Chemical heterogeneity of insoluble organic matter in Ryugu grains

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Introduction: The Hayabusa2 mission has returned to Earth 5.42 g of samples collected at the surface of asteroid Ryugu (Yada et al., 2022). Two touchdowns were operated: the first on February 21 2019 to collect material from the top surface, and the second on July 11 2019, ~20 m north from the artificial crater generated by the impact experiment a few months ago, for probing ejecta coming from deeper in the subsurface (Tsuda et al., 2020). The bulk and multi-instrumental mineralogical and isotopic characterization of Ryugu samples show that they are related to CI chondrites, but experienced a lower stage of hydrothermalism resulting in a more reduced mineralogy (e.g. Nakamura et al., 2022). Insoluble organic matter (hereafter IOM) has been extracted from Ryugu's samples, and infrared spectroscopic analyses have revealed differences with respect to IOMs extracted from historical falls as Alais, Ivuna and Orgueil (Yabuta et al., 2022; Kebukawa et al., 2022). Here, we investigate the chemical heterogeneity of IOM in a series of Ryugu grains selected from the A and C chambers, corresponding to the first and second touchdowns, respectively. Small grains (100-500 µm) were processed with an HF/HCl extraction protocol and characterized by micro-FTIR. Some of these grains were also analyzed by Raman micro-spectroscopy (Bonal et al. 2022).

Experimental: IOM samples were extracted with the HF/HCl protocol (Durand and Nicaise 1980), adapted to micro-sized grains. Infrared transmission spectra were collected with a Bruker HYPERION 3000 micro-FTIR, equipped with a MCT-detector. The spot size at the sample was ~50 µm x 50 µm and the spectral resolution was 4 cm^{-1}. Measurements were run with an environmental cell maintained under secondary vacuum (~ 10^{-6} mbar) and the sample was heated at 80°C to remove adsorbed terrestrial water.

Results and discussion: The samples are presented in Tab. 1 and some infrared spectra in Fig. 1. The spectra collected from the series of samples show significant chemical variations, which can have different origins : (1) Terrestrial weathering versus sample freshness; (2) Analytical artefacts; (3) Accretion of distinct organic precursors and (4) Post-accretional processes. Ryugu samples are extremely fresh and have experienced little interactions with the terrestrial atmosphere. In contrast, the historical falls Alais, Orgueil and Ivuna fell in 1804, 1864 and 1938, respectively, and storage conditions in old times were not optimized. However, systematic measurements on finds and falls covering a long period of time, including recent falls (e.g. Tagish Lake, Mukundupura), do not support an IOM evolution controlled by terrestrial weathering (Alexander et al. 2007; Cody et al. 2005; Kebukawa et al., 2011; Orthous-Daunay et al., 2013; Quirico et al. 2018). The HF/HCl digestion protocol could be subjected to analytical artifacts, such as oxidation and contamination (e.g. viton particles from the wires). However, we cross-checked the extraction quality by extracting IOM from well known chondrites (e.g. Orgueil), and in some cases in parallel with two reactors filled from the same solvents and reagents. In the past, comparison with IOM samples obtained independently with the CsF-technique developed at Carnegie Institute showed little difference with HF/HCl IOMs (Cody and Alexander 2005; Quirico et al., 2018). Artifact measurements are known to arise with infrared micro-FTIR because IOM samples contain insoluble minerals with varying sizes that generate scattering, which can blur the absorption signal. We have suspicions for C109-12, as the baseline correction was uncertain in the region 1700-1600 cm^{-1}. The accretion of different organic precursors is difficult to address here as no insights into petrography was available for our samples, and we cannot infer the presence of xenolithic clasts. Last, post-accretional processes are a potential source of heterogeneity, as observed in recent falls like Tagish Lake and Sutter's Mills (e.g. Herd et a., 2011; Quirico et al., 2018). Mineralogy, bulk and isotopic compositions of Ryugu samples are consistent with a CI chondrite, more reduced than the least altered CI Alais, and which experienced a hydrothermal event of lower intensity. Therefore, we do not expect a significant impact of fluid circulation, regarding the similarities of IOM composition across CM and CI chondrites when covering a broad range of petrologic subtypes. Last, a possible source of heterogeneity is short-duration thermal metamorphism, rated as stages from I to IV (Nakamura, 2005). According to systematics on a broad array of C1 and C2 chondrites, I_{CH2}/I_{CH3} appears as a suitable tracer of this process, while the aliphatic and carbonyl abundances are less accurate. In this respect, C0109-12, A0108-6, A0108-10 and A0106-23,24,25 appear inconsistent with the CI chondrites Alais, Ivuna and

