Geochemical Perspectives Letters

Interaction between clay minerals and organics in asteroid Ryugu

J.-C. Viennet[1*], M. Roskosz[1], T. Nakamura[2], P. Beck[3], B. Baptiste[1], B. Lavina[4,5], E.E. Alp[5], M.Y. Hu[5], J. Zhao[5], M. Gounelle[1], R. Brunetto[6], H. Yurimoto[7], T. Noguchi[8], R. Okazaki[9], H. Yabuta[10], H. Naraoka[9], K. Sakamoto[11], S. Tachibana[12], T. Yada[11], M. Nishimura[11], A. Nakato[11], A. Miyazaki[11], K. Yogata[11], M. Abe[11], T. Okada[11], T. Usui[11], M. Yoshikawa[11], T. Saiki[11], S. Tanaka[11], F. Terui[13], S. Nakazawa[11], S.-I. Watanabe[14], Y. Tsuda[11]

Abstract

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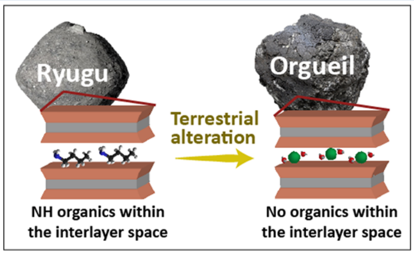

The Hayabusa 2 spacecraft brought back to Earth grains of the carbonaceous asteroid Ryugu. Such grains represent the pristine state of CI chondritic materials and have been preserved from exposure to Earth's atmosphere. Here, we show evidence of the presence of organics trapped within the interlayer space of smectite layers in Ryugu grains. No such organics are found in the Orgueil CI meteorite. We put forward that the organics within the interlayer space of smectite in Orgueil CI meteorite were lost during their oxidation on Earth. Also, we propose that the presence of organics within the interlayers space of smectite might be responsible for the possible NH infrared signature observed in Ryugu particles and potentially to a few large C-type asteroids including Ceres.

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Letter

The sample return mission Hayabusa 2 brought back to Earth the most pristine chondritic material to date, from the C-type asteroid Ryugu (Ito *et al.*, 2022; E. Nakamura *et al.*, 2022; T. Nakamura *et al.*, 2022). Indeed, unlike meteorites or interplanetary dust particles, the Ryugu grains have never been exposed to terrestrial atmosphere and are kept under N_2 in the JAXA Curation Facility at ISAS, Sagamihara. Ryugu grains share numerous features with the chemically primitive but also highly aqueously altered CI group chondrites (E. Nakamura *et al.*, 2022; T. Nakamura *et al.*, 2022; Yada *et al.*, 2022; Yokoyama *et al.*, 2022), hence offering invaluable insights into the protoplanetary disk and asteroidal alteration processes. They also offer a chance to better characterise the terrestrial alteration that CI meteorites underwent since their fall on Earth (Gounelle and Zolensky, 2001; E. Nakamura *et al.*, 2022; T. Nakamura *et al.*, 2022; Yada *et al.*, 2022; Yokoyama *et al.*, 2022).

A puzzling spectroscopic feature of essentially the entire collection of Ryugu grains is the infrared signature of NH-rich compounds as evidenced by the presence of an absorption band at ~3.06–3.1 μm (Fig. 1a; Pilorget *et al.*, 2022; Yada *et al.*, 2022). This feature is observed by two independent instruments in the Hayabusa 2 Curation Facility, both on bulk samples and on several individual grains. The current interpretation of this feature calls for either NH_4^+ phyllosilicates, NH_4^+ hydrated salts and/or nitrogen-rich organics (Pilorget *et al.*, 2022). However, such an infrared signature has never been observed in any meteorite on Earth, but strikingly similar signatures are reported for Ceres (King *et al.*, 1992; De Sanctis *et al.*, 2015; Yada *et al.*, 2022) and a few other asteroids (Takir and Emery, 2012).

