UBIQUITOUS PRESENCE OF SODIUM-BEARING MAGNESIUM PHOSPHATE IN CI CHONDRITIC MATERIALS.

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Introduction: The discovery that the asteroid Ryugu samples returned by the JAXA Hayabusa2 spacecraft are chemically and mineralogically nearly identical to CI chondrites has made us re-recognize the importance of CI chondrites in the early solar system [e.g., 1]. These CI chondritic materials have undergone strong aqueous alteration in their parent bodies, resulting in the formation of abundant Mg-Fe phyllosilicates along with other altered minerals such as carbonates, magnetite, and pyrrhotite. Initial and subsequent AO analyses of the Ryugu samples have found that they are brecciated on the mm~μm scale and that a small amount of forsterite and other primary minerals survive in some of the brecciated clasts with evidence of less degrees of aqueous alteration (“less altered clast”) [e.g., 1]. In addition, these less altered clasts contain a rare Na-bearing Mg phosphate that is still poorly characterized. Despite the analytical attempt to identify its mineral species, their identity has not been clarified yet [2]. These rare Mg phosphates could be one of the key phases to understanding the evolution of CI chondritic bodies since a similar Na-bearing Mg phosphate has been reported from the asteroid Bennu sample returned by the NASA OSIRIS REx mission [3,4], and the importance of these materials has been suddenly highlighted. Since the initial analysis of the Ryugu sample, we have been paying attention to these Mg phosphates in CI chondrites as well as Ryugu samples, and here we report the present results on their mineralogical analysis.

Samples and Methods: Polished sections of Ryugu particles (mainly C0002 and C0040 by the initial analysis and C0032 distributed for the AO1 study from JAXA) and three CI chondrites (Ivuna, Orgueil, and Alais) were analyzed. JEOL JXA-8530F FE-EPMA at Dept. Earth & Planet. Sci., Univ. of Tokyo was employed for both WDS mapping and quantitative analyses (quantitative analysis of Mg phosphate: 15 kV/6 nA/2 μm beam). We also performed micro-Raman spectroscopy of Mg phosphate at Geochem. Res. Center at Univ. of Tokyo. As a reference terrestrial mineral phase, bobierrite ($Mg_3(PO_4)_2 \cdot 8H_2O$) from the Kola Peninsula, Russia (#810001 of Mineral Collection at Univ. Museum, Univ. of Tokyo) was analyzed.

Results and Discussion: In Ryugu samples, the largest Mg phosphate grain is up to 150 x 100 μm which forms an irregularly shaped cluster reaching 400 x 300 μm in total size (Fig. 1a) [2]. The overall abundance of Mg phosphate in Ryugu is well below 0.1% and does not exceed 1% even in the less altered clasts except C0040-01 (~10% Mg phosphate). The characteristic texture of Mg phosphate is the presence of cleavage-like fractures (up to 1 μm wide) sometimes developing along two directions but thin fractures with random orientations are also present (Fig. 1a-b).

In our CI chondrite sections analyzed, Mg phosphate was found in Ivuna and Orgueil. Mg phosphate in these CI chondrites is a rare phase (<0.1%) similar to Ryugu samples. The largest grain is 200 x 100 μm in size and is equivalent to the Ryugu Mg phosphate (Fig. 1c). The cleavage-like fractures are also observed for some large Mg phosphate grains (Fig. 1c). As is the case for Ryugu samples, the presence of Mg phosphate in CI chondrites appears associated with less altered clasts. Although our Alais section is mostly composed of such less altered clasts, we did not find Mg phosphate probably because of the small size of the Alais section (~3.5 x 2 mm).

We note the obvious terrestrial alteration of Mg phosphate in Ivuna after the polished sections were made even though they were stored in a vacuum dessicator. The Ivuna Mg phosphate shows the growth of the secondary Na sulfate phase on its surface 1.5 years after preparation of the polished sections (Fig. 1d), which likely affects the original phosphate chemical composition as discussed below. The Ivuna Mg phosphate clearly shows open spaces between the surrounding minerals, suggesting volume decrease by terrestrial alteration (Fig. 1d). The internal texture of the Ivuna Mg phosphate also appears slightly different from Mg phosphates in other samples.

The chemical composition of Mg phosphate obtained by FE-EPMA is summarized in Table 1. The Ryugu Mg phosphate contains 3-4 wt% Na_2O and can be considered as a Na-bearing Mg phosphate. It is also noted that it contains 2-6 wt% of F. The Cl abundance is small (0.1-0.2 wt%). As discussed in [2], its low total mass (up to 72 wt%) indicates the presence of water. Mg phosphates in CI chondrites show slightly different chemical compositions from that of the Ryugu Mg phosphate. In Ivuna the Mg phosphate contains abundant SO_3 (up to 24 wt% SO_3), probably some of the PO_4 has been replaced with SO_3. Also, the Mn abundance is notably high, up to 6.6 wt%. There is a positive correlation between SO_3 and MnO abundance.

