

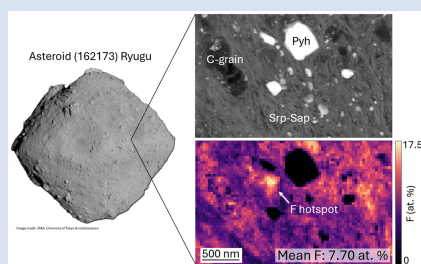
Fluorine in the late fluids of asteroid Ryugu

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<https://doi.org/10.7185/geochemlet.2637>

Abstract



Fluorine is a highly reactive halogen whose distribution and speciation may provide key insights into fluid evolution and element mobility in planetary materials. Yet, despite its cosmochemical significance, the phase carrier(s) of fluorine, its speciation and behaviour during fluid-rock interactions are still enigmatic. Here, we report the occurrence of fluorine associated with phyllosilicates at the nanometre scale in Ryugu samples. We carefully evaluated the possibility of exogenous contamination, but several lines of evidence indicate that fluorine is most likely indigenous. It is concentrated in particular in saponite, possibly *via* OH-F substitution, and/or as interstitial fluoride salts. These observations are interpreted as the result of fluorine release from primary carrier(s) and its subsequent concentration within late stage, highly saline

fluids. Limited phosphorus and sodium availability likely restricted apatite, Mg, Na phosphates and Na carbonate formation, preventing them from acting as a major sink for fluorine and favouring its retention within phyllosilicates. This finding expands the scope of previously documented brine related mineral assemblages in Ryugu and Bennu and reveals an unexpected behaviour of halogens in primitive Solar System bodies.

Received 11 July 2026 | Accepted 7 September 2026 | Published 22 October 2026

Introduction

Fluorine and other halogens play important roles in geo-, bio-, and cosmo-chemistry (Harlov and Aranovich, 2018). Their abundances in primitive extraterrestrial materials, such as carbonaceous chondrites, provide valuable constraints on the chemical and physical conditions of the early Solar System. However, uncertainties remain regarding their behaviour during its formation and evolution. For instance, it is unclear which phases host these elements during the nebular phase and how they respond to alteration processes in the asteroidal parent bodies (Brearley and Jones, 2018; Barnes and Zolensky, 2022).

The most recent estimates for halogen contents in CI chondrites are Cl = 717 ± 110 µg/g, F = 92 ± 20 µg/g, Br = 3.77 ± 0.90 µg/g, and I = 0.77 ± 0.31 µg/g (Lodders and Fegley, 2023). Although CI chondrites exhibit the highest chlorine and F contents among carbonaceous chondrites, only a single report exists of a fluorite (CaF₂) grain occurring in a CI-like clast within the Tsukuba ordinary chondrite (Nakashima *et al.*, 2003), and while F-rich apatite occurs in Orgueil, no chlorine bearing phases have been identified (Brearley and Jones, 2018; Harrison *et al.*, 2025). Recently, Mg, Na phosphates have been reported in a CI-like clast in Cold Bokkeveld (CM2 chondrite) and in Oued Chebeika 002, with chlorine detected in the former and both F and chlorine in the

latter (Gattacceca *et al.*, 2025; Lee *et al.*, 2025a). This apparent discrepancy between bulk halogen abundances and the scarcity of discrete halogen bearing phases has led to debate regarding the mineralogical hosts of halogens in these meteorites. The identification of halogen bearing phases in CI chondrites is complicated by their extensive aqueous alteration, which has deeply modified the original mineralogy (Lee *et al.*, 2025b), consuming primary halogen bearing phases and redistributing halogens into secondary minerals. For example, chlorine has been observed in association with phyllosilicates and organic matter (Schöler *et al.*, 2005; Le Guillou *et al.*, 2014; Brearley and Jones, 2018), although these associations may also reflect the result of terrestrial weathering. Consequently, the distribution of halogens in CI chondrite parent bodies remains a key unresolved question.

Samples returned by the Hayabusa2 and OSIRIS-REX missions, which delivered material from the CI-like asteroids Ryugu and Bennu, allowed the study of pristine CI-like materials unaffected by terrestrial weathering. Ryugu samples contain chlorine bearing organics, halite and Na carbonates, and Mg, Na phosphates containing F (Nakamura *et al.*, 2023; Matsumoto *et al.*, 2024). Na carbonates and Mg, Na phosphates containing F, halite and Na fluoride have also been identified in Bennu samples (McCoy *et al.*, 2025; Singerling *et al.*, 2025). The

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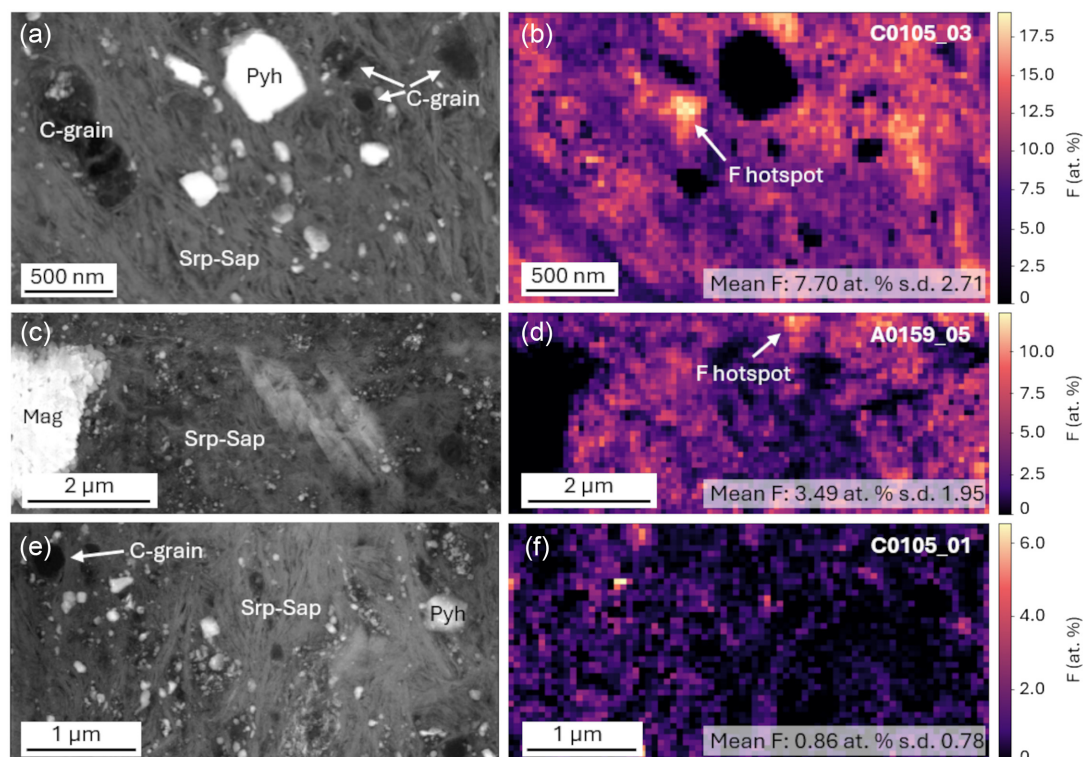


Figure 1 Distribution of F within the phyllosilicates. (a, c, e) High angle annular dark field (HAADF) images of three different FIB sections (C0105_03, A0159_05, and C0105_01). (b, d, f) Corresponding STEM-EDS F concentration maps (in at. %). Map pixel sizes are 34 nm (b), 85 nm (d), and 60 nm (f). Colour scales are linear. Fluorine is associated with the phyllosilicates (Srp-Sap), whereas organic particles (C-grain), magnetite (Mag), and sulphides (Pyh) do not show detectable F. The F signal within the organic grain in (b) results from its intergrowth with phyllosilicates, as visible in the HAADF image in (a). Fluorine content varies between samples and within individual sections, ranging from areas with no detectable F to localised hotspots reaching an average of ~14.5 at. %. Mean F values (at. %) and standard deviations (s.d.) are reported for each FIB section and were calculated using only pixels attributed to phyllosilicates; pixels corresponding to other phases were excluded.

identification of these phases in returned samples confirms that the halogen content of CI chondrites is intrinsic and not the result of terrestrial weathering or contamination. Moreover, these minerals have been interpreted to have formed from late brines, highlighting the role of such fluids in concentrating alkalis and halogens and the potential of halogens to serve as tracers of late stage aqueous processes.

Here, we present analyses of Ryugu samples revealing locally high F abundances in phyllosilicates. These observations open the discussion on F speciation and partitioning, providing insights on the geochemical processes that occurred during the latest stages of aqueous alteration on CI parent bodies.

Material and Methods

The Ryugu samples are from chambers A (sample A0159) and C (sample C0105-045). Eight focused ion beam (FIB) sections were prepared from grain A0159, six from the main grain and two from detached grains found alongside. Four FIB sections were prepared from grain C0105-045. Analyses were conducted using scanning transmission X-ray microscopy (STXM) coupled with X-ray absorption near-edge structure (XANES) spectroscopy, scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR), see details in [Supplementary Information](#).

Fluorine Distribution and Contamination Assessment

Fluorine is preferentially associated with phyllosilicates (Fig. 1). The mean F concentration measured for the phyllosilicates within each FIB section ranges from undetectable to ~7.70 at. % (Table S-2, Fig. S-5), with pronounced spatial variability, as shown by the STEM-EDS maps (Fig. 1). The Mg/Si ratios suggest that at least two thirds of the phyllosilicates are saponite. This represents a conservative estimate, as many data points are close to the saponite end member, suggesting that the proportion of saponite may be higher in some of the samples (Figs. 2a, S-5). Fluorine is also detected within one carbonate grain (average 1.05 at. %; Fig. S-6), but is otherwise absent from oxides, sulphides and individual organic particles (Figs. 1, S-6).