In order to provide an explanation for this puzzling spectroscopic feature of Ryugu, we measured a ~500 μm-sized sub-part of the grain C-0061 of Ryugu, and grains several hundred μm in size of the Orgueil CI chondrite meteorite (fell

1. Muséum National d'Histoire Naturelle, Sorbonne Université, UMR CNRS 7590, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Paris, France
2. Tohoku University, Sendai 980-8578, Japan
3. Université Grenoble Alpes, Grenoble 38058, France
4. Center for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60439, USA
5. Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA
6. Institut d'Astrophysique Spatiale, CNRS, Université Paris-Saclay, Orsay 91405, France
7. Hokkaido University, Sapporo 060-0810, Japan
8. Kyoto University, Kyoto 606-8502, Japan
9. Kyushu University, Fukuoka 812-8581, Japan
10. Hiroshima University, Higashi-Hiroshima 739-8526, Japan
11. Institute of Space and Astronautical Science (ISAS), Japan Aerospace Exploration Agency (JAXA), Sagamihara 252-5210, Japan
12. The University of Tokyo, Tokyo 113-0033, Japan
13. Kanagawa Institute of Technology, Atsugi 243-0292, Japan
14. Nagoya University, Nagoya 464-8601, Japan
* Corresponding author (email: jean.christophe.viennet25@gmail.com)

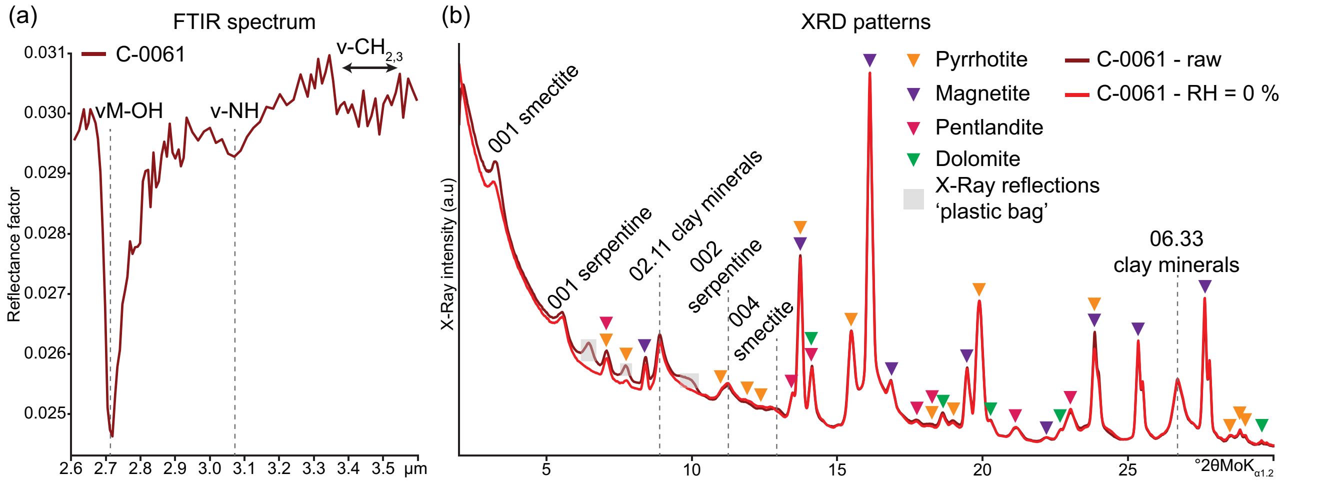

Figure 1 **(a)** FTIR spectrum of the grain C-0061 acquired within the Curation Facility with the MicrOmega instrument (Pilorget *et al.*, 2022) and obtained from the Astromaterials Science Research Group (ASRG *et al.*, 2022). **(b)** XRD measurements and the corresponding peak assignation of the grain C-0061 under "raw" and 0 % relative humidity conditions.

in 1864) by X-Ray diffraction (XRD) under different relative humidities. Such XRD experiments allow investigation of the presence of water molecules or organics within the interlayer space of smectite layers (Viennet *et al.*, 2019, 2020, 2022; Lanson *et al.*, 2022).

