Interpreting the thermal alteration history from organic matter in Ryugu samples

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Introduction: The Hayabusa2 mission visited the near-Earth Cb-type asteroid (162173) Ryugu and has returned to Earth with the surface material of Ryugu. Ryugu is an airless rubble pile asteroid exposed to space weathering [1]. Near infrared remote observations recorded an absorption feature at 2.72 μm indicating the presence of OH–bearing hydrous components. However, the 2.72 μm feature is weak, suggesting that Ryugu was once organic- and water-rich and subsequently dehydrated by a brief period of surficial heating. This feature has also been observed in "thermally metamorphosed carbonaceous chondrites", "CI-/CM-like", or "CY" chondrites [2, 3]. Initial examination of the returned samples did not identify any significant heating at >150 °C [4, 5]; however, amino acid analyses suggested similarities to thermally-altered meteorites on the grounds of the predominant straight-chain *n*-ω-amino acid abundances [6]. It remains unclear as to what caused the nonconformal interpretations of the thermal alteration history of Ryugu.

Here we investigate the alteration history of Ryugu by comparing the organic composition of fresh Ryugu samples to that of naturally and experimentally heated chondritic meteorites. This study describes a coordinated effort in analysing organic matter in Ryugu samples using micro–x-ray computed tomography (μ-CT), micro-Raman spectroscopy, focused ion beam (FIB), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), micro-X-ray diffraction (μ-XRD), scanning transmission X-ray microscopy (STXM), X-ray absorption near edge structure (XANES), and synchrotron radiation-based X-ray computed tomography (SR-CT).

Samples and Analytical Techniques: We studied Ryugu samples allocated during the Hayabusa2 preliminary examination (A0063-FC016, A0063-FC017, A0064-FO012, A0067-FC008, C0002-FC014, C0002-FC015, C0025-FC003, C0033-FC003, C0046-FO003) and AO1 (A0009 and C0011), plus raw fragments of naturally long-term (CIs: Orgueil, Ivuna; CMs: Murchison, Murray; CV: Allende; CRs: Grosvenor Mountains 95577; OCs: Yamato (Y)-74191, Queen Alexandra Range 93010) and short-term heated meteorites (Belgica-7904, Jbilet Winselwan, Y-793321, Y-86720, Y-982086) [7, 8]. We also analysed samples of Murchison, Murray and Orgueil experimentally heated to 300, 400, 500, 600, 700 and 900 °C for 1, 10, 50, 100, 500 and 1000 hours. Raman analyses were conducted using a Jobin-Yvon Horiba LabRAM HR Raman microprobe with a 514 nm laser for which the power was maintained at <100 μW at the sample surface. The mineralogy of the raw Ryugu samples was characterised using low-voltage SEM-EDS (FEI Quanta 650) and μ-XRD. We identified regions of interest (ROIs) within A0009 and C0011 by conducting μ-CT analysis using a cabinet-based industrial Zeiss Xradia Versa 520 CT system. Targeted ROIs were picked using sterile tools, pressed into indium, and prepared into electron-transparent sections (~100 nm thick) mounted on TEM Cu grids using a FEI Quanta 3D 600 dual beam FIB-SEM, which were studied by STXM-XANES to determine the organic composition. Euhedral sulphide crystals were lifted and mounted on W-needles by the FIB-SEM, and potential fluid inclusions within them were then located by SR-CT conducted at SPring-8 BL47XU at the X-ray energy of 7 keV.

Results and Discussion: Increased heating of carbonaceous materials results in a transition from amorphous to graphitic carbon, and such ordering is traceable using Raman spectroscopy as a cosmothermometer [9]. Raman spectroscopic analysis of the Ryugu samples indicates significant heterogeneity (Figure 1), evident by Raman spectral features that are comparable to the organic matter in both relatively unheated primitive chondrites and those that experienced short duration heating like Y-793321, a Stage II heated chondrite [10].