Fluorine also shows an anticorrelation with O (Figs. 2b, S-7), consistent with substitution of OH^- by F^- in phyllosilicates. However, the observed O-F anticorrelation does not follow the expected 1:1 trend, but rather shows a ~1.5:1 trend. This deviation may reflect the complex intergrowth of serpentine and saponite, which have different O/OH ratios, as well as the preferential loss of F relative to O under the electron beam (Fig. S-8). No clear correlations are observed with other elements, except carbon. Concentrations of chlorine and Na range from undetectable to 0.8 at. % and 1.25 at. %, respectively (Fig. S-9).

Some highly localised hotspots (<100 nm) show elevated F concentrations relative to the surrounding area,

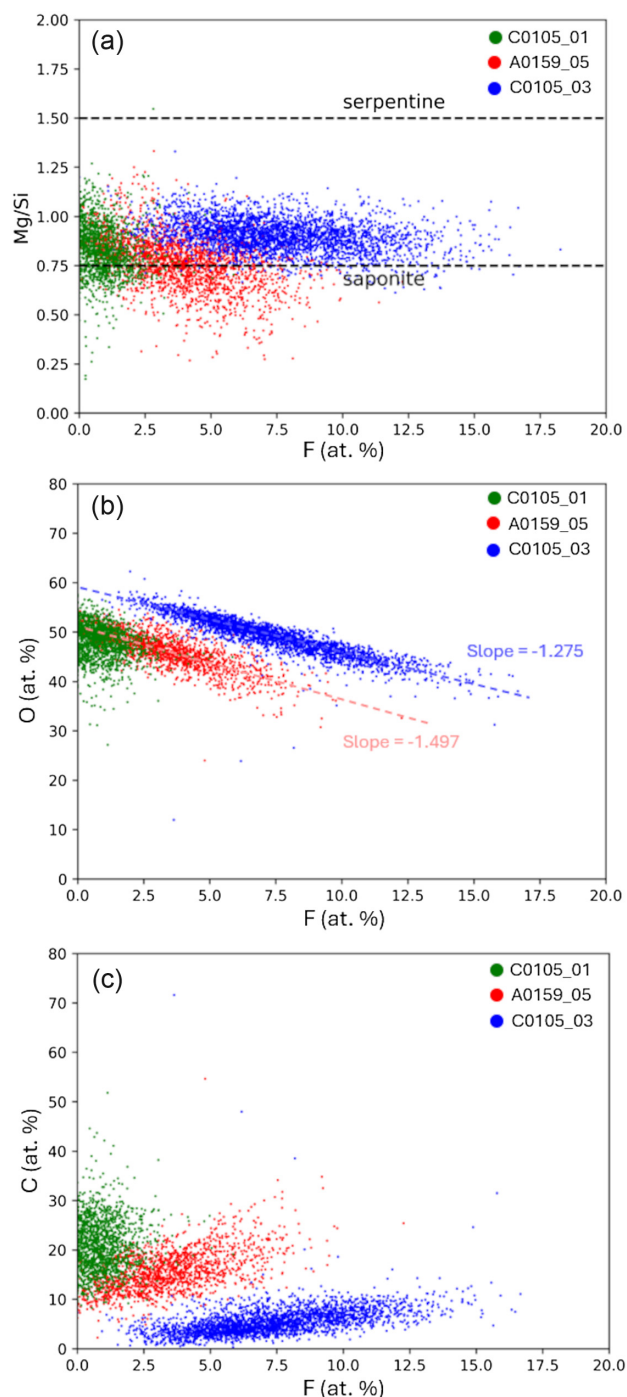


Figure 2 Relationship between F and Mg/Si (a), O (b) and C (c) in the three samples shown in Figure 1. Each dot corresponds to one phyllosilicate pixel in a STEM-EDS map. The Mg/Si ratios indicate that saponite dominates over serpentine, suggesting that F preferentially associates with saponite. The dashed line at Mg/Si = 0.75 marks the low charge saponite end member. The anticorrelation between F and O indicates substitution of OH by F, while the non-ideal 1:1 relationship likely reflects partial loss of F and O during analysis and the complex saponite-serpentine intergrowth. The positive F-C trend supports either co-incorporation of F and soluble organics within porous phyllosilicates or, less likely, the presence of fluorinated organics.

accompanied by an increase in C but no increase in other elements (Fig. 2c). These areas appear darker in the HAADF images (Fig. 1) possibly reflecting organic matter within the phyllosilicate porosity.

Given that the F-C correlation could reflect the presence of fluorinated organic compounds, which are common contaminants (Roesch *et al.*, 2023), we carefully evaluated this hypothesis. However, several lines of evidence support an indigenous origin for the detected F: (i) All samples were prepared and stored under identical conditions, yet F is detected in FIB sections from grains A0159 and C0105-045, but not in FIB sections from the detached grains associated with A0159 (Fig. S-5), suggesting that its occurrence is not related to preparation or handling. (ii) Neither XANES nor FTIR analyses reveal unambiguous C-F signatures, making the presence of fluorinated organic contaminants unlikely (Figs. S-10, S-11). (iii) Fluorine has previously been reported in Bennu and Ryugu samples, where it occurs in halides and Na carbonates (Matsumoto *et al.*, 2024; McCoy *et al.*, 2025; Singerling *et al.*, 2025).

Fluorine Speciation

The STXM based XANES spectra collected at the F K-edge exhibit a broad absorption feature between 691–695 eV (Fig. 3), with no difference between F hotspots and the surrounding matrix (Fig. S-10). In contrast, synthetic F bearing smectite (hectorite; see SI) shows two distinct peaks at 690 and 694 eV (Fig. 3). This discrepancy may reflect the small domain size and low crystallinity of Ryugu phyllosilicates, which may contribute to the broadening of the spectral features. In addition, F in Ryugu may be predominantly adsorbed on phyllosilicate surfaces rather than being incorporated in the structure, as in synthetic hectorite, which could further modify the F K-edge spectral response. Moreover, Ryugu phyllosilicates have been described as an intergrowth of smectite (saponite) and serpentine (Nakamura *et al.*, 2023). Thus, differences in phyllosilicate mineralogy and F speciation may both contribute to the distinct spectral response observed in Ryugu. The broad absorption observed in Ryugu also shares similarities with reference MgF_2 (sellaite) and fluorinated organic reference spectra (Roesch *et al.*, 2023), although notable differences persist (Fig. 3), particularly an additional low energy absorption shoulder absent from MgF_2 and fluorinated organic spectra.

The FTIR analysis reveals spectra similar to those reported for other Ryugu particles, with the main bands in the 1000–1800 cm^{-1} region assigned to phyllosilicates and organic matter (Fig. S-11). This region also overlaps with the spectral range in which C-F vibrations are typically observed (1000–1400 cm^{-1}). However, no distinct bands that can be unambiguously attributed to C-F species are clearly visible, even in sample C0105_03, which exhibits the highest F content (Fig. S-11).

The exact speciation of F remains uncertain, but combining XANES, FTIR and EDS observations, the following hypotheses can be considered. 1) F may be incorporated into phyllosilicates by substituting for OH groups. Substitution at the OH site has been occasionally reported in extraterrestrial materials. Recently, Topping *et al.* (2025) reported sulphur bearing serpentine in several carbonaceous chondrites, including Ryugu, while chlorine bearing smectite has been described in the ordinary chondrite Bishunpur (Alexander *et al.*, 1989). The OH-F substitution in phyllosilicate involves two mechanisms: (i) F could be incorporated directly into the forming phyllosilicate if the F activity in the mineralising fluid is high enough (Thomas *et al.*, 1977), and (ii) F may substitute surficial OH groups by adsorption after phyllosilicate formation (Du *et al.*, 2011). Based on mass balance and mixing calculations, the inferred degree of OH-F substitution in our samples ranges from ~4 % to 50 % (Fig. S-12). 2) F may occur as nanoscale fluoride salts, including cryolite-like (Na_3AlF_6) phases formed through interaction between F-rich fluids and phyllosilicates (Du *et al.*, 2011), or

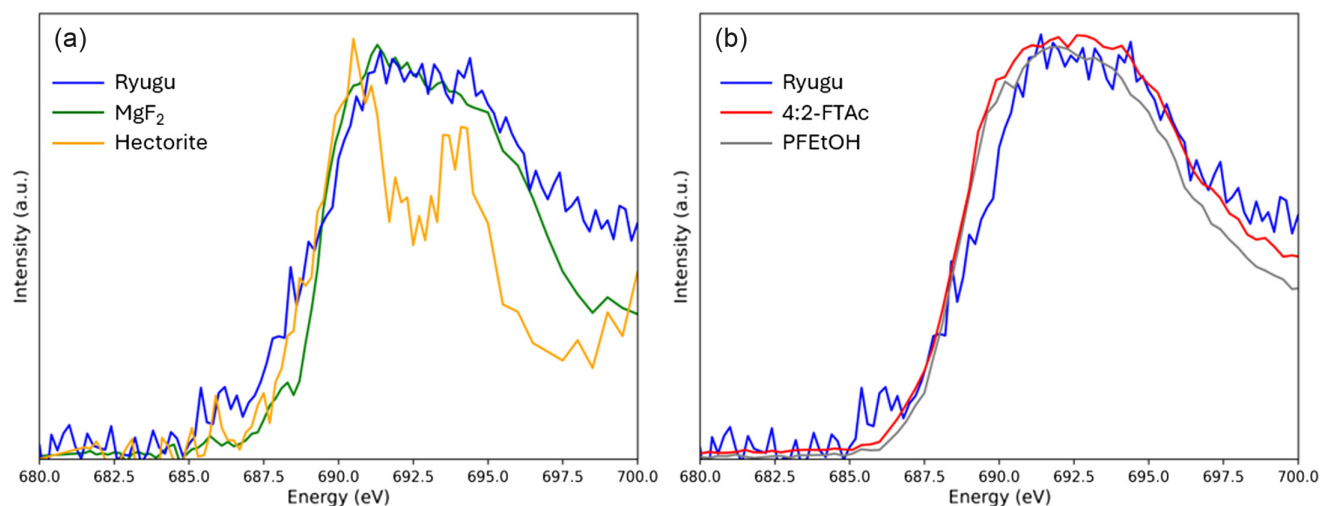


Figure 3 STXM based XANES spectra at the F K-edge of Ryugu's matrix and different inorganic and organic compounds. **(a)** Spectra of the F bearing phase in Ryugu (blue), a synthetic hectorite (orange), and MgF_2 (green). **(b)** Spectra of the F bearing phase in Ryugu (blue), and two fluorinated organic compounds from Roesch *et al.* (2023): 4:2-FTAc (4:2-fluorotelomeracrylate; red) and PFtEtOH (trifluoroethanol; grey).

