Interaction between clay minerals and organics in asteroid Ryugu


Abstract

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 layers in Ryugu 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.

Letter

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 NH4+ phyllosilicates, NH4+ 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

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in 1864) by X-Ray diffraction (XRD) under different relative humidities. Such XRD experiments allow investigation of the presence of water molecules or organic substances 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, and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view. Clay minerals are trioctahedral it can be considered a typical Ryugu grain from a mineralogical and petrological point of view.

The 002 reflection amplitudes of smectite layers (for details please refer to the Supplementary Information) are rational, indicating the essentially monohydrated state of the smectite layers (for details please refer to the Supplementary Information). 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. 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 13.13 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 Å reflection band related to “OH vibrations in H2O 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...
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 (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.

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).

![Figure 2](image2.png)

Figure 2 XRD measurements and the corresponding peak assignment of the 001 reflection 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.

![Figure 3](image3.png)

Figure 3 XRD measurements and the corresponding peak assignment of the 001 reflection of the smectite layers of Orgueil under “raw” and 0 % relative humidity conditions.
NH4+ phyllosilicates, NH4+ hydrated salts and/or nitrogen-rich organics are the likely candidates to explain the infrared NH signature of Ryugu (Pløger 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 NH4+ 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 NH4+complexing with organics or other constituents (Ehlmann et al., 2018). Furthermore, NH4+ 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 NH4+ within the interlayer space (Gautier et al., 2017) or is due to the presence of NH4+ 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 NH4+ (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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References


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Supplementary Information

The Supplementary Information includes:
- Materials and Methods
- Supplementary Information
- Figures S-1 to S-3
- Supplementary Information References

Materials and Methods

Ryugu Grain C-0061
Grain C-0061 of the asteroid Ryugu was provided by the Curation Center at the Extraterrestrial Sample Curation Center, ISAS, JAXA, Japan (P1C). It comes from Chamber C of the Hayabusa2 spacecraft, i.e. samples that were collected at the second collection site on the asteroid, close to the ejecta of the SCI artificial crater. The grain was millimetre-scale in size. Half of the grain was cut and sealed in an airtight plastic container in a N₂ atmosphere glove box at the Curation Center.

Smectite Synthesis
Smectite of saponite composition (Na₀.₄(Mg₃)[Si₃.₆,Al₀.₄]O₁₀(OH)₂) was synthesised from a hydrogel obtained by mixing Na₂SiO₃ ∙ 5H₂O (Sigma Aldrich, >95 %), AlCl₃ ∙ 6H₂O (Sigma Aldrich, 99 %) and MgCl₂ ∙ 6H₂O (Sigma Aldrich, >99 %) in distilled water (18.2 MΩ cm). The hydrogel was mixed at room temperature, then filtered and rinsed (with distilled water) with a vacuum suction filter device. The gel was then placed in 23 mL Teflon reactors and placed in an oven at 230 °C for 4 days, under equilibrium vapor pressure at ~28 Bar. After cooling down, the synthesised smectite was filtered, washed with distilled water and dried at room temperature.

Orgueil Grain
The grain of the Orgueil meteorite was provided by the Museum National d’Histoire Naturelle, Paris, France; it was ~500 µm in diameter.
**XRD Measurements**

Laboratory X-ray diffraction experiments were performed at the X-ray diffraction facility of the Institut de Minéralogie, de Physique des Matériaux et Cosmochimie (IMPMC), Sorbonne Université (Paris, France). A Rigaku MM007HF diffractometer equipped with Varimax focusing optics, a RAXIS4++ image plate detector placed at a distance of 350 mm from the sample and a Mo rotating anode ($\lambda_{K\alpha 1} = 0.709319$ Å and $\lambda_{K\alpha 2} = 0.713609$ Å) at 50 KeV and 24 mA was used, with a scan range of 3–31°2θ and the acquisition time of 45 minutes. The FIT2D program (Hammersley, 2016) was used for the integration of 2D images into 1D patterns after a calibration using a LaB$_6$ standard crystalline sample. The XRD beam size was ~70 µm in diameter. In order to ensure that the measurements are representative of the samples, three XRD patterns were taken for each sample and then the final XRD patterns represent the average of the three measurements.

**XRD Experiments**

XRD experiments under 0% relative humidity (RH) were carried out using capillary made of borosilicate glass. The grains (Ryugu C-0061, Orgueil) and the synthetic smectite were transferred in a dry glove (<0.5 ppm H$_2$O and <0.5 ppm O$_2$) and under 0.9 mbar of Ar atmosphere operating at IMPMC. Then the samples equilibrate with the atmosphere in the glovebox for 1.5 days to allow the desorption of labile the water molecules. Finally, the samples were transferred, in the glove box, into a borosilicate capillary and sealed with cyanoacrylate glue. The sealed capillaries were taken out from the glove box and the XRD measurements were performed immediately after.

**Simulation of XRD patterns**

The simulated XRD patterns were obtained thanks to the Sybilla software developed by Chevron (Aplin et al., 2006). The XRD profile calculation is based on the algorithm initially developed by Sakharov and Drits (1973) and detailed theory of the XRD calculation can be found in Sakharov and Lanson (2013). The program allows to simulate XRD 00ℓ reflections of either pure clay minerals or mixed layers minerals (see Viennet et al., 2015, and references therein). Smectite layers were modelled by using a composition of saponite ($n$(H$_2$O) · Ca$_{0.15}$(Mg$_3$)[Si$_3.7$Al$_{0.3}$]O$_{10}$(OH)$_2$$. For the simulation, a coherent scattering domain size of 14.8 was chosen for all of the clay phases to avoid apparent irrationality. The dehydrated state was simulated with a saponite layer without water molecule and a layer-to-layer distance of 10.0 Å. The monohydrated state was simulated with a saponite layer with one sheet of water molecules in the middle plane of the interlayer space, a content of 3.5 water molecules per unit cell and a layer-to-layer distance set at 12.5 Å. The bihydrated state was simulated with a layer with two sheets of water molecules in the middle plane of the interlayer space, a content of 3.5 water molecules per unit cell and a layer-to-layer distance set at 15.0 Å. The mixed layer mineral was simulated by using the same layer structures described above with a relative proportion 50% for each layer and a random stacking defined according to Markovian statistics.

