Revision 1

The first meteoritic ammonium mineral: discovery of boussingaultite in the Orgueil CI1 carbonaceous chondrite

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ABSTRACT

The enigma of ammonium mineral speciation in solar system has no proven solution due to the lack of data on the real minerals serving as space ammonium carriers. We herein report on discovery of the first ammonium mineral in meteoritic substance and show its relevance to compositional and spectral characteristics ascribed to hypothetic ammonium phases in cometary and asteroidal bodies. Chemically distant from previously inferred volatile organics or ammoniated phyllosilicates, the mineral is an aqueous metal-ammonium sulfate related to the picromerite group – a family of so-called Tutton's salts. Nickeloan boussingaultite, $(NH_4)_2(Mg,Ni)(SO_4)_2\cdot6H_2O$, was discovered in Orgueil, a primitive carbonaceous chondrite closely related to (162173) Ryugu and (101955) Bennu, the C-type asteroids. The available spectroscopic, chemical and mineralogical data signify that natural sulfates related to boussingaultite-nickelboussingaultite series perfectly fit into the role of bound ammonia carriers under conditions of cometary nuclei and carbonaceous asteroids. The problems of possible technogenic contamination of astromaterial samples and the difficulties of microprobe determination of ammonium are discussed in connection with recently published reports on the discovery of lunar and asteroidal ammonium-containing minerals.

Keywords: ammonium; boussingaultite; Tutton's salt; carbonaceous chondrite; asteroid; comet; sulfate; nickel

INTRODUCTION

Elucidating the evolution of cosmic nitrogen is one of the challenges of modern planetary science. Ammonia and ammonium, the simplest carriers of reduced, life-essential nitrogen, are believed to be abundant on the icy Solar System bodies (Pizzarello and Williams 2012; Pizzarello and Bose 2015; Altwegg et al. 2019; Poch et al. 2020; Grewal et al. 2021). Spectroscopic observations indicate the likely occurrence of ammonium salts in surficial deposits of (1) Ceres, a dwarf planet (King et al. 1992; De Sanctis et al. 2015), and in cometary bodies (Poch et al. 2020; Lewis et al. 2023). However, all reported interpretations remain ambiguous since they are based solely on remote sensing and laboratory simulations (Marion et al. 2012; De Sanctis et al. 2015; Berg et al. 2016; Poch et al. 2020), without the knowledge of real minerals – natural ammonium carriers that might constitute the celestial bodies.

The absence of recognizable ammonium minerals in meteorites, cometary and asteroid sample returns lead to the opinion that such indigenous salts could disappear – either sublimated or thermally decomposed already in space (Poch et al. 2020; Matsumoto et al. 2024). The questionable point of such opinion is that a variety of aqueous minerals, many of them as unstable as ammonium ones, are successfully delivered on Earth with meteorite influx (Rubin and Ma 2017). In addition, traces of water-soluble ammonium were confirmed in primitive meteorites – aqueously altered carbonaceous chondrites (Pizzarello and Williams 2012; Pizzarello and Bose 2015) and in the samples returned from Ryugu, a C-type asteroid (Pilorget et al. 2022; Schmitt-Kopplin et al. 2023). Unfortunately, all ammonium determinations in the samples of extraterrestrial origin are based on the analyses of leachates or evolved gases released from bulk probes. The identification of real ammonium minerals is an uncharted area of space research. It may take place that native ammonium salts, being much scarce than aqueous minerals, are simply overlooked during conventional analytical procedures. A recent reports of ammonium mineral from Lunar regolith (Jin et al. 2024) and a possible ammonium-bearing phase in the Ryugu samples (Pilorget et al. 2024) supports such an assumption. To elucidate the problem, our team re-examined the material of Orgueil, a primitive CI1 carbonaceous chondrite that contains ammonium of definitely extraterrestrial origin (Laize-Générat et al. 2024). We herein report the discovery of the first meteoritic ammonium mineral and demonstrate that it may serve as the likely carrier of bound ammonia in cometary and asteroidal bodies.

SAMPLES AND METHODS

Samples. A 4×4×5 mm^3 piece of Orgueil from the collections of Vernadsky Institute of Geochemistry was crushed between flat glass plates. The material was inspected under binocular microscope at 120× magnification. The boussingaultite crystals could be distinguished from other near-colorless minerals (dolomite, hexahydrite, gypsum, sulfur) due to euhedral isometric crystal shape and the greenish tint. The crystals were handpicked from the sample for subsequent study.