as NaF and MgF_2 precipitated from late stage brines. Although MgF_2 would be expected to produce a positive Mg-F correlation, variations in the serpentine/smectite ratio may mask this relationship, allowing minor MgF_2 to occur without generating a clear positive Mg-F correlation (Fig. S-13). A possible Na-F relationship is also observed in some data sets, with the most F-rich samples showing slightly elevated Na (Fig. S-9), consistent with the possible presence of Na bearing fluoride phases such as NaF or cryolite. The identification of NaF in asteroid Bennu supports this interpretation (McCoy *et al.*, 2025). However, Na concentrations are low (<1.25 at. %). Thus, if Na bearing fluoride phases are present, they are likely to be very minor. 3) F could be organic in nature, as suggested by the F-C correlation in the EDS data (Fig. 2c). However, fluorination of organic matter is complex, and as discussed above, neither XANES nor FTIR analyses show distinct spectral signatures unequivocally attributable to C-F bonds (Figs. S-10, S-11). Therefore, although the presence of minor amounts of F bonded to C cannot be completely excluded, the apparent correlation observed in the EDS data more likely reflects the late stage percolation of fluids enriched in both F and soluble organic compounds through phyllosilicate porosity (Le Guillou *et al.*, 2014; Viennet *et al.*, 2023). These hypotheses are not mutually exclusive, but incorporation of F through substitution for OH in phyllosilicates, possibly with an additional contribution from fluoride salts, is considered the most likely explanation for the observed F in the samples.

Source of Fluorine and Late Fluid Enrichment

The bulk halogen inventory of Ryugu is poorly constrained, except for chlorine, the abundance of which ($776 \pm 21 \mu\text{g/g}$; Yokoyama *et al.*, 2022) is nearly identical to that of CI chondrites ($717 \mu\text{g/g}$; Lodders and Fegley, 2023). Given this similarity, it can be hypothesised that the F content of Ryugu should fall within the range measured for CI chondrites ($92 \pm 20 \mu\text{g/g}$; Lodders and Fegley, 2023). Instead, the F content observed in our samples is markedly higher (at least two orders of magnitude higher than CI chondrite value), pointing to a significant enrichment relative to CI chondrite and suggesting local enrichment.

Regarding the origin of F, it is likely that one or more F bearing phases were incorporated into the matrix protolith,

which consisted, among other components, of amorphous and anhydrous silicates, sulphides, organic matter, and ices. However, the exact nature of these F bearing phases, formed under nebular conditions, remains uncertain. Fluorine has first been proposed to condense as fluorapatite (Lodders, 2003). However, nebular reactions required to form fluorapatite are complex, involving diffusion of cations and anions between different mineral phases, and are unlikely to occur efficiently in the solar nebula and fluorapatite is more likely to form during parent body evolution (Lodders and Fegley, 2023), as supported by petrological evidence (Lewis and Jones, 2016; Brearley and Jones, 2018; Harrison *et al.*, 2025). Another possibility is that F condensed through reactions of HF with silicate minerals and metal alloys, forming metal fluorides such as NaF, CaF_2 , MgF_2 , and FeF_2 (Lodders and Fegley, 2023). The presence of MgF_2 has been proposed in enstatite chondrites, although no direct mineralogical evidence has been reported (Rubin and Choi, 2009). Zolotov and Mironenko (2007) suggested that chlorine could have been accreted in chondrites as HCl hydrates, raising the possibility that HF hydrates were also present in the solar nebula.

Regardless of the identity of the primary F bearing phases, extensive aqueous alteration on the parent body likely led to their alteration and F release into the fluid. Because F enrichment is necessarily localised, a mechanism is required to explain its concentration in specific regions.

Previous studies of Ryugu and Bennu have reported localised elemental enrichments, particularly in Ca and Na, which have been interpreted as part of an evaporitic sequence precipitated from brines (Matsumoto *et al.*, 2024; McCoy *et al.*, 2025; Singerling *et al.*, 2025). Na carbonates and Mg, Na phosphates commonly occur as veins within Na-rich phyllosilicates, suggesting precipitation within fractures (Matsumoto *et al.*, 2024; McCoy *et al.*, 2025). The same is true for Ca, as in Ryugu sample A0159 a millimetre scale dolomite vein has been identified. This grain is strongly enriched in carbonates relative to the average Ryugu abundance (22.7 vol. % *vs.* 3 vol. %; Jossé *et al.*, 2025). Dolomite, like Na carbonates, may have formed from brines (Libourel *et al.*, 2026). These textural and chemical features indicate that late stage brines played a key role in elemental enrichment, with fracture/pore-controlled fluid flow promoting localised concentration of dissolved species (Iizuka *et al.*, 2025). Moreover, Na carbonates show F concentration comparable to those observed in our samples, ranging from 3.31 to 6.01 at. %

(Matsumoto *et al.*, 2024; Singerling *et al.*, 2025), suggesting that F was available in the fluid and became concentrated during late stage brines evolution.

Although Na carbonates were not observed in our samples, possibly reflecting limited Na availability, the most F-rich samples exhibit slightly elevated Na relative to those with lower F abundances (Fig. S-9). This relationship suggests coupling between alkaline elements and F, consistent with brine mediated concentration processes. We therefore propose that F enrichment occurred during the latest stages of aqueous alteration, with F concentrated in residual brines within pore spaces and fractures. Because Na carbonates did not form in our samples, and because limited phosphorus availability likely restricted the formation of apatite and Mg, Na phosphates, phosphate phases may have remained spatially decoupled from F-rich fluids, thereby limiting F uptake. Under these conditions, F was preferentially incorporated into saponite, replacing OH groups by absorption, and may also have precipitated as F bearing salts.

Conclusions

We observed heterogeneous F enrichments in phyllosilicates in Ryugu grains, suggesting the importance of late stage fluids in concentrating this element. However, further studies on additional Ryugu samples, and possibly on Benu and Oued Chebeika 002, are needed to better constrain F variability, its speciation, and the enrichment mechanism. In addition, measuring bulk F concentration in Ryugu samples, as recommended by the Ryugu Reference Project (Yokoyama *et al.*, 2026), will help clarify whether the observed F enrichment is restricted to specific samples or is more widespread among Ryugu materials. A clearer understanding of fluorine's cosmo-/geo-chemical behaviour will also provide insights into halogen fractionation, thermodynamical modelling of fluorine in fluid-rock interactions, and the evolution of volatile elements in the early Solar System.

Acknowledgements

We wish to thank David Troadec for the preparation of the FIB sections, as well as Christian Vogel for providing the raw XANES data of published fluorinated organic compounds. We are particularly thankful to Rachid Belkou, Sufal Swaraj and Stefan Stenescu for their help on the HERMES STXM beamline at the SOLEIL synchrotron. We also thank all the members of the Hayabusa2 project for their technical and scientific contributions. The Ryugu grain A0159 analysed in this study was allocated to the Institut d'Astrophysique Spatiale (IAS, Orsay). Small fragments found alongside A0159 were prepared in Japan by Kentaro Hatakeda and transferred by IAS to University of Lille in the framework of the LARCAS French collaboration project. We are grateful to K. Hatakeda and the JAXA Curation team for their efforts in preparing and transferring the A0159 fragments. We also thank the LARCAS members for useful discussions. This work was carried out at the electron microscopy facility of the Advanced Characterization Platform of the Chevreul Institute, University of Lille-CNRS. This project has been funded by ISITE ULNE and the "Métropole Européenne de Lille" through the "TEM-Aster project", and the ANR project LARCAS under grant ANR-22-CE49-0009-01 of the French Agence Nationale de la Recherche. The Chevreul Institute is thanked for its help in the development of this work through the CHEMACT project supported by the "Ministère de l'Enseignement Supérieur de la Recherche et de l'Innovation", the region "Hauts-de-France" and the "Métropole Européenne de Lille". Finally, we sincerely thank Editor

Romain Tartèse for handling the manuscript, and Rhian Jones and Martin Lee for their thoughtful and constructive reviews, which helped improve the manuscript.

Editor: Romain Tartèse

Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2637>.



