLab G3 CX). Scanning transmission X-ray microscopy (STXM) imaging was performed to obtain X-ray absorption near edge structure (XANES) spectra from the sections. The bonding structure of carbon was investigated using XANES spectra at the carbon K-edge (at 280 eV-320 eV). After STXM analysis, the sections were observed using field-emission transmission electron microscope (TEM) (JEOL JEM2100F).

Results: Backscattered electron images of the grain surface show the concentration of organic matter embedded in the phyllosilicate matrix (Fig. 1a). Several carbon-rich spots were found on the grain surface. We investigated the largest carbon-rich region with approximately $17 \times 8 \times 9 \,\mu$ m in size (Fig.1ab). Carbon-XANES spectra of the carbon-rich region include major peaks of aromatic carbon (285 eV) and carboxyl carbon (288.5 eV), and those of phyllosilicate matrix in the vicinity of the carbon-rich region show peaks of aromatic carbon (285 eV), carboxyl carbon (288.5 eV), aliphatic carbon (287.5 eV), and carbonates (290.4 eV). TEM analysis showed that organic materials and fibrous phyllosilicates are finely intermixed in the carbon-rich region. Hereafter, we call the carbon-rich region as the carbon-phyllosilicate aggregate (CPA). Distinct morphologies of organic materials, such as the organic globules, were not identified in the CPA. The surrounding matrix consists mainly of fibrous phyllosilicates (Fig. 1c) enabled us to investigate the interlayer distance of the phyllosilicates. The majority of the fibrous phyllosilicates in the CPA and the matrix have interlayer distances of $0.7 \sim 0.75$ nm, and 1.0-1.2nm. These values correspond to typical interlayer distances of serpentine and saponite in Ryugu samples, respectively [2]. On the other hand, fibrous phyllosilicates with interlayer distances of 1.23-1.35 nm were occasionally observed in the CPA and in the matrix close to the carbon-rich region (Fig.1c).

Discussion: The enrichment of aromatic and carboxylic carbon in the XANES spectra from the CPA is similar to the spectral features of highly-aromatic or aromatic macromolecular carbon in Ryugu samples [3]. The concentration of aromatic organic matter may have occurred by redistribution and/or synthesis of organic matter during fluid activity in the parent body. It is also possible that large chunks of organic matter have been incorporated during the initial accretion of the parent body, in the form of primitive materials originated from the outer solar system [7]. The appearance of aliphatic carbon in the matrix is consistent with the previous XANES study of Ryugu samples, in which aliphatic organics were detected in association with phyllosilicates [8]. Previous X-ray diffraction measurements of Ryugu samples detected 001 reflection of smectite at 1.26 nm [4]. The relatively large interlayer distance was interpreted as the expansion of the interlayer space due to the presence of organic molecules [4]. Accordingly, the interlayer distances of 1.25-1.35 nm found in our sample suggest that organic species

are intercalated into the phyllosilicates. The spatial relationship between the CPA and the possibly organic-bearing phyllosilicates suggests that macromolecular organic matter could have interacted with surrounding phyllosilicates during aqueous alteration, as suggested by analyses of carbonaceous chondrites [9, 10].



Figure 1. SEM and TEM analysis of the carbon-rich region of Ryugu grain (A0142). Backscattered electron image (a) and bright-field TEM image (b) of the carbon-phyllosilicate aggregate (CPA). Arrows indicate the interface between the CPA and surrounding phyllosilicate matrix. (c) High-resolution TEM image of fibrous phyllosilicates near the CPA. Interlayer distances are shown in the figure.

References: [1] Yokoyama et al. 2022. Science 379.6634, eabn7850. [2] Nakamura et al. 2022. Science 379.6634, eabn8671. [3] Yabuta et al. 2023. Science 379. 6634, eabn9057. [4] Viennet et al. 2023. Geochem. Persp. Let. 25, 8-12. [5] Damien et al. 2023. Meteoritics & Planetary Science under review. [6] Pilorget et al. 2022. Nat. Astron. 6, 221-225. [7] Duprat et al. 2010. Science 328, 742-745. [8] Ito et al. 2020. Nature Astron. 6:1163-1171. [9] Garvie and Buseck, 2007. Meteoritics & Planetary Science 42, 2111-2117. [10] Guillou et al. 2014. Geochim. Cosmochim. Acta, 131, 368-392.