X-ray single-crystal study and crystal structure. The single-crystal X-ray dataset was collected by means of a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer equipped with a microfocus X-ray tube (Mo*K*α) and HyPix-6000 hybrid photon counting detector. Boussingaultite is stable at ambient conditions, therefore data were collected at ambient temperature and pressure, as in previous X-ray studies (Margulis and Templeton 1962; Montgomery and Lingafelter 1964; Zhitova et al. 2024). Unit-cell parameters were refined from 3879 reflections. Data collection, processing and reduction routines were performed with CrysAlisPro v.171.42 software (Rigaku Oxford Diffraction 2023). The crystal structure was solved and refined using *SHELX*-2018 set of programs (Sheldrick 2015) incorporated into Olex2 v.1.5 graphical user interface (Dolomanov et al. 2009). The results of the study are provided in the crystallographic information file (CIF) included in supplemental materials.

Electron microprobe analysis. The mineral was found to be extremely unstable under the electron beam. In particular, application of wavelength-dispersive analyzer (WDX) was not possible, owing to instantaneous decomposition (burning out) of the crystals even under the de-focused beam. The energy-dispersive analysis (EDX) was carried out on the same crystal which was used for X-ray single crystal study. The analyzed crystal was glued onto carbon tape and vacuum-coated by conductive carbon film. The analyses were carried out by means of a Hitachi S-3400N SEM with an attached EDX spectrometer, using Oxford Instruments INCA software and the following standards and lines: diopside (Mg*K*α), metal Ni (Ni*K*α), anhydrite (S*K*α), orthoclase (K*K*α), chkalovite (Na*K*α) and TiN (N*K*α). With the used EDX setup (acceleration voltage 20 kV, beam current 1 nA, beam diameter 2 μm), the mineral could withstand until full decomposition for ~30 seconds per analytical point.

Infrared spectroscopy. FT-IR spectra of the mineral were obtained using a Bruker Hyperion 2000 IR-microscope with a liquid-nitrogen cooled MCT detector attached to a Bruker Vertex 70 spectrometer. The mid-IR spectrum in transmission mode was recorded from a 30 μm crystal which was placed onto and than smeared over the flat polished surface of KBr crystal disc. The 15× reflector objective and 15 μm rectangular field aperture was used. The spectra were recorded over the range of 4000 to 600 cm^{-1} with spectral resolution of 4 cm^{-1}. The resultant profile was obtained by averaging of 320 scans. FT-IR spectrum in reflectance mode was obtained from the same mineral film smeared over the KBr disc. The spectrum was recorded using the same instrument setup, but the KBr crystal was placed on a liquid-nitrogen cooled metal table, which allowed to cool the sample and recording the spectrum at 200±20 K. All spectra were processed using Bruker OPUS v. 6.5 software.

OCCURRENCE

Orgueil, a witnessed fall (1864, Midi-Pyrenees, France), is a biggest (13 kg) carbonaceous chondrite belonging to most primitive meteorites incorporated into the C1I (Ivuna) group (Gounelle and Zolensky 2014). The latter, consisting just of 10 meteorites, attracts enormous interest owing to mineralogical and chemical features, such as extremely high water content (Court and Sephton 2014) and the occurrence of diverse organic compounds of extraterrestrial origin, including nitrogen-bearing moieties (e.g., Remusat et al. 2005; Aponte et al. 2015; Pizzarello and Yarnes 2016). Orgueil is the closest relative of the samples recently returned from asteroids (162173) Ryugu and (101955) Bennu (Ito et al. 2022; Yokoyama et al. 2023; Lauretta et al. 2024). Due to its large mass, Orgueil is the most accessible C1I chondrite distributed among museums and laboratories worldwide (Grady 2000)· Owing to the striking compositional similarity to the solar photosphere, Orgueil is an international standard used for normalization of elemental abundances in geochemical and cosmochemical studies (Lodders 2003). The meteorite consists entirely of matrix, with no traces of chondrules or Ca,Al-rich inclusions (CAIs). The matrix constituents are Mg-rich, Fe-bearing serpentine and smectite, magnetite, and a poorly crystallized ferrihydrite (a ferric hydroxide) (Tomeoka and Buseck 1988). Accessory minerals are comprised by irregular grains of Ca-Mg-Fe carbonates, olivine, pyroxene, sulfides. Sulfate minerals, in form of veinlets infilling the cracks in the matrix, are represented by gypsum, magnesium sulfate hydrates, sometimes with admixture of Na and Ni (Fredriksson and Kerridge 1988; Gounelle and Zolensky 2014). Ammonium-bearing salts (probably sal ammoniac) were originally described on the fusion crust of Orgueil immediately after the fall (Daubrée 1864; Cloëz 1864), but were not confirmed by subsequent studies, leading to the assumption that they were lost upon meteorite storage (Gounelle and Zolensky 2014).