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Cite this letter as: Conconi, R., Le Guillou, C., Laforet, S., Marinova, M., Leroux, H., Jossé, L., Aléon-Toppini, A., Dionnet, Z., Brunetto, R., Bernard, S., Dazas, B., Miyake, A., Noguchi, T. (2026) Fluorine in the late fluids of asteroid Ryugu. *Geochem. Persp. Let.* 42, 21–26. <https://doi.org/10.7185/geochemlet.2637>

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Fluorine in the late fluids of asteroid Ryugu

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Supplementary Information

The Supplementary Information includes:

- Materials
- Methods
- Table S-1 and S-2
- Figures S-1 to S-12
- Supplementary Information References

Materials

Ryugu samples

In 2020, the Japan Aerospace Exploration Agency (JAXA)'s Hayabusa2 mission delivered to Earth 5.4 g of samples from the carbonaceous asteroid (162173) Ryugu (*e.g.*, Yada *et al.*, 2022; Yokoyama *et al.*, 2022). The Hayabusa2 spacecraft collected two sets of samples: one from the surface (Chamber A), representing the outermost layer of Ryugu and therefore affected by space weathering, and one from the subsurface (Chamber C), excavated from a crater created by an impact device. The latter provides access to material that has potentially less been exposed to space weathering. Samples from both chambers (sample A0159 and sample C0105-45) are analysed in this study.

Hectorite sample

A synthetic hectorite sample was used to compare the STXM data with that of Ryugu. The hectorite has been synthesized and characterized by Dazas *et al.* (2013; 2024), with a reported composition, measured by particle-induced gamma- and X-ray emissions, of $\text{Na}_{0.69}\text{Mg}_{5.31}\text{Li}_{0.69}\text{Si}_{8.0}\text{O}_{20}(\text{OH})_{0.76}\text{F}_{3.24}$. Minor quartz (SiO_2), sellaite (MgF_2), and enstatite (MgSiO_3) were also reported, attributed to synthesis residues. Our STEM-EDS analyses on the same material reveal a similar composition (Table S-1), with contamination by MgF_2 and CaF_2 (Fig. S-1). The slight differences arise from the different characterization approaches, bulk versus localized, and from the fact that Li cannot be detected by EDS.

Table S-1 Composition of hectorite and MgF_2 in atoms per formula unit (a.p.f.u.) as reported by Dazas *et al.* (2013) and as measured in this study by STEM-EDS analysis. The a.p.f.u. values were calculated on the basis of 8 Si atoms, and the O content was determined by subtracting the F value from a total of 24 O.

El.	Hectorite (a.p.f.u.; Dazas <i>et al.</i> , 2013)	Hectorite (a.p.f.u.; this study)	MgF_2 (a.p.f.u.; this study)
Al	Not reported	0.09	
Ca	Not reported	0.39	
Na	0.69	0.03	
Li	0.69	Not measured	
Mg	5.31	5.18	7.80
Si	8.00	8.00	
F	3.24	4.40	14.54
O	20.76	19.60	

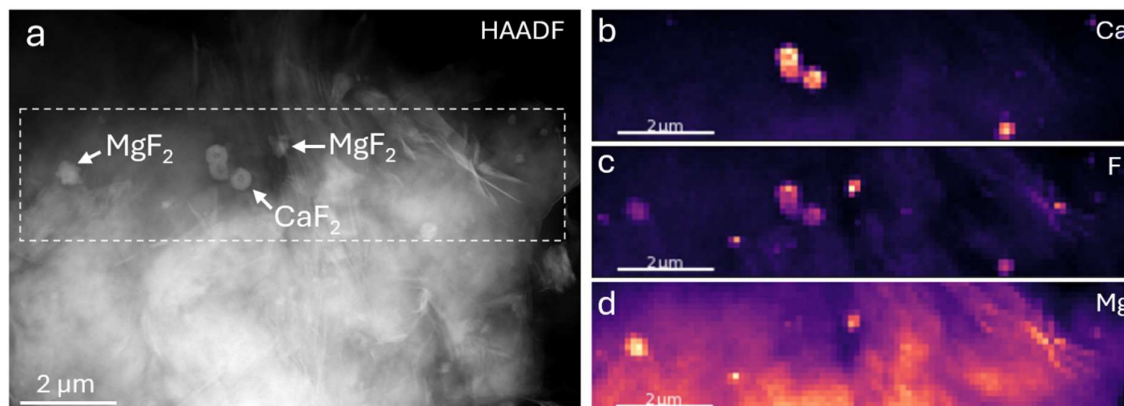


Figure S-1 STEM-EDS maps of hectorite. **(a)** HAADF image showing presence of MgF_2 and CaF_2 . The dashed white rectangle indicates where the EDS analysis was performed. **(b–d)** Elemental distribution maps of Ca, F, and Mg in the sample, highlighting the presence of MgF_2 and CaF_2 . Pixel size: 121 nm.

Methods

FIB extraction

FIB lamellae (approximately $20 \times 6 \mu\text{m}$) were extracted at the Institute of Electronics, Microelectronics and Nanotechnology (IEMN) of the University of Lille using a Zeiss Crossbeam 550 L instrument. The FIB sections were extracted from rough grains (C0105 and small grains found alongside A0159) and from grains with a plasma-FIB-polished surface (A0159; Jossé *et al.*, 2025). The grains were secured using C-tape during FIB cuts. The sections were first excavated using a 30 keV Ga beam, then thinned down to ~ 100 nm using a 10 keV beam and polished at 2 keV to remove surface implantation damage.

Transmission electron microscopy

TEM observations were performed at the Electron Microscopy Facility of the Chevreul Institute at the University of Lille, using a Thermo Fisher TITAN Themis operating at 300 keV in scanning TEM mode (STEM). The microscope is equipped with a high-brightness Schottky field emission gun (FEG), a super-X windowless four-quadrant silicon

drift detector (SDD) EDS system, different annular dark field detectors, a Wien filter type monochromator and a probe aberration corrector, allowing a spatial resolution of 70 pm and flexibility in choosing the electron dose. High annular dark field (HAADF) images were collected with a probe semi-convergence angle of 20 mrad and a probe current of 50 pA. STEM-EDS maps were collected with a probe semi-convergence angle of 5 mrad, a spot size of 2 nm and a probe current between 300 and 500 pA.

Fluorine is known to volatilize during TEM observations due to the strong interaction of the electron beam with the sample (Capitani, 2019). For this reason, to avoid beam damage and analytical artifacts, EDS maps were collected in multi-frame mode with a dwell time between 2 and 20 μ s and continuous scanning over a total time of 5-12 hours for large maps (A0159_02; A0159_05; A0159_06; C0105_01; C0105_03) and 1-2 hours for smaller maps (A0159_01; A0159_03; A0159_04; A0159_g13; A0159_g14; C0105_02; C0105_04). Although this approach minimizes F volatilization, some F loss still occurred. As illustrated in Figure S-2, a slight variation in F content is observed from the first 500 frames to the last 500 frames (10000 frames in total; sample A0159_05). Quantification reveals that the F concentration in the first 500 frames is 3.14 at. %, whereas in the last 500 frames it decreases to 2.45 at. %, corresponding to a 22% loss. Oxygen also shows a minor variation from the first to the last frames, a well-documented phenomenon in 2:1 dioctahedral phyllosilicates, where dehydroxylation can occur under electron-beam (Kogure, 2007). All frames were used for quantification, so the reported fluorine and oxygen values may be slightly underestimated due to volatilization. Quantification of the EDS data were done applying absorption correction using experimentally derived *k*-factors (Conconi *et al.*, 2023, 2025; Le Guillou *et al.*, 2024). EDS data were processed using the open-source software Python package HyperSpy (de la Peña *et al.*, 2017). Background fitting and subtraction were done using a Bremsstrahlung model (Zanetta *et al.*, 2019). Peak fitting and deconvolution were performed with a Gaussian function, and the integrated intensity were used for quantification. The $F_{K\alpha}$ line and $Fe_{L\alpha}$ partially overlap, being centred at 677 eV and 705 eV, respectively. To assess that the measured F signal is real and not an artifact from the $Fe_{L\alpha}$ contribution, we compared residuals of the fitting performed with and without $F_{K\alpha}$ in the model. This test was applied to average spectra from two samples: C0105_1 (low F content, average 0.86 at. %) and C0105_3 (high F content, average 7.70 at. %). In sample C0105_3, omission of F from the model results in a clear misfit of the peak (Fig. S-3). A similar, although less pronounced, effect is observed in sample C0105_1 (Fig. S-4), due to the weaker intensity of the $F_{K\alpha}$ line. In both cases, the residual to peak intensity ratio is consistently higher when F is excluded. These results demonstrate that the F signal is real and confirm the robustness of our quantification.