The mineralogy of grain C-0061 was first determined by XRD measurement prior to any exposure to air. The grain was transferred under nitrogen from the Curation Facility to Tohoku University, and there it was sealed in an airtight plastic container (referred to as "raw") in a glove box with a low dew point (<−60 °C) and low oxygen pressure (<10 ppm). Like other Ryugu grains, grain C-0061 mainly contains clay minerals, magnetite, pentlandite, pyrrhotite and dolomite (Fig. 1b; E. Nakamura *et al.*, 2022; T. Nakamura *et al.*, 2022), which implies it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral because of their 02.11 and 06.33 reflections at 4.59 and 1.537 Å, respectively. This is consistent with the Fourier Transform Infrared (FTIR) feature at 2.7 μm related to metal-OH vibration of trioctahedral clay minerals (Fig. 1a; Pilorget *et al.*, 2022; Yada *et al.*, 2022) and with their Mg-rich chemical composition (E. Nakamura *et al.*, 2022; T. Nakamura *et al.*, 2022). The XRD peaks at 7.29 and 3.62 Å correspond to the 001 and 002 reflections of serpentine. The positions of the 001 reflection at 12.55 Å (Fig. 2a) and the 004 reflection at 3.15 Å (Fig. 2b) are almost rational, indicating the essentially monohydrated state of the smectite layers (for details please refer to the Supplementary Information; Ferrage, 2016). However, based on thermogravimetric analyses coupled with mass spectrometry on representative Ryugu grains (Yokoyama *et al.*, 2022), the water molecule content within the interlayer space of smectite in the Ryugu samples is low (<0.3 wt. %). Indeed, a monohydrated state for typical saponite would account for ∼2 wt. % of water (Ferrage *et al.*, 2010).

In order to assess the presence (or absence) of water molecules within the interlayer space, XRD measurements under 0 % of relative humidity (referred as 0 % RH) were carried out (see materials and methods and Fig. S-3 in Supplementary Information for details). The 001 reflection shifts from 12.55 Å under raw conditions to 12.66 Å under 0 % RH (Fig. 2a). Furthermore, the intensity of the XRD peak decreases and a fraction of the intensity shifts toward higher angle (*i.e.* toward a dehydrated smectite position; see Supplementary Information). The 00ℓ reflections splitting shows that there are, at least, two populations of smectite phases. While there is only one broad peak centred at 3.15 Å under raw conditions, this peak moves partially to 3.19 Å and a shoulder appears at 3.13 Å at 0 % RH (Fig. 2b). The XRD peak at 3.19 Å corresponds to the smectite layers with water molecules desorbing during the process. Such XRD behaviour could be related to the presence of the mixed layering of dehydrated and monohydrated layers (Ferrage *et al.*, 2010). Hence, such a smectite phase is responsible for the broadening toward higher angles and the intensity drop of the 001 reflection at 12.55 Å under 0 % RH. Nonetheless, the main contribution to the 001 reflection of smectite under 0 % RH is the peak at 12.66 Å. The shoulder centred at 3.13 Å (which does not move at 0 % RH), corresponds to its 004 reflection. The XRD behaviour of these 001 and 004 reflections indicates that water molecules are not present within the interlayer space of these smectite layers of Ryugu.

What could be the species accommodated in the interlayer space of smectite layers at ∼12.6 Å? Among clay minerals, the smectite family is a pivotal agent driving organic carbon sequestration/preservation on Earth and asteroids (Blattmann *et al.*, 2019). The clay/organic interactions occur either at the edges, or within the interlayer space, of expandable clay minerals. When organic molecules are present within the interlayer space of smectite layers, the layer to layer distance of smectite is modified according to the type of organic molecules and their arrangement (Lagaly *et al.*, 2013) and the organics lock the interlayer space by preventing water molecules from entering (Lagaly *et al.*, 2013; Viennet *et al.*, 2019, 2020, 2022). Thus, the XRD behaviour observed for the 001 reflection at 12.66 Å of grain C-0061 under 0 % RH is characteristic of the presence of organic matter within the interlayer space. Such a result also explains both the low water molecule content of the interlayer space of Ryugu grains (0.3 wt. %; Yokoyama *et al.*, 2022) and the lack of a 1.9 μm combination band related to "OH vibrations in H_2O molecules" (Pilorget *et al.*, 2022).