RESULTS

Nickeloan boussingaultite in Orgueil

Our results evidence that the source of surficial ammonium evaporates detected by Daubrée (1864) and Cloëz (1864), as well as of water-soluble ammonium in Orgueil leachates (Laize-Générat et al. 2024) is nickeloan boussingaultite, $(NH_4)_2(Mg,Ni)(SO_4)_2 \cdot 6H_2O$. We identified this mineral as an accessory phase in the studied Orgueil sample. The mineral occurs as euhedral isometric, isolated faceted crystals and their intergrowths up to 30 µm in size (Fig. 1) disseminated within phyllosilicate matrix. Of the 4-5 mm meteorite piece crushed between the glass slides, one could recognize eight Ni-boussingaultite crystals. The mineral is nearly colorless with a distinct greenish tint due to significant amount of Ni in its composition. It is readily soluble in water.

Chemical composition

Nickeloan boussingaultite is very unstable under the electron beam and readily decomposes (burns out) within 30 s of analysis per analytical point. The damage is clearly visible in the SEM photograph before and after the EDX analysis (Fig. 1a,b): the beam impact sites appear as deep pits (craters) on the crystal surface (Fig. 1b). Therefore, the obtained electron microprobe data (Table 1) can be assessed as semi-quantitative. In this regard, the goal of the EMPA analysis was not to obtain quantitative results but to prove that (1) the mineral contains nitrogen; (2) it does not contain essential alkali metals substituting for ammonium; (3) determine the elements (metals) that populate the *M*-site in the crystal structure; (4) after completing task (3), determine the Mg to Ni ratio in order to compare it with the results obtained by the single-crystal structure refinement. The presence of nitrogen (N-$K\alpha_2$ line at 392.4 eV) was confirmed (Fig. 1c), which is consistent with the presence of ammonium determined by both X-ray structural analysis and infrared spectroscopy (see the corresponding sections). The content of potassium and sodium substituting for ammonium was found insignificant (0.4 wt.% K, 0.1 wt.% Na). Divalent metal cations other than Mg^{2+} and Ni^{2+} were not detected. The atomic ratio of Mg to Ni, 0.63/0.37, was found almost identical to that determined by X-ray structure refinement.

X-ray single-crystal study and crystal structure

The unit-cell parameters of nickeloan boussingaultite from Orgueil are consistent with previously published data on the synthetic and natural members of the boussingaultite-nickelboussingaultite solid solutions, $(NH_4)_2M^{2+}(SO_4)_2 \cdot 6H_2O$, where M^{2+} is either Mg or Ni, respectively (Table 2). Notably, the cell parameters of the mineral from Orgueil are intermediate between the larger Mg end-member values and the smaller values of Ni end-member, consistent with the smaller ionic radius of Ni^{2+} (0.69 Å) compared to Mg^{2+} (0.72 Å) (Shannon 1976). Refinement of the crystal structure was converged at $R_1 = 0.029$ for 1175 unique observed reflections, yielding the chemical formula $(NH_4)_2(Mg_{0.65}Ni_{0.35})_{1.00}(SO_4)_2·6H_2O$, where the Mg/Ni atomic ratio is in agreement with the electron microprobe data (Table 1).

Boussingaultite belongs to a wide family of hydrated sulfates of the general formula $A^+_2M^{2+}(SO_4)_2·6H_2O$, where A^+ is either ammonium or alkali cation (except for Na^+ and Li^+); M^{2+} is a medium-sized metal cation. In mineralogy, these sulfates are incorporated into the picromerite group (Bosi et al. 2009; Diego Gatta et al. 2023), whereas in chemistry and materials science they are known as the Tutton's or Tutton salts (Tutton 1893; Manomenova et al. 2016; Ghosh et al. 2018; Smith et al. 2024a,b). Like other ammonium-bearing Tutton's salts, the crystal structure of the mineral from Orgueil, illustrated in Fig. 2, is a framework composed of $[(Mg,Ni)(H_2O)_6]$ octahedra, sulfate tetrahedra and ammonium ions. It is noteworthy that studied nickeloan boussingaultite is the first example of a structurally characterized intermediate member of solid solution between the Mg and Ni end-members. The interatomic bond lengths of the mineral follow the same general trend as its unit-cell parameters, occupying a position between corresponding values of Mg and Ni end-members (Table 3).