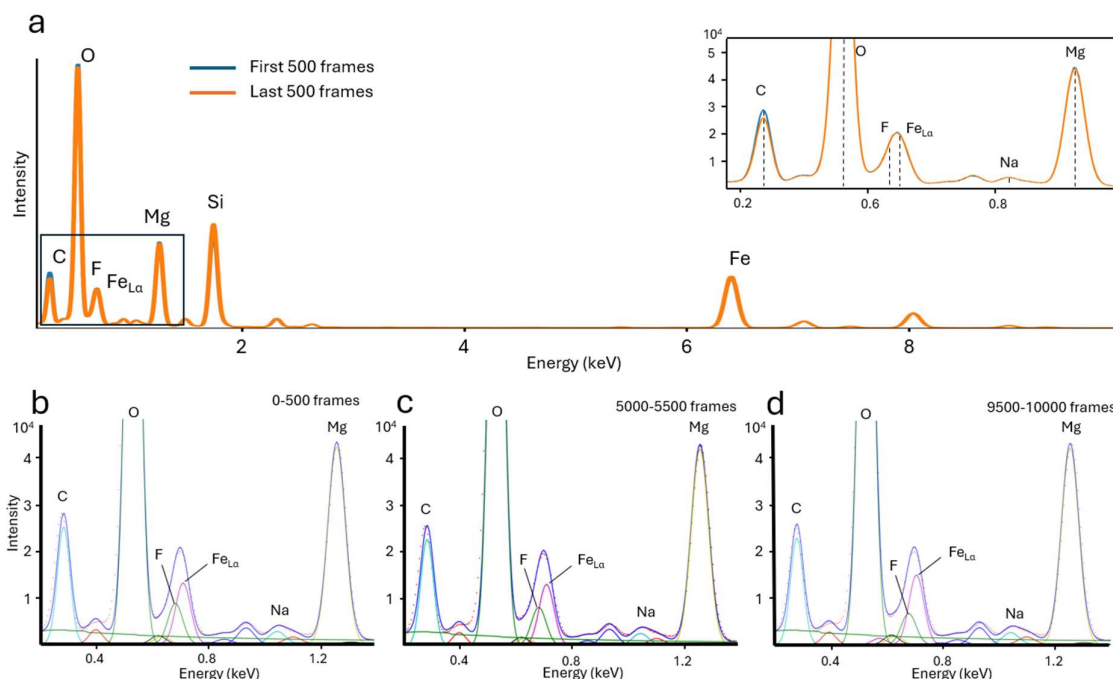


Figure S-2 Average EDS spectrum of sample A0159_05. **(a)** Comparison between the summed spectrum of the first 500 frames (blue) and the summed spectrum of the last 500 frames (orange). Only minimal changes occurred between the start and end of the acquisition, these changes mainly affect carbon, oxygen and fluorine. The inset shows the presence of F since the peak is not centred on the $\text{Fe}_{\text{L}\alpha}$ but is slightly shifted to lower energy. **(b, c, d)** Quantification of the summed spectra for the first 500 frames **(b)** a middle set of 500 frames (frames 5000-5500) **(c)** and the last 500 frames **(d)**. Spectral deconvolution confirms the presence of F, and its intensity decreases slightly from the start to the end of the acquisition.

C0105_03: high F content

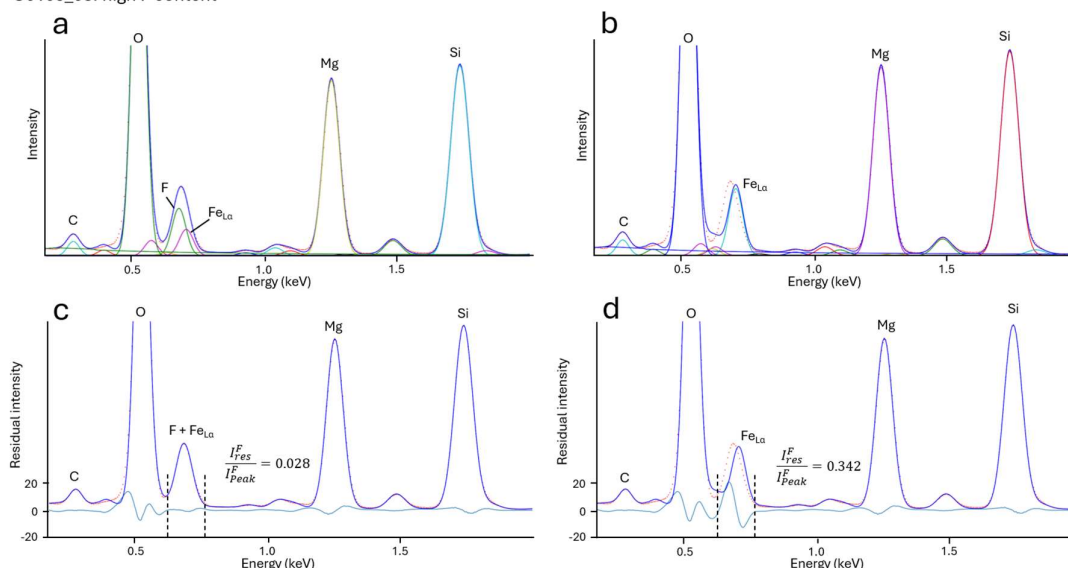


Figure S-3 Average spectrum of sample C0105_03. **(a)** Spectrum with background model and peak fitting including F; **(b)** the same spectrum fitted without F in the model, showing a clear misfit of the peak. The corresponding residuals are shown in **(c)** and **(d)**, illustrating that the residual is significantly lower when F is included **(c)** than when it is omitted **(d)**. Residuals were calculated by integrating the area of the residual ($I_{\text{res}}^{\text{F}}$) and the area of the peak ($I_{\text{Peak}}^{\text{F}}$) between the two black dashed lines (0.63-0.77 keV).

C0105_01: low F content

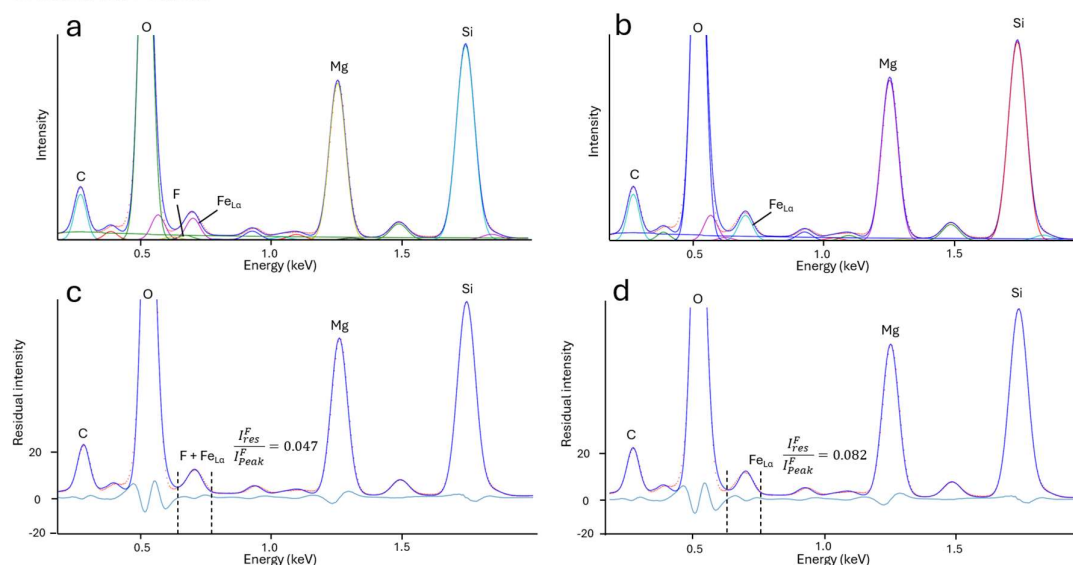


Figure S-4 Average spectrum of sample C0105_01. **(a)** Spectrum with background model and peak fitting including F; **(b)** the same spectrum fitted without F in the model. Because F is present at low concentration (average 0.86 at. %), the difference is less pronounced than in Figure S-3. However, a closer look shows that the left shoulder of the peak is better fitted when F is included. The corresponding residuals are shown in **(c)** and **(d)**, illustrating that the residual is lower when F is included (c) than when it is omitted (d). Residuals were calculated by integrating the area of the residual (I_{res}^F) and the area of the peak (I_{Peak}^F) between the two black dashed lines (0.63-0.77 keV).

Scanning transmission X-ray microscopy coupled with X-ray absorption near-edge structure at the F-edge STXM-based XANES measurement were obtained on the HERMES Beamline at the SOLEIL synchrotron (Belkhou *et al.*, 2015; Swaraj *et al.*, 2017). The microscope is first pumped to high vacuum before Helium is introduced into the chamber to perform the measurements. We acquired image stacks at energy increments of 0.2 eV over the F K-edge (685-700 eV) and 0.1 eV over C K-edge (280-295 eV) using a dwell time of 2 ms per pixel. Energy calibration was performed using CO₂ absorption bands for the C K-edge, and thanks to an internal hematite sample for the F K-edge (Fe³⁺ peak at 710 eV). Calibration are further confirmed with cross comparison from published CaF₂ data (Roesch *et al.*, 2023). Data reduction workflow and spectra extraction was made using the HyperSpy python package. A power law background was subtracted and spectrum normalization to the F content was performed by integrating the optical density up to 695 eV (Le Guillou *et al.*, 2018). Spectra of Ryugu are obtained from one FIB section (C0105_03) and the hectorite reference was measured on a microtomed preparation.

Fourier Transform Infrared Spectroscopy

Mid-infrared (MIR) hyperspectral maps were collected using an Agilent Cary 670 Fourier-Transform IR (FTIR) microscope equipped with a Focal Plane Array Detector (FPA) installed at the SOLEIL synchrotron (France). The configuration was very similar to the one used by Aléon-Toppani *et al.* (2024). We measured in transmission mode with a spectral resolution of 4 cm⁻¹, and a spectral range from 800 to 3900 cm⁻¹, typically averaging 512 scans for each map. We used a 25× objective in combination with a high magnification system placed in front of the FPA detector, which was resized to 64×64 pixels. In this configuration, the size of the projected pixel size was ~0.66 μm and the field of view was ~42 μm, but the spatial resolution was diffraction-limited in the whole spectral range. Each map was ratioed to a reference map acquired on an empty field of view before each analysis. The average spectrum of each section was obtained by first selecting only pixels where the silicate bands were observed, and then by averaging only the central part (typically less than 100 pixels) in order to avoid the edges of the sections. A rubber

band baseline correction was then applied to the 850-1950 cm^{-1} range to produce the absorbance spectra shown in Figure S-11.

Supplementary Tables

Table S-2 Average values in at. % with relative errors for F, Si, and Mg for phyllosilicates in each sample shown in Figure S-5. The reported values were obtained by quantifying the average phyllosilicates contribution from the STEM-EDS maps, excluding other phases such as, carbonates, magnetite, sulphides and large organic particles. Errors were calculated by considering both the uncertainty associated with counting statistics (3σ) and the uncertainty in the k -factors, assumed to be 3% for Mg (experimentally derived k -factor) and 10% for F (manufacturer-provided k -factor).