We also performed the same measurements on the CI meteorite Orgueil. While the results obtained on Ryugu point toward organic molecules fixed within the interlayer space of smectite layers, the XRD measurements on Orgueil show that there are no organic molecules within the interlayer space of smectites. Indeed, the XRD peak at 13.27 Å under 42 % RH, which corresponds mainly to the 001 reflection of monohydrated smectite, shifts toward dehydrated smectite layers after exposure

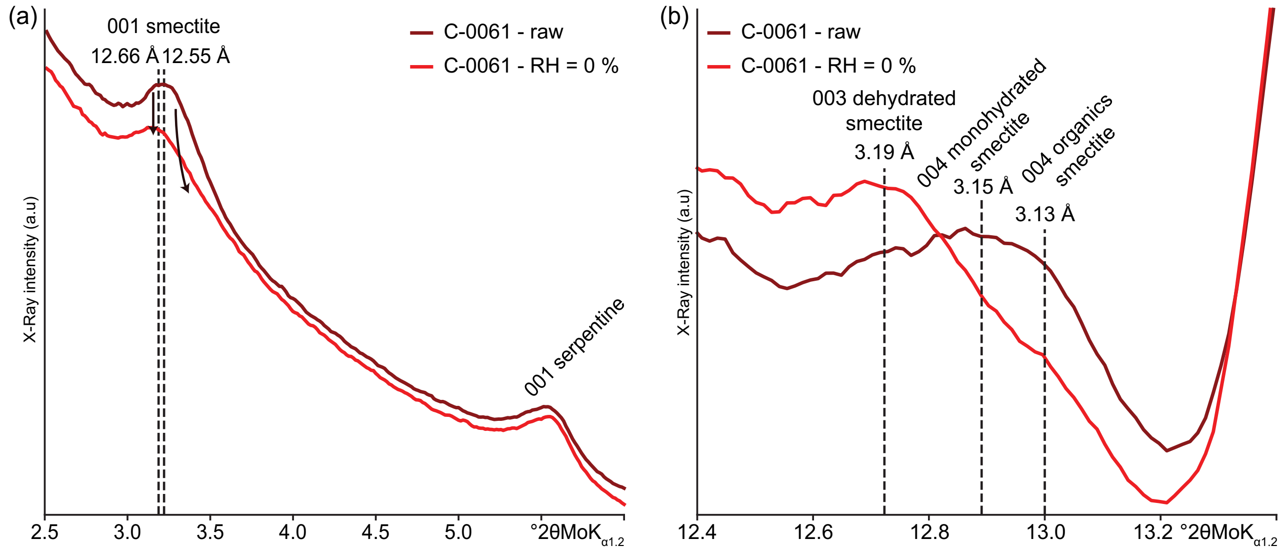

Figure 2 XRD measurements and the corresponding peak assignation of the 00ℓ reflections of the smectite layers of the grain C-0061 under "raw" and 0 % relative humidity (RH) conditions. The arrows indicate the XRD behaviour of the two smectite phases after exposure to 0 % RH.

to 0 % RH (Fig. 3). Hence, there are no organics within the interlayer space of the smectite layers of Orgueil.