The overall integrity of the structure is maintained solely by a very dense network of hydrogen bonds (Fig. 3; Supplemental Table S1). The strong hydrogen bonding in boussingaultite, studied in detail by Gatta et al. (2023) using single-crystal neutron diffraction, results in a stability of the structure under ambient conditions, preserving a fixed hydration stage of $6H_2O$ per formula unit. On the other hand, however, the destruction of hydrogen bonds already at 90–100 °C leads to a complete and irreversible stepwise dehydration and collapse of the entire structure (Kosova et al., 2018; Zhitova et al. 2024).

Infrared spectroscopy

Infrared spectrum of nickeloan boussingaultite from Orgueil is consistent with the spectra of the minerals of boussingaultite-nickelboussingaultite series (Culka et al. 2009). In context of the ammonium detection problem, of particular significance are the absorption bands characteristic of ammonium ion: 2888 and 2840 cm^{-1} ≡ 3.46 and 3.52 μm (stretching modes of N–H bonds in NH_4^+); 1471 and 1432 cm^{-1} ≡ 6.80 and 6.98 μm (bending vibrations of NH_4^+) (Fig. 3, Table 4). Infrared spectrum of the mineral from Orgueil recorded in the diffuse reflectance mode (Fig. 4, Table 5) bears the same absorption bands in the N–H/O–H stretching region.

DISCUSSION

Boussingaultite as a carrier of indigenous meteoritic ammonium in Orgueil

The discovery of nickeloan boussingaultite in Orgueil confirms the existence of a suspected but previously poorly defined crystalline ammonium salt in this meteorite (Daubrée 1864). It is noteworthy that Cloëz (1864) reported 0.1 wt.% of ammonium in aqueous leachates collected shortly after the Orgueil witnessed fall. The latest analytical data almost exactly replicate the above value, giving ~0.07 wt% NH_4 in leachates (Laize-Générat et al. 2024). It is significant that this water-soluble ammonium has distinct extraterrestrial signature (Laize-Générat et al. 2024), consistent with $\delta^{15}N$ values in the samples returned from asteroids Ryugu (Naraoka et al. 2023) and Bennu (Lauretta et al. 2024). However, the nature of mineral carrier of ammonium in CI1 chondrites was previously unknown. In view that Orgueil, likewise other CI1 chondrites, experienced terrestrial aerial alteration (Gounelle and Zolensky 2001; Airieau et al. 2005), the genesis of nickeloan boussingaultite should be discussed in conjunction with the previously known sulfate assemblages in these meteorites. The main sulfate carrier in CI1 chondrites is $MgSO_4 \cdot nH_2O$; it was detected in the aqueous leachates of Orgueil, Alais and Ivuna shortly after their witnessed falls (Fredriksson and Kerridge 1988; Gounelle and Zolensky 2001 and references cited therein). A second, much less abundant sulfate is gypsum, $CaSO_4 \cdot 2H_2O$. It is known that $MgSO_4 \cdot nH_2O$ is prone to a reversible hydration, where n can vary from 1 (kieserite) 2 (sanderite), 4 (starkeyite or cranswickite), 5 (pentahydrite), 6 (hexahydrite) to 7 (epsomite). The humidity-dependent phase relations between these hydrates have been experimentally studied in connection with their inferred presence on Mars (Chipera and Vaniman 2007). It is therefore obvious that magnesium sulfates in CI1 chondrites could have rehydrated on Earth depending on air humidity. This does not mean, however, that the indigenous sulfates, i.e., the SO_4^{2-} anion as such, could not have existed on the parent asteroids. With such high abundances in CI1 chondrites (up to several wt.%) (Fredriksson and Kerridge 1988; Gounelle and Zolensky 2001), sulfates could not have formed due to terrestrial oxidation of the modern, rather scarce accessory pyrrhotite with simultaneous decomposition of rock-forming phyllosilicates as a source of magnesium. An asteroidal origin of sulfate sulfur in CI1 chondrites is supported by isotopic evidence (Bullock et al. 2005; 2010). It seems obvious, therefore, that sulfates already existed on the parent asteroid(s) of CI1 chondrites, but could have been reversibly hydrated-dehydrated on Earth. It is important that in this case the hydration processes did not affect ammonium, which retains indigenous meteoritic origin (Laize-Générat et al. 2024).