Sample	F (at. %)	Si (at. %)	Mg (at. %)
C0105_01	0.86 ± 0.09	13.58 ± 0.01	11.30 ± 0.34
C0105_02	2.18 ± 0.23	13.72 ± 0.09	11.76 ± 0.36
C0105_03	7.70 ± 0.77	16.11 ± 0.02	14.61 ± 0.44
C0105_04	1.76 ± 0.20	13.33 ± 0.13	10.08 ± 0.33
A0159_01	0.62 ± 0.07	13.45 ± 0.12	9.96 ± 0.32
A0159_02	2.29 ± 0.23	13.19 ± 0.02	10.56 ± 0.32
A0159_03	0.71 ± 0.08	14.04 ± 0.10	9.76 ± 0.31
A0159_04	4.50 ± 0.48	13.43 ± 0.21	10.72 ± 0.38
A0159_05	3.49 ± 0.35	15.11 ± 0.02	11.72 ± 0.35
A0159_06	3.66 ± 0.37	14.43 ± 0.05	11.18 ± 0.34
A0159_g13	-	12.29 ± 0.15	9.02 ± 0.10
A0159_g14	-	11.39 ± 0.05	9.46 ± 0.10

Supplementary Figures

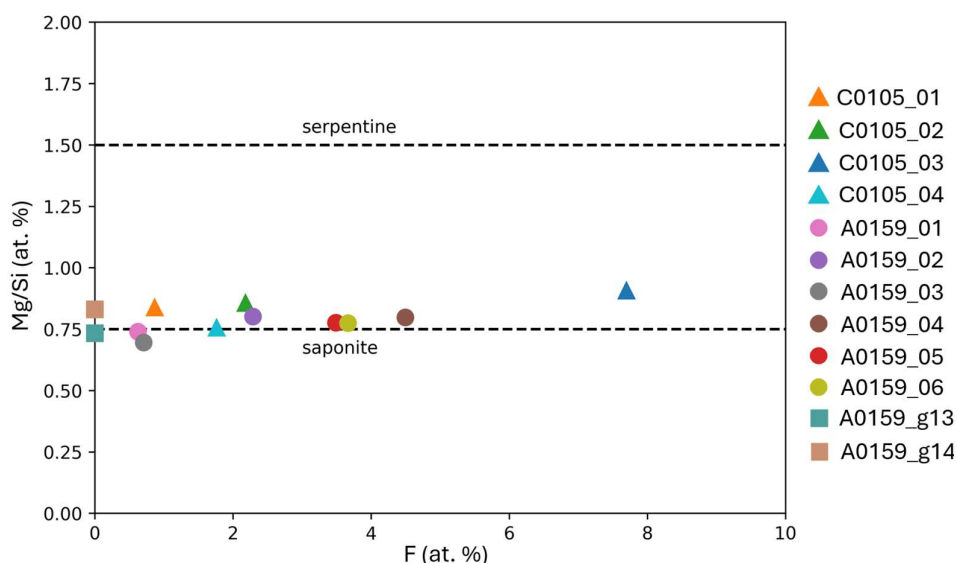


Figure S-5 F vs. Mg/Si plot for all the FIB sections studied. The F, Mg and Si concentrations are reported in at. % and were obtained by quantifying the average phyllosilicates contribution from the STEM-EDS maps, excluding other phases such as, carbonates, magnetite, sulphides and large organic particles. The F concentration varies from not detected (samples A0159_g13/g14, corresponding to FIB sections from the small detached grains found alongside A0159) to 7.70 at. % (sample C0105_3). The Mg/Si ratio varies between 0.70 (sample A0159_03) to 0.91 (sample C0105_03), indicating that the matrix is dominated by saponite rather than serpentine. Values below the ideal Mg/Si ratio of saponite (0.75) may reflect the presence of silica within the phyllosilicate porosity (Leroux *et al.*, 2024). The dashed line at Mg/Si = 0.75 marks the low-charge saponite end-member

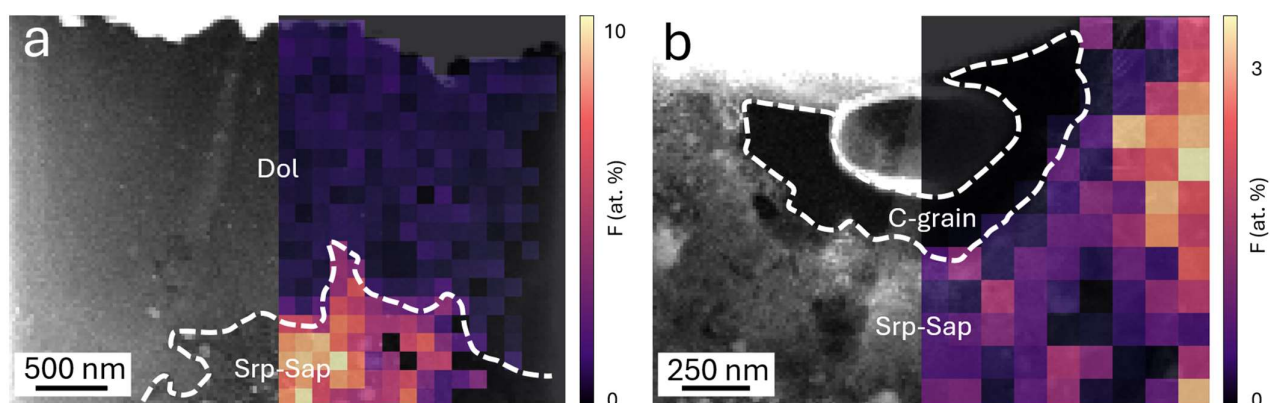


Figure S-6 Fluorine content in dolomite (Dol) and an organic grain (C-grain) compared with that of the surrounding phyllosilicate matrix (Srp-Sap). Dolomite contains minor amounts of F (average 1.05 at. %), while the organic grain show no detectable fluorine. Pixel size for both maps is 121 nm.

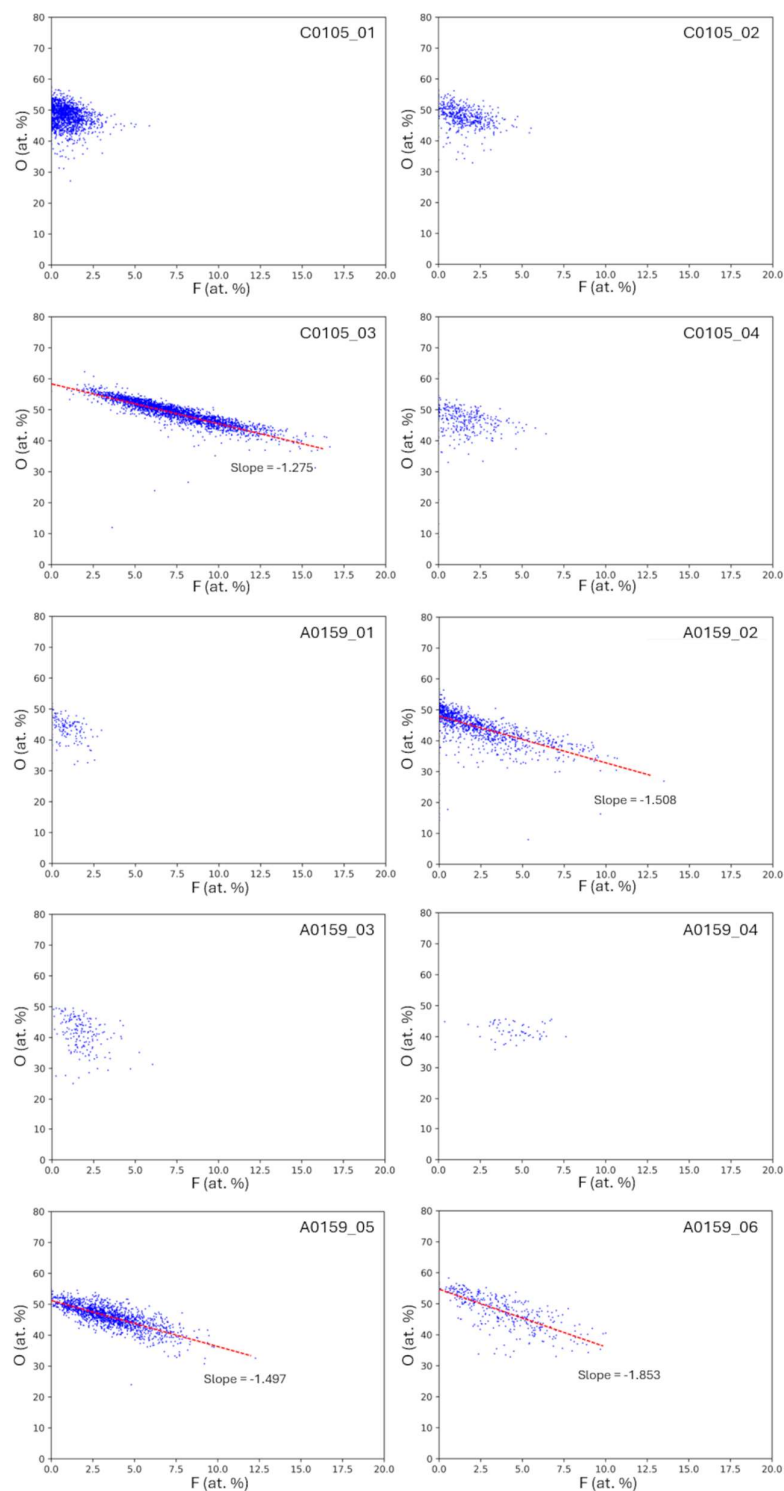


Figure S-7 Relationship between O and F contents for each phyllosilicate pixels of the STEM-EDS maps. The F content varies from not detected up to ~17 at. % depending on the section. The dashed red line represents the regression line for samples with the best statistics. The slope ranges from -1.275 (C0105_03) to -1.853 (A0159_06), with an average value of approximately -1.5. This suggests that the substitution between F and O is not strictly 1:1, likely due to partial volatilization of F and OH groups under the electron beam and the variable mixing degree of

saponite and serpentine. The higher slope observed for sample A0159_06 is consistent with it being the longest map acquired, comprising approximately 162,000 frames.