The source of S is Fe sulfide, however, it is uncertain for Mn, but is most likely from Mn-rich carbonate. Our Orgueil sample shows less terrestrial weathering relative to Ivuna, nevertheless Mg phosphate contains ~7 wt% SO_3. Unlike Mg phosphates in Ryugu and Ivuna, the Orgueil Mg phosphate does not contain F. The Mn abundance reaches ~2 wt% MnO, again suggesting coupling with SO_3. In CI chondrites, Mg phosphate contains less amounts of Na_2O compared to the Ryugu Mg phosphate, which is also related to Na resorption by terrestrial weathering. If we take the Ryugu Mg phosphate as an original phase, its chemical formula is slightly different from those proposed in [2] since Na appears to be a significant component. The (P+Na) atomic abundance is ~1.2-1.3x higher than P, and this phase could be similar to bakhchisaraitsevite ($Na_2Mg_5(PO_4)_4 \cdot 7H_2O$). However, this formula is still not a perfect match with the EPMA data and there is no matching mineral in the mineral database [e.g., 5].

To further characterize these Mg phosphates, we attempted micro-Raman analysis, however, the polished sections gave high fluorescence, and a clear Raman signal was not obtained. Some Ryugu Mg phosphate grains exhibit weak Raman peaks (560, 896, 1045, 1112, 1170, 1290 cm^{-1}), suggesting a crystalline phase (Fig. 2). Some Orgueil Mg phosphate grains show similar Raman spectra, suggesting an identical crystalline state despite high SO_3 content. However, these Raman peaks do not match with either bobierrite or bakhchisaraitsevite (Fig. 2). We also tried to search for a matching Mg phosphate mineral in the Raman database [6], but none of them gives a good match. The spectra of the Ivuna Mg phosphate are different from the others, consistent with large compositional differences.

Conclusions: We found that Na-bearing Mg phosphate is ubiquitously present in CI chondritic materials although those in CI chondrites experienced terrestrial weathering and contain high SO_3 and MnO components. This observation suggests that in CI chondritic materials Na-bearing Mg phosphate is unstable during terrestrial weathering of pyrrhotite. Although there is no matching mineral in the literature, the phse appears to be crystalline. More analysis of Ryugu and Bennu samples will be necessary to confirm their mineralogy and crystallography and will be useful to further constrain the evolutional history of CI chondritic bodies in the early solar system.

References: [1] Nakamura T. et al. (2022) *Science*, eabn8671. [2] Ma C. et al. (2022) *85th Annual Meeting of Meteorit. Soc*. (Glasgow), #6134. [3] Voosen P. (2023) *Science*, doi:10.1126/science.zcys97n. [4] Witze A. (2023) Nature, doi:10.1038/d41586-023-03978-4. [5] Mindat.org database website (https://www.mindat.org/). [6] RRUFF database website (https://rruff.info/).

Table 1. Average chemical compositions (wt%) of Mg phosphates in Ryugu samples and CI chondrites

	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Cr_2O_3	P_2O_5	SO_3	F	Cl	Total
Ryugu C0032 (*n*=11)	0.34	0.02	0.03	0.59	0.05	21.86	0.03	3.50	0.14	0.01	38.21	0.23	4.06	0.15	67.46
Orgueil (*n*=4)	0.18	0.01	0.01	0.58	1.63	25.89	0.19	1.12	0.13	0.03	39.76	7.00	0.00	0.05	76.55
Ivuna (*n*=8)	0.42	0.01	0.07	0.96	4.75	20.91	0.28	1.49	0.16	0.02	26.15	20.12	1.76	0.07	76.40

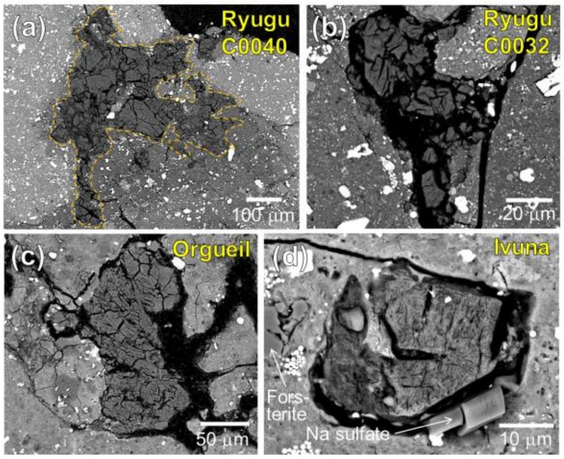

Fig. 1. Mg phosphates in (a) Ryugu C0040-01 (the cluster is shown by orange dashed lines), (b) Ryugu C0032, (c) Orgueil, and (d) Ivuna.

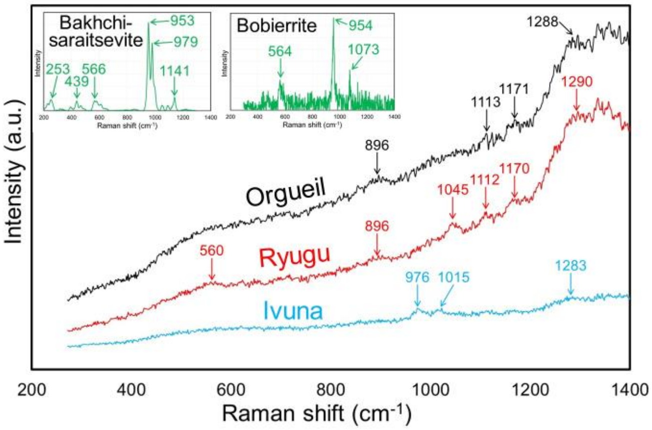

Fig. 2. Raman spectra of Mg phosphates in CI chondritic materials (Ryugu C0032, Orgueil, and Ivuna) The Raman spectra of bakhchisaraitsevite and bobierrite [6] are also shown for comparison.