Boussingaultite is the only known hydrated Mg-NH_4 sulfate compound, and therefore appears in all aqueous systems with excess Mg^{2+}, SO_4^{2-} and H_2O and subordinate NH_4^+, as observed in Orgueil. Once formed, boussingaultite, unlike $MgSO_4$ hydrates, maintains a fixed hydration state (see the crystal structure section). The possibility that boussingaultite in Orgueil could be formed by hydration of the as yet unknown nickel-bearing efremovite, $(NH_4)_2(Mg,Ni)_2(SO_4)_3$, was suggested by one of the referees (Michael Zolensky) during the review process. Efremovite, $(NH_4)_2Mg_2(SO_4)_3$, a classic representative of the “Anthropocene Epoch” mineralogy (Hazen et al. 2017), was discovered in the burnt waste dumps of the Chelyabinsk coal basin (Shcherbakova and Bazhenova 1989). The mineral was subsequently recognized in numerous similar localities worldwide (Nasdala and Pekov 1993; Szakáll and Kristály 2008; Shimobayashi et al. 2011; Žáček et al. 2019; Parafiniuk et al. 2021). Efremovite of natural origin was found in fumaroles of the Tolbachik volcano, Kamchatka, Russia (Bulakh et al. 2023). Efremovite is known to decompose by hydration in a humid atmosphere into boussingaultite and hydrous magnesium sulfates (Highfield et al. 2012). However, it has been shown experimentally that efremovite as such only crystallizes at temperatures exceeding 370 °C. Below this temperature, in the presence of chemically bound water in the form of serpentine, boussingaultite always crystallizes (Highfield et al. 2012). Therefore, even the Orgueil parent body could have been accreted and altered at temperatures above 370 °C, its cooling in space would inevitably result in the crystallization of boussingaultite rather than efremovite.

Previous reports of ammonium-bearing phases in astromaterials

Boussingaultite is the first ammonium mineral definitely confirmed in meteorites. Considering other types of astromaterials, the inferences about the composition of ammonium-bearing phases in asteroids and comets have long been based on infrared remote sensing data, which are discussed in detail in a separate chapter. At the same time, recent advances in space missions have opened the frame for new studies of lunar soil (Tian et al. 2023) and even direct sampling of asteroidal material (Yokoyama et al. 2023). We herein examine published papers on this topic, focusing on some challenges that may accompany the study of such objects.

The first mineral discussed is novograblenovite, $NH_4MgCl_3 \cdot 6H_2O$, from the Moon. This phase was initially described as an anthropogenic product from the burnt dumps of the Chelyabinsk coal basin, Urals, Russia (Chesnokov et al. 1988), than in the same environment in Silesia, Poland (Parafiniuk et al. 2021) and as a new mineral of volcanic (fumarolic) origin (Okrugin et al. 2019). A single loose grain of $NH_4MgCl_3 \cdot 6H_2O$ was identified in a lunar soil sample returned by the Chang'e-5 space mission (Jin et al. 2024). Taking into account a strange occurrence of the mineral, the likelyhood of technogenic contamination is discussed by Jin et al. (2024) from several points of view, including the possible reaction(s) of rocket propellant exhaust with basaltic rock at the lunar landing site. Unfortunately, the authors do not pay attention to the pyrotechnically actuated separation devices (pyrotechnic fasteners) that were installed in the active docking mechanism (ADM) of the lander (Wang et al. 2023). It can be seen (Fig. 1 in Wang et al. 2023) that the ADM is directly attachable to the Chang'e-5a soil sampling container, namely through the aforementioned pyrotechnic fasteners. Although the chemical composition of the pyrotechnics used in the Chang'e-5 ADM has not been disclosed, the most reliable formulations, by analogy with known devices (Seeholzer et al. 1995), are perchlorate-metal mixtures. In this regard, ammonium perchlorate/magnesium metal, NH_4ClO_4/Mg formulation (e.g., Nishiwaki et al. 2019; Ao et al. 2023) is one of candidates that can explain well the emergence of $NH_4MgCl_3{\cdot}6H_2O$ as a contaminant in the Chang'e-5 returned sample. Incomplete reductive decomposition of NH_4ClO_4 results in the formation of NH_3, HCl and H_2O vapor, while chloridation of Mg yields $MgCl_2$, all the necessary components for the synthesis of $NH_4MgCl_3{\cdot}6H_2O$ (Doll and Lund 1992). Note that in this case, the $^{37}Cl/^{35}Cl$ ratios (Jin et al. 2024) are useless for resolving the origin of the phase, since they have to be compared not with natural chlorine sources but with the isotopic ratio of chlorine used in the production of a particular propellant composition.