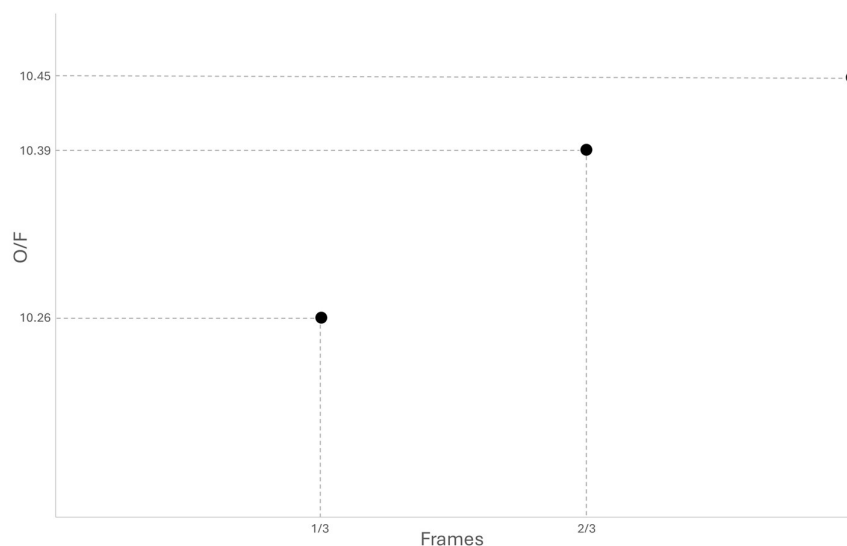


Figure S-8 O/F ratio quantified at different acquisition stages (frames) for map A0159_05 to evaluate the evolution of F and O. The x-axis corresponds to the fraction of the total number of frames (10,000). The O/F ratio does not remain constant and shows an increasing trend, suggesting that F is lost more rapidly than O.

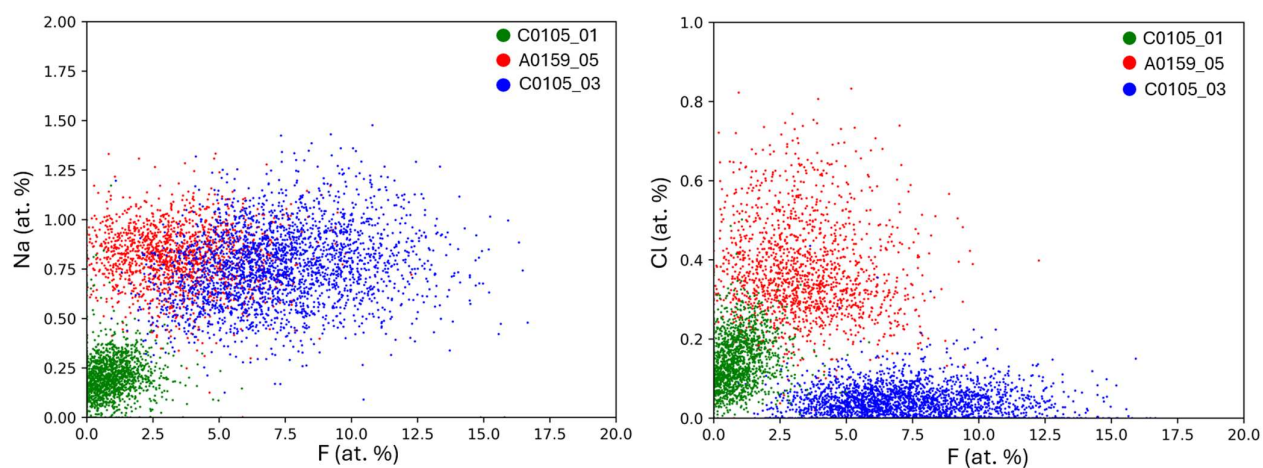


Figure S-9 Relationship of F with Na and Cl. No clear correlations are present and the concentrations of Na and Cl are minimal, ranging from undetectable to 1.25 at. % and undetectable to 0.8 at. %, respectively.

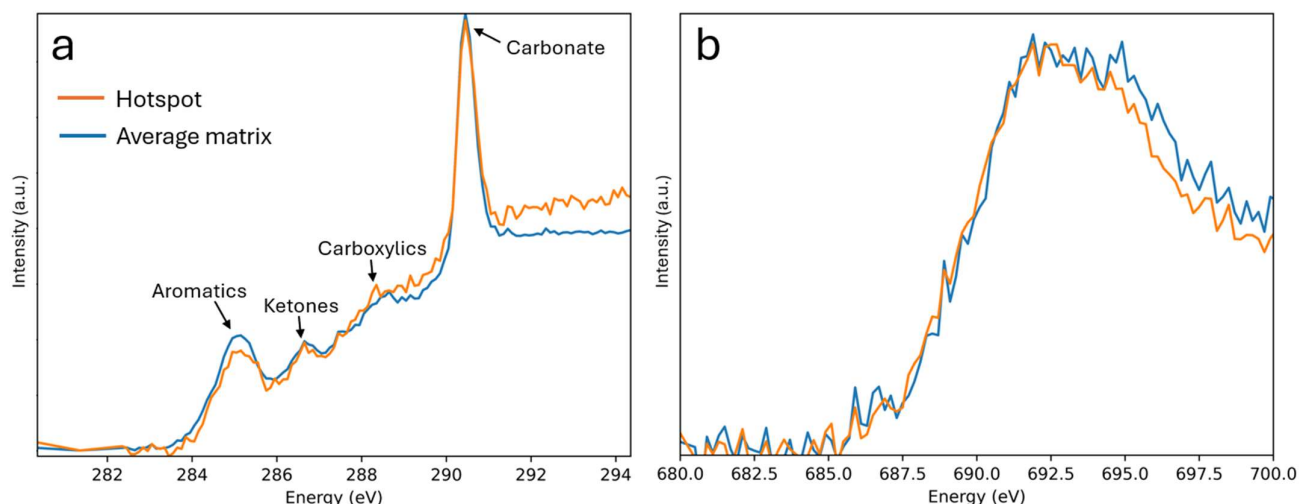


Figure S-10 STXM-based XANES spectra of Ryugu phyllosilicates. **(a)** C K-edge spectra extracted from the F hotspot (orange) and from the surrounding matrix (blue). The two spectra are similar and show only signals attributable to organic matter, with no distinct features indicative of C–F bonding. The intense band around 290.3 eV is only observed after STEM-EDS measurements and is thus related to beam damage. **(b)** F K-edge spectra extracted from the F hotspot (orange) and the surrounding matrix (blue). The two spectra are similar showing a broad absorption feature between 691–695 eV and a low energy absorption shoulder around 686–687.5 eV. The F K-edge spectra were collected before STEM-EDS analysis.

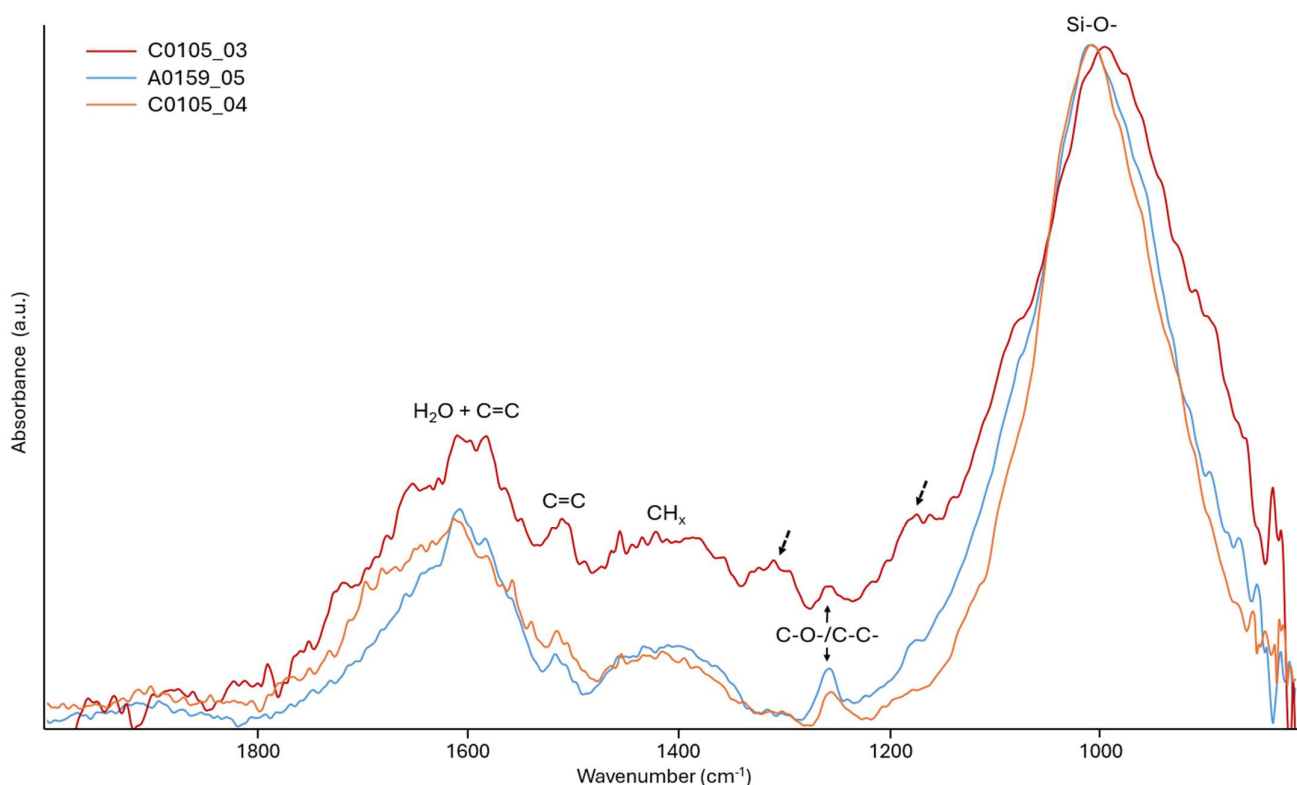


Figure S-11 FTIR spectra of samples C0105_03 (red; average F = 7.70 at. %), A0159_05 (cyan; average F = 3.49 at. %), and C0105_04 (orange; average F = 1.76 at. %). The spectra were normalized to the most intense band at