Orgueil. C0109-12 displays a high I_{CH2}/I_{CH3}, a low intensity aliphatic band and a low intensity carbonyl band (Fig. 2). However, short-duration metamorphism is not confirmed by Raman spectroscopy and the baseline correction of the spectra of this sample are questionable. A0108-6 and A0108-10 display a high I_{CH2}/I_{CH3}, but they were very thin and translucent samples, optically very different than other IOMs. In addition, they display a strong OH band, which does not appear in other IOMs as well. Regarding A0106-23,24,25, it looks similar to IOM from heated stage II C1 and C2 chondrites, but once again Raman spectroscopy does not report short-duration heating for A0108-10, A0106-23,24,25. Accordingly, the spectral heterogeneity cannot be firmly interpreted as the result of short duration heating. Last, the sample C0109-9 seems to depart from other samples in terms of Raman characteristics. However, its infrared spectrum is similar to that of unheated C2s, and the Raman data likely suffer from a statistical bias.

Conclusion: Our data reveal chemical heterogeneity across the IOM samples extracted from a series of Ryugu grains and aggregates. No clear differences are observed between the two chambers A and C. 6 samples are consistent with the IOMs of the three historical CI falls Alais, Ivuna and Orgueil, and strengthens the link with this chondrite class. 4 samples show substantial differences, which cannot be firmly interpreted as the evidence of short duration heating.

Table 1
Samples investigated.

Sample	Grain size	FTIR -IOM	CI-like?
A108-6	~100 µm	y	≠
A108-10	~100 µm	y	≠
A106-4	~500 µm	y	=
A106-6	~500 µm	y	=
A106-23,24,25	~500 µm	y	≠
A108-61	~500 µm	y	=
A108-60	~500 µm	y	=
C0057-6	~500 µm	y	=
C109-5	~500 µm	opaque	
C109-9	~500 µm	y	=
C109-12	~500 µm	y	≠
Orgueil	100-1000 µm	y	

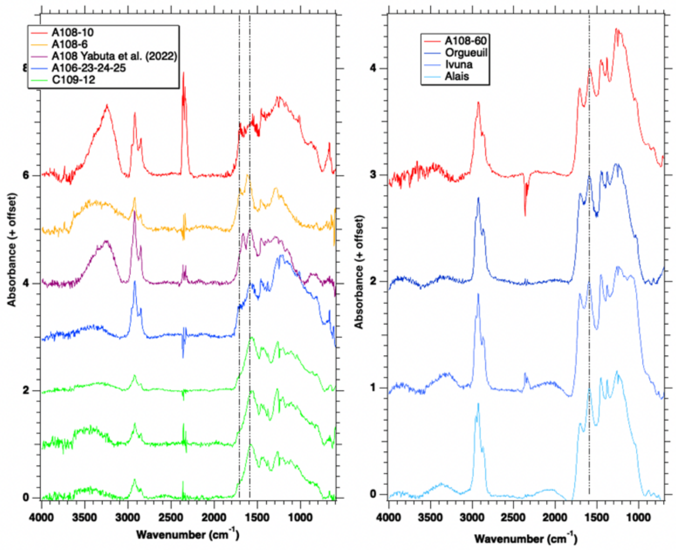

Figure 1: Micro-FTIR of IOM from Ryugu grains and CI chondrites

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