The next phase under discussion is the so-called HAMP (high ammonium phosphate) or "struvite", which has been detected in samples returned from Ryugu, a C-type asteroid (Pilorget et al. 2024). This X-ray amorphous substance was supposed to be ammonium-bearing mineral, presumably struvite, $NH_4MgPO_4{\cdot}6H_2O$, on the basis of a band at ~1450 cm^{-1} (6.9 μm) in diffuse reflectance infrared spectra of its mixtures with a phyllosilicate matrix. It is noteworthy in this regard that the EDX spectrum of the HAMP phase does not contain the diagnostic $K\alpha$-line of nitrogen (Pilorget et al. 2024). Meanwhile, struvite contains 5.7 wt.% of *elemental* nitrogen, whereas dittmarite, $NH_4MgPO_4{\cdot}6H_2O$, a likely dehydration product of struvite under the conditions of EDX analysis (Bayuseno and Schmahl 2018; Feng et al. 2021), contains even 9 wt.% elemental nitrogen. At those contents the N-$K\alpha_2$ line of nitrogen at 392.4 eV is clearly visible in the EDX spectra (see Fig. 1 in our paper; Jin et al. 2024). Moreover, the reference

EDX spectra of struvite contain this well-resolved N-*K*α line (Zhang et al. 2020; Sittipunsakda et al. 2021; Wang et al. 2022). Based on the absence of the N-*K*α line, it can therefore be concluded that the HAMP phase in the Ryugu samples (Pilorget et al. 2024) is, at first, definitely not struvite and next, is devoid of ammonium, at least at the levels detectable by EDX (ca. 2 wt.%). The appearance of a band at ~1450 cm^{-1} (6.9 μm) in the IR-spectrum of this phase does not necessarily signify the presence of ammonium: it can equally be explained by the presence of hydrous magnesium carbonates, such as nesquehonite $MgCO_3·3H_2O$, lansfordite $MgCO_3·5H_2O$, artinite $Mg_2(CO_3)(OH)_2·3H_2O$, or dypingite, $Mg_5(CO_3)_4(OH)_2·5H_2O$ (White 1971; Hill et al. 1982; Frost et al. 2008).

The non-ammonium origin of 3.2 μm feature in the IR-spectra of comets and asteroids

In view of recent advances in space research, in particular the challenge of ammonium reservoirs in comets and asteroids, we attempted a comparison of infrared spectra of comet 67P/Churyumov-Gerasimenko (Rubin et al. 2020) with corresponding spectra of nickeloan boussingaultite from Orgueil. The choice of comet 67P is connected with the availability of a quality spectrum in the 2.5 – 4 μm region (Raponi et al. 2020) that supposedly evidences for ammonium salts in the composition of comet 67P (Poch et al. 2020; Altwegg et al. 2020). In the context of the problem, it is important that infrared spectra of the Tutton's salts exhibit significant red shift of the bands corresponding to O–H stretching vibrations relative to the commonly encountered O–H frequences (Culka et al. 2009; Belogub et al. 2015; Chukanov et al. 2018). The effect is caused by a pronounced network of cross-linked hydrogen bonds (Fig. 2). The O–H bands offset towards smaller wavenumbers (i.e., longer wavelengths) reaches 150–200 cm^{-1}, down to ~3200 cm^{-1}, well displaced from the values of 3400–3600 cm^{-1} in the IR-spectra of the most water-bearing minerals (Chukanov 2014). The magnitude of displacement is of the same order for the different Tutton's salts, independent on the nature of A^+ or M^{2+} cation (Fig. 3) (e.g., Belogub et al. 2015; Souamti et al. 2016; Chukanov et al. 2018). As a result, the O–H stretching bands in the IR-spectrum of nickeloan boussingaultite from Orgueil, as well as other Tutton's salts, match the position of a so-called "3.2 μm feature" observed in the infrared spectra of comets and asteroids (Poch et al. 2020). This enigmatic split band (Capaccioni et al. 2015) was assigned to ammonium in cometary nucleus of 67P (Poch et al. 2020), because its position and shape corresponds to N–H stretching vibrations in the spectra of simulants prepared from the mixtures of pyrrhotite, $Fe_{1-x}S$, and anhydrous ammonium salts (Poch et al. 2020). Several candidate compounds were checked for the role of ammonium reservoir in comet 67P, the best suited one was ammonium formate, $HCOONH_4$ (Poch et al. 2020). Our infrared reflectance data (Fig. 4, Table 5) evidence that the 3.2 μm feature can be equally attributed to the presence of the Tutton's salts. Curiously in this case, the 3.2 μm band is not assigned to ammonium, but to crystal hydrate water of the Tutton's salt, the only known meteoritic one is boussingaultite.