around 1000 cm^{-1} . All three spectra display absorption bands similar to those reported for other Ryugu particles (*e.g.*, Aléon-Toppani *et al.*, 2024). Specifically, the band around 1000 cm^{-1} , together with the small shoulder at $\sim 1080\text{ cm}^{-1}$ (Si–O–), represents the main and secondary SiO_4 stretching modes in phyllosilicates (Salisbury *et al.*, 1991; Beck *et al.*, 2014), while the remaining bands are characteristic of organic matter (see Aléon-Toppani *et al.*, 2024 and references therein for a detailed discussion). The bands around 1180 and 1310 cm^{-1} (dashed arrows) remain unassigned. The $1000\text{--}1400\text{ cm}^{-1}$ region also overlaps with the spectral range in which C–F vibrations are typically observed. However, C–F species generally produce multiple absorption bands, with the most intense features occurring around $1150\text{--}1250\text{ cm}^{-1}$ (Weiblen, 1954). Thus, although the presence of some C–F bonding cannot be completely ruled out, no unequivocal spectral evidence for C–F bonding is observed in the FTIR spectra. Any potential C–F bands may be either too weak to be resolved or overlap with the broad absorption features associated with phyllosilicates and organic matter, making their unambiguous identification difficult.

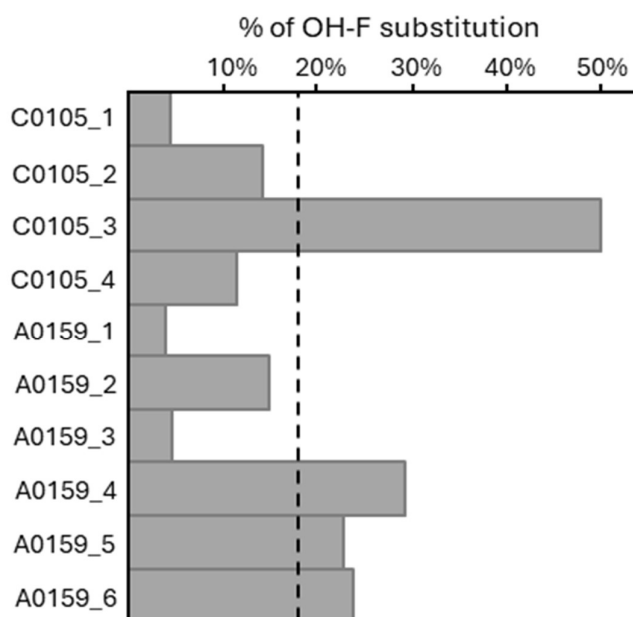


Figure S-12 Estimate of the degree of OH-F substitution in the phyllosilicate of the different FIB sections, assuming that the phyllosilicate consists of two-thirds saponite and one-third serpentine. This proportion represents a simplified and conservative estimate based on the Mg/Si ratio of section C0105_03 (~ 0.9); the actual proportion of saponite may be higher, particularly in sections with lower Mg/Si ratios. Consequently, the OH–F substitution for these samples may differ slightly from the values reported here. Section C0105-03 exhibits the highest degree of substitution, reaching 50%, whereas section A0159_01 shows the lowest degree, at 4%. The dashed line represents the mean value of 17.9%.

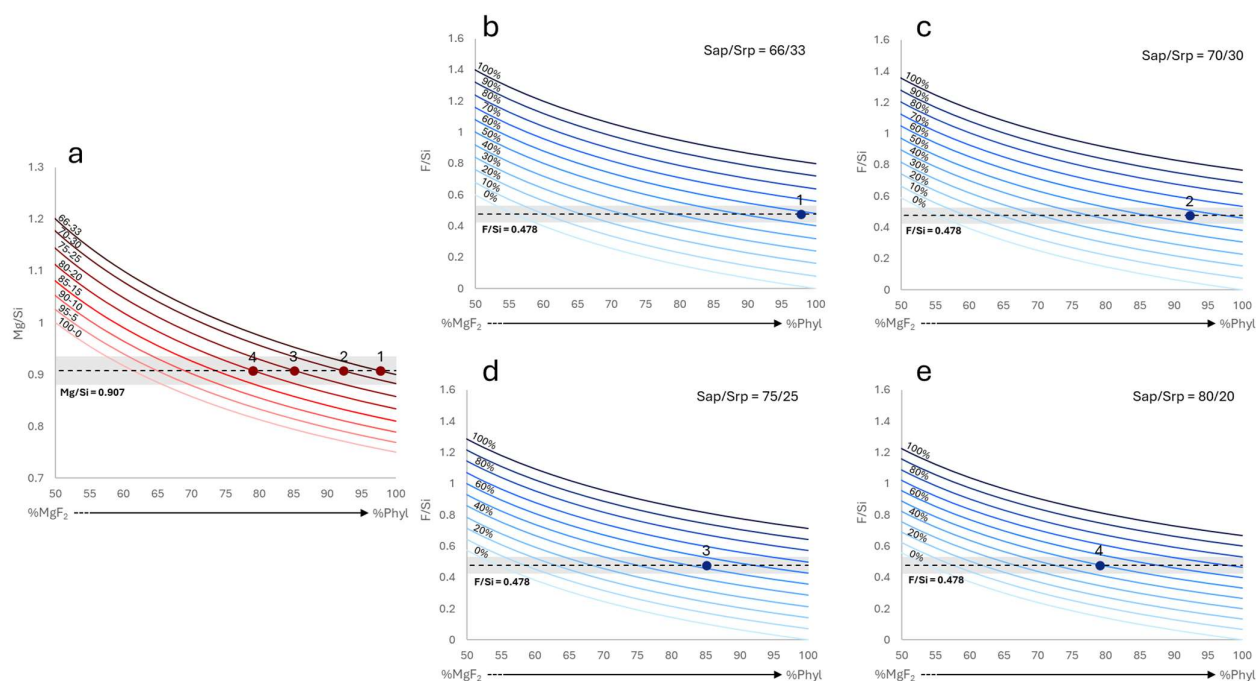


Figure S-13 Diagram showing how Mg/Si and F/Si ratios vary with different proportions of saponite-serpentine (Phyl), their mixtures with MgF₂, and the degree of OH-F substitution for sample C0105_03. (a) Variation of the Mg/Si ratio (y-axis) as a function of the MgF₂-Phyl mixing proportion (x-axis) for different saponite-serpentine compositions (red curves). The black dashed line represents the average Mg/Si ratio measured in sample C0105_03, and the shaded area the associated uncertainty (see Table S-2). Red dots mark the intersections between the measured Mg/Si ratio and the model curves. For example, the 66-33 curve (two-thirds saponite and one-third serpentine) intersects the dashed line at ~98% (point 1), indicating that the Mg/Si ratio of 0.907 in sample C0105_03 can be explained by a mixture of ~98% phyllosilicate (66.66% saponite + 33.33% serpentine) and ~2% MgF₂. Similarly, the 70-30 curve intersects the dashed line at ~92% (point 2), corresponding to ~92% phyllosilicate (70% saponite + 30% serpentine) and ~8% MgF₂. These results show that the observed Mg/Si ratio can be reproduced by different Sap/Srp proportions combined with variable amounts of MgF₂, and that the MgF₂ proportion increases with increasing saponite content. Panels (b-e) show the variation of F/Si ratios for different Sap/Srp compositions (b: 66.66-33.33; c: 70-30; d: 75-25; e: 80-20) as a function of both MgF₂-Phyl mixing and the degree of OH-F substitution in the phyllosilicates (blue curves). A value of 0% indicates fully hydroxylated phyllosilicates, whereas 100% indicates complete substitution of OH by F. The black dashed line represents the average F/Si ratio measured in sample C0105_03, and the shaded area the associated uncertainty. For example, in panel (b), point 1 corresponds to the ~98% Phyl and ~2% MgF₂ mixture identified in panel (a), and it lies within the 50% and 60% OH-F substitution curves, in agreement with the degree of OH-F substitution measured in Figure S-12 (~50%). Overall, the model does not unambiguously demonstrate the presence of MgF₂. Nevertheless, it shows that MgF₂ could be present without producing a clear Mg-F correlation in the EDS maps, depending on the saponite-serpentine proportion. The model assumes ideal compositions for saponite [(Mg₃Si₄O₁₀(OH)₂] and serpentine [(Mg₃Si₂O₅(OH)₄], deviations from these ideal compositions may slightly modify the model curves.

Supplementary Information References

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