Given the strong geochemical, mineralogical and petrological similarities between the Orgueil meteorite and the grains of Ryugu (E. Nakamura *et al.*, 2022; T. Nakamura *et al.*, 2022; Yada *et al.*, 2022), it appears unlikely that this difference could be explained in terms of asteroidal geochemical processes. On the other hand, Orgueil suffered strong terrestrial alteration. Indeed, abundant sulfates form in Orgueil and in other carbonaceous chondrites by reaction of sulfides with atmospheric water in the meteorite (Gounelle and Zolensky, 2001, 2014; Ito *et al.*, 2022; T. Nakamura *et al.*, 2022). Furthermore, Mössbauer analysis shows that Ryugu is overall more reduced than Orgueil (T. Nakamura *et al.*, 2022). Magnetites from Ryugu are stoichiometric while magnetites from Orgueil are anomalously oxidised

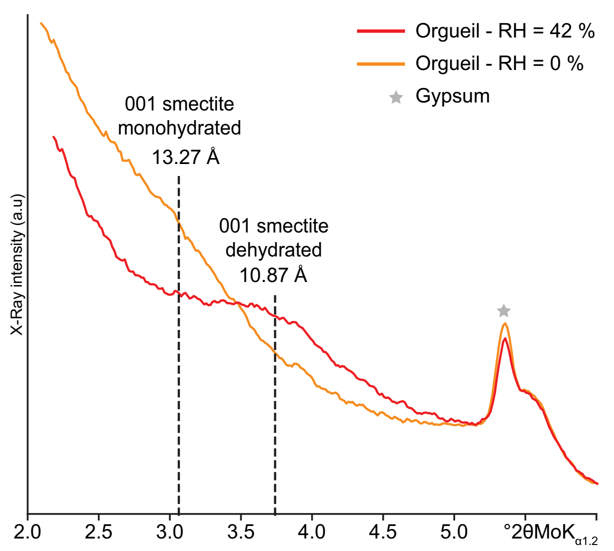

Figure 3 XRD measurements and the corresponding peak assignation of the 001 reflection of the smectite layers of Orgueil under "raw" and 0 % relative humidity conditions.

(Gunnlaugsson *et al.*, 1994; T. Nakamura *et al.*, 2022). Clay minerals from Ryugu are also more reduced than typical CI and CM carbonaceous chondrites found on Earth so far and ferrihydrite is absent in Ryugu samples (T. Nakamura *et al.*, 2022). Degradation of organic molecules could occur *via* Fe oxidation of clay minerals by the formation of hydroxyl radicals (•OH) which then degrade organics (Chen *et al.*, 2019; Huang *et al.*, 2020; Thomas *et al.*, 2021). Moreover, the oxidation of structural Fe in smectite decreases its permanent charge, which in turn decreases the capacity of smectite to adsorb positively charged molecules within their interlayer space. This strongly suggests that the terrestrial alteration of most primitive extraterrestrial samples is even more pervasive than previously suggested. Indeed, in addition to Fe-bearing minerals, organics of carbonaceous chondritic materials can also be modified due to terrestrial oxidation, explaining in part the differences in alkali-bearing organic molecules between Ryugu and Orgueil (E. Nakamura *et al.*, 2022). Note that, recently, XRD revealed variability of the smectite structure in some Ryugu grains (T. Nakamura *et al.*, 2022). Since this variability may point to a diversity of interlayer species, it would be necessary, in the near future, to determine the exact fraction of Ryugu's smectites containing organics within the interlayer space.

The presence of organics within the interlayer space of smectite could help better understand the origins of organics within CI objects. For instance, it has been proposed that the hydrothermal alteration of soluble organics within asteroids could be the origin of insoluble organic matter (IOM) (Cody *et al.*, 2011). Yet, in presence of smectite, the formation of IOM is inhibited by the fixation of a part of the organic molecules in solution within the interlayer space of smectite, preventing the necessary reaction of polymerisation and condensation steps for the formation of IOM (Viennet *et al.*, 2022). Here, due to the presence of organic molecules within the interlayer space, we infer that potentially less IOM was formed during the asteroidal alteration of the parent body of Ryugu and more soluble organic matter was locked down within the interlayer space of smectite layers. Such observations would also argue for origins of IOM prior to parent body processing (Alexander *et al.*, 2007; E. Nakamura *et al.*, 2022).