The Tutton's salts as the likely space ammonium carriers

The 3.2–3.1 μm feature similar to that observed in the infrared spectrum of comet 67P was detected in the spectra of (1) Ceres and several asteroids (King et al. 1992; De Sanctis et al. 2015; Poch *et al.* 2020). It was suggested that, together with a strong 2.7 μm band, this argues for the wide distribution of ammoniated phyllosilicates in these space bodies (De Sanctis et al. 2015). We suggest that like in case of comet 67P, the infrared spectra of (1) Ceres can be interpreted in terms of superposition of ordinary (ammonium-free) phyllosilicates abundant in carbonaceous chondrites and asteroids (Gounelle and Zolensky 2014; Ito et al. 2022; Yokoyama et al. 2023; Lauretta et al. 2024), and naturally confirmed ammonian Tutton's salts like that discovered in our work. Cometary mineralogy share many common features with primitive carbonaceous chondrites and their closest relatives – carbonaceous asteroids (162173) Ryugu and (101955) Bennu (Westphal et al. 2009; Berger et al. 2011; Filacchione et al. 2019; Ito et al. 2022; Yokoyama et al. 2023; Lauretta et al. 2024). In the context of the present work, it is notably that all these bodies contain noticeable amounts of sulfides, including pyrrhotite, $Fe_{1-x}S$, pentlandite, $(Fe,Ni)_9S_8$, and cubanite, $CuFe_2S_3$. The former two sulfides bear notable to very high Ni contents (Berger et al. 2011); therefore, they might serve as a source of Ni for Tutton's salts. Nickelboussingaultite, $(NH_4)_2(Ni,Mg)(SO_4)_2 \cdot 6H_2O$ where Ni>Mg, is known on Earth as an aqueous alteration product of Ni-sulfide ores (Yakhontova et al. 1976; Chukanov et al. 2018) and as a rare product of volcanic fumarolic activity (Campostrini et al. 2024). The origin of nickel-rich boussingaultite in Orgueil could be invoked by the asteroidal alteration of Ni-bearing sulfides. This corroborates with the known pronounced aqueous alteration of carbonaceous asteroids (Ito et al. 2022; Yokoyama et al. 2023; Lauretta et al. 2024). The presence of abundant molecular oxygen and SO_2 in the composition of the coma of 67P (Bieler et al. 2015) supports the likelihood of the low-temperature aqueous oxidation of sulfides. Phyllosilicates would act as a source of Mg, whereas Fe, being predominant in sulfides, is dumped out into ferric iron-bearing minerals (phyllosilicates, framboidal magnetite) abundant both in CI1 chondrites and asteroid samples from Ryugu and Bennu (Tomeoka and Buseck 1988; Sutton et al. 2017; Ito et al. 2022; Yokoyama et al. 2023; Lauretta et al., 2024; Roskosz et al. 2023). This mechanism explains the emergence of Mg-Ni sulfates completely devoid of Fe. In this respect, the latest finding of iron-free newberyite, $MgHPO_4 \cdot 3H_2O$, in the fresh samples returned from asteroid Bennu (Lauretta et al., 2024) evidences that oxidative Mg/Fe aqueous fractionation also took place on this asteroid. The only but significant feature that can not be explained by the in-situ oxidation of native sulfides is the complete absence of Cu in sulfates of Orgueil. Cubanite $CuFe_2S_3$, an accessory phase in both Orgueil and comet Wild2 (Macdougall and Kerridge 1977; Bullock et al. 2005; Berger et al. 2011) occurs in Orgueil as very fresh, sharp, unaltered twinned crystals (Fig. 5). It appears unlikely that cubanite was not affected by oxidative alteration whereas pentlandite, being quite resistant to oxidation, would oxidize, acting as a source of Ni released into sulfates. Therefore it is also possible that nickeloan boussingaultite in Orgueil is in fact a remnant of the early solutions which were not directly connected with the oxidation of Fe-Ni sulfides.