The Raman spectral features of the organic matter in most of the Ryugu samples are similar to those observed from CIs, consistent with previous studies [11]. However, localised areas within several Ryugu samples show a wider G band, comparable to organic matter processed by short duration heating. The Raman features of the organic matter in broad areas within A0009, A0064 and C0011 clearly deviate from that observed from the other Ryugu samples and Orgueil, with significantly lower D band positions and D band widths that are comparable to chondritic organics that had been heated at elevated temperatures [9], and larger G band widths that are not observed in naturally metamorphosed chondritic meteorites (Figure 1). These trends are similar to those exhibited by astromaterials heated by short-term heating, like interplanetary dust particles [12] and some meteorites [13]. The Raman spectra of A0009, A0064 and C0011 are similar to those of Orgueil experimentally heated to 300 °C for 500 h.

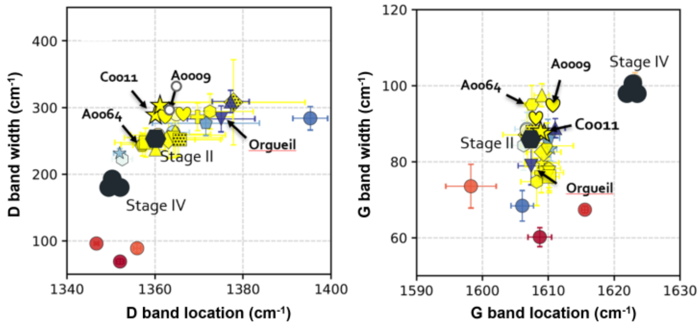

Figure 1. Comparison of the Raman D and G band parameters of Ryugu samples (yellow symbols), and naturally short-term heated samples (black symbols; Stage II CCs peak heating temperature ~250–500°C; Stage IV CCs >750°C). Γ=Full width half maximum; ω = Peak location.

Analysis of A0064 by SEM-EDS and μ-XRD shows the presence of hydrated phyllosilicates, suggesting that the particle did not experience significant heating above ~300–400 °C. Moreover, the SR-CT data validated the μ-CT scans, and indicate that C0011 contains a sulphide grain hosting an inclusion with X-ray attenuation that is clearly distinct from air (Figure 2). Previous studies have revealed H_2O and CO_2 within such inclusions [14], suggesting that they have not been metamorphosed after aqueous alteration. Analysing these more "evolved" particles with STXM-XANES helped us understand the organic structure corresponding to the Raman features. C-XANES spectra of A0009 and C0011 indicate the presence of aromatic or olefinic groups (C=C) at ~285 eV and carboxylic groups (COOH) at ~288.5 eV within the matrix associated with carbonate grains (CO_3 absorption at 290.3 eV). While thermally stable oxygenated functional groups were observed in short term (impact induced) heated meteorites [15], the association of the organic matter with carbonates is comparable to the carboxylic-rich diffuse organic matter in CM and CI chondrites [16]. Based on our coordinated investigation, we have drawn two possible scenarios that can explain our observations: (1) some carbonaceous matter in Ryugu had experienced post aqueous alteration short duration heating (impact induced and/or solar irradiation), resulting in the presence of thermally stable oxygenated moieties like furan and phenol that were formed via dehydration and cyclisation of polyalcohols. These "evolved" materials were subsequently disrupted and redistributed by impacts, thermal fatigue, and/or mass wasting processes [17], intermixed with fresh, undisturbed and pristine Ryugu materials. Alternatively, (2) the formation of the macromolecular organic matter occurred at the final stages of aqueous alteration in low-temperature, highly oxidizing fluids, e.g., fluid with OH radicals contributing through H_2O_2 dissociation [18], co-precipitating carboxylic enriched components in the immediate vicinity of carbonate.

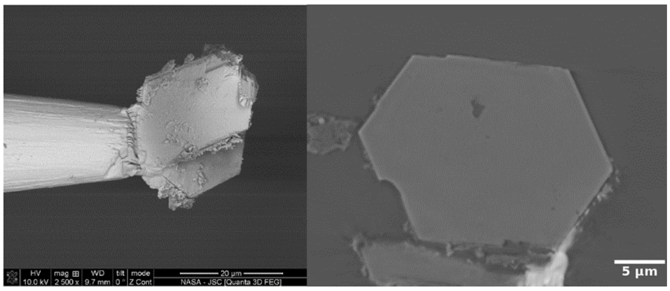

Figure 2. SR-CT images of a sulphide grain picked from C0011.

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