**IR Measurements**

The IR spectrum of C-0061 shown in Figure 1 was acquired by the MicrOmega hyperspectral imaging instrument installed at the Hayabusa2 Curation Center in Sagamihara (Pilorget et al., 2022). It is an average spectrum of the mm-sized grain, thus representative of the bulk composition of C-0061. The spectrum was obtained by averaging spectra from several hundred pixels (each 22 µm wide), acquired in diffused reflectance geometry. Details of the MicrOmega experiment, calibrations and protocols are provided by Riu et al. (2022).
Supplementary Information

XRD Measurements of Grain C-0061

![XRD Measurements](image)

**Figure S-1** The three XRD measurements taken on grain C-0061 under (a) raw condition and (b) 0% relative humidity (RH).

Structure and Hydration of Smectite Layers

The structure of smectite layer is made of a TOT (T, tetrahedral; O, octahedral) or 2:1 layer and is a part of the family of expandable clay minerals. Isomorphic substitutions in variable amounts by lower charge cations in tetrahedral and/or octahedral sheets induce negatively charged 2:1 layers, the so-called “permanent charge”. This permanent charge is in turn compensated by hydrated exchangeable cations in the interlayer space that are responsible for the hydration properties leading to the expansion of the layer-to-layer distance determined by the position of the 001 reflection (Ferrage, 2016). The layer-to-layer distance is dependent on various factors such as the hydration properties of cations, RH or the permanent charge (Ferrage, 2016). Three states of hydrations exist, corresponding to the intercalation of 1, 2, and 3 planes of water molecules in smectite interlayers leading to a monohydrated ($d_{001} = 11.6–12.9 \text{Å}$), a bihydrated ($d_{001} = 14.9–15.7 \text{Å}$), and a trihydrated ($d_{001} = 18–19 \text{Å}$) hydration states, in addition to the dehydrated one ($d_{001} = 9.6–10.2 \text{Å}$) (Ferrage, 2016). Note that, for a given expandable clay mineral and given environmental conditions, different states of hydrations of smectitic layers could occur within the same crystal that leads to mixed layering. For mixed layer minerals, the $\ell \times d_{00\ell}$ product is not constant and the series of 00$\ell$ reflections is called irrational ($\ell \times d_{00\ell} \neq d_{001}$).

XRD Behaviour of Pure and Mixed Layer Minerals

Figure S-2 shows that for pure clay minerals phases the 00$\ell$ reflection are rational. For instance, the position of the 001 reflection of the bihydrated smectite is equal to 3 multiplied by the position of the 003 reflection ($i.e. d_{001} = 3 \times d_{003}, 15.00 \text{Å} = 3 \times 5.00 \text{Å}$) and so on for the 004 and 005 reflections. In comparison, for mixed layer minerals, the positions of the series of 00$\ell$ reflections are irrational ($i.e. 11.38 \text{Å} \neq 3 \times 3.21 \text{Å}$). Note that the intensity of each XRD pattern correspond to a simulated mixture of 25% bihydrated smectite, 25% monohydrated smectite, 25% dehydrated smectite and 25% random mixed layer mineral composed of 50% monohydrated and 50% dehydrated smectite layers.
Simulated X-Ray diffraction patterns showing the position in Angstrom and the 00ℓ for bihydrated, monohydrated, dehydrated smectites and random mixed layer mineral composed of 50% of monohydrated and 50% of dehydrated smectite layers.

**XRD Experiments on a Reference Synthetic Smectite**

A saponite (Na0.4(Mg3)Si3.6Al0.4O10(OH)2) was analysed by XRD in air and then prepared according to the procedure described in the method part. Under 42% RH (room humidity), the reference smectite presents a 001 reflection at 12.76 Å and a 004 reflection at 3.14 Å (Fig. S-3). The irrationality of the 00ℓ reflections is probably due to both a low coherent scattering domain size (leading to apparent irrationality, shift to lower angle of the 001 reflection) and to mixed layering between monohydrated and bihydrated layers (Ferrage et al., 2010). Hence, such XRD peak positions mainly indicates that smectite has a monohydrated state (Ferrage et al., 2010). After equilibrium under 0% RH, the 001 reflection shifts to 10.43 Å and its 003 reflection shift at 3.25 Å. Again, the irrationality of the 00ℓ reflections could be attributed to both a low coherent scattering domain size and mixed layering between dehydrated and monohydrated layers (Ferrage et al., 2010). Typically, such XRD peak positions correspond mainly to dehydrated smectite (Ferrage et al., 2010). We note that the 004 reflection of dehydrated smectite and the 003 reflection of monohydrated smectite are not detectable on our reference synthetic material due to the structural factor of smectite that leads to low or absence of such reflection (such XRD behaviours are illustrated in the simulated XRD patterns for smectite in Fig. S-2). This reference experiment demonstrates the efficient removal of the water molecules from the interlayer space of smectites.
Figure S-3  XRD measurements and the corresponding peak assignment of the 00ℓ reflections of the synthetic smectite under 42 % and 0 % RH conditions for (a) 001 reflections and (b) 003 and 004 reflections of smectite.

Supplementary Information References