IMPLICATIONS

The discovery of the first ammonium mineral in meteoritic matter might call for the overall reassessment of the analytical techniques implemented to extraterrestrial objects. It is shown in our paper that crystalline ammonium minerals can be scarce in meteoritic, cometary or asteroidal matter. They are generally water-soluble. In addition, these phases may have very low thermal decomposition thresholds. The rarity and inherent instability of ammonium minerals under conditions of focused electron/ion beam in vacuum (electron or ion microprobe) may result in the omissions of these important phases during conventional analytical procedures (e.g., preparation and study of thin sections). The possibility of technogenic contamination, especially in the samples returned by space missions, can not be ruled out. The novel approaches, like single-crystal studies implemented in this work, could facilitate to overcome the existing problems in the study of extraterrestrial matter.

CONCLUSION

The existence of Tutton salts in both cometary nuclei and carbonaceous asteroids looks quite arguable, based on the fact of their natural occurrence in mineralogically relevant carbonaceous chondrite. From this point of view, the naturally confirmed mineral appears to be a potent candidate for the role of ammonium reservoir, superior to the previously proposed ephemeral compounds not yet confirmed in nature.

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Figure 1. Nickeloan boussingaultite (the NH_4-Mg-Ni Tutton's salt) handpicked from Orgueil. (**a**) General view of the crystal intergrowth in scanning electron microscope (BSE image) before EDX analyses. (**b**) The same crystal after EDX analyses. The beam impacted sites appear as deep pits on the crystal surface (outlined by white squares). (**c**) Low-energy region of the EDX spectrum acquired from the same crystal, evident for the presence of nitrogen, magnesium and nickel.

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Tables

Table 1. Semi-quantitative chemical composition of boussingaultite from Orgueil (electron microprobe, wt. %, *apfu*) vs. that obtained by the structure refinement

Point	$(NH_4)_2O$	K_2O	Na_2O	MgO	NiO	SO_3
1	2.71	0.41	0.11	4.01	8.17	33.86
2	4.78	0.42	0.00	6.70	7.61	39.18
3	5.60	0.34	0.15	9.54	6.81	42.53
4	2.86	0.41	0.00	6.67	7.28	38.88
Average	3.99	0.40	0.07	6.73	7.47	38.61

Formula amounts

	NH_4	K	Na	Mg	Ni	S
Average microprobe, based on (Mg+Ni)=1						
	0.57	0.03	0.01	0.63	0.37	1.81
Crystal structure refinement						
	2.00	–	–	0.650(4)	0.350(4)	2.00

Table 2. Unit-cell parameters of some reported boussingaultite and nickelboussingaultite [a]

M site [b]	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	*V* (Å^3)	Locality and ref. [c]
Mg	9.316(2)	12.580(4)	6.202(1)	107.094(5)	694.7(1)	Synthetic [1]
Mg	9.3183(4)	12.6070(4)	6.2054(3)	107.115(5)	696.70(5)	Kladno [2]
$Mg_{0.65}Ni_{0.35}$	9.2526(5)	12.5213(7)	6.2137(3)	106.934(6)	688.67(7)	Orgueil [3]
$Ni_{0.84}Mg_{0.22}$ $Cu_{0.12}Fe_{0.02}$	9.21(2)	12.46(2)	6.25(3) [d]	106.9	686.3	Norilsk [4]
Ni [e]	9.195(3)	12.469(4)	6.244(2)	106.98(3)	684.7(1)	Synthetic [5]

[a] All crystallize in monoclinic system, space group $P2_1/a$. [b] The records are ordered by Ni contents in the *M* site. [c] References: [1] Margulis and Templeton (1962); [2] Zhitova et al. (2024); [3] This work; [4] The holotype nickelboussingaultite, Yakhontova et al. (1976); [5] Tahirov et al. (1994). [d] Yakhontova et al. (1976) gives a doubled *c*-parameter, which was not confirmed in other studies. [e] Cell setting was transformed from $P2_1/c$ to $P2_1/a$.

Table 3. Non-hydrogen bond distances in boussingaultite from Orgueil and related Tutton's salts $(NH_4)_2M^{2+}(SO_4)_2\cdot 6H_2O$ [a]

Bond	Mg [1] [b]	$Mg_{0.65}Ni_{0.35}$ [2]	Ni [3]
	Synthetic	Orgueil	Synthetic