NH_4^+ phyllosilicates, NH_4^+ hydrated salts and/or nitrogen-rich organics are the likely candidates to explain the infrared NH signature of Ryugu (Pilorget *et al.*, 2022). Yet, ammonium-bearing smectites allow the absorption of water molecules within their interlayer space which will give a XRD behaviour similar to the reference smectite considered here (Supplementary Information Fig. S-3) and a collapsed interlayer space at ~10 Å under 0 % RH (Gautier *et al.*, 2010; Viennet *et al.*, 2019). In addition, the experimental ammoniation of the Orgueil meteorite produced weak absorptions between 3.0 and 3.1 μm while the XRD data demonstrated the NH_4^+ adsorption within the interlayer space of smectite (Ehlmann *et al.*, 2018). Yet, it remains unclear if the attempt at producing the 3.06–3.1 μm infrared feature could be related to particular Orgueil smectite properties or NH_4^+ complexing with organics or other constituents (Ehlmann *et al.*, 2018). Furthermore, NH_4^+ hydrated salts have not been observed so far in Ryugu and are not present in grain C-0061 based on XRD data (Fig. 1b). Instead, the fixation of NH-rich organic compounds in the interlayer space can explain the position of the NH stretching vibration in Ryugu (Fig. 1a), which is shifted to higher wavelengths when organics interact with NH_4^+ within the interlayer space (Gautier *et al.*, 2017) or is due to the presence of NH_3^+ groups (Liu *et al.*, 2013). In addition, the fixation of NH organics within the interlayer space of smectite could offer an alternative hypothesis to the difficulty of producing a clear 3.06–3.1 μm feature by ammoniation of the Orgueil CI meteorite (Ehlmann *et al.*, 2018). We therefore postulate that the XRD behaviour observed here is related to a nitrogen-rich organic matter trapped within the interlayer space of Ryugu smectites. The exact nature of the interactions between the smectite layers and organics remains difficult to determine. Yet when positively charged, NH organics can compensate the permanent charge of smectite (Lagaly *et al.*, 2013; Viennet *et al.*, 2019, 2020, 2022). N heterocyclic compounds, which can form positively charged ions, were found in Ryugu (E. Nakamura *et al.*, 2022) and N-bearing organic compounds were detected in a fluid inclusion in a Ryugu pyrrhotite crystal (T. Nakamura *et al.*, 2022). Note that, similar d-spacing can be obtained for different types of organic molecules and smectite structures (Lanson *et al.*, 2022), which does not allow us to investigate further the nature of organics within the interlayer space of Ryugu's smectite. Achieving a better understanding of the link between the nature of NH organics and smectite structure related to FTIR and XRD behaviours will require many additional experimental studies. By extension, we propose that the reflectance spectra of Ceres may be interpreted as a signature of NH-rich organics within the interlayer space of phyllosilicates instead of NH_4^+ (King *et al.*, 1992; De Sanctis *et al.*, 2015; Yada *et al.*, 2022). Given the ability of smectite layers to adsorb, concentrate, protect and serve as polymerisation templates for organic molecules, they might play a key role for prebiotic reactions which are necessary steps in the origin of life (Bernal, 1951; Viennet *et al.*, 2021), further increasing the astrobiological potential of the dwarf planet Ceres. More IR experimental work on NH-bearing organics and their adsorption within the interlayer space of smectite and comparison to Ceres reflectance spectra would allow a more comprehensive view of the nature of the NH stretching vibrations of Ceres.

Altogether, the results of the present study show that the nitrogen-rich infrared signature in Ryugu could be attributed to NH-bearing organic molecules trapped within the interlayer space of smectite layers in Ryugu. This signature is no longer observed in the Orgueil CI meteorite and perhaps other CI meteorites, most likely because of terrestrial oxidation leading to the oxidation and the desorption of organic molecules within their interlayer space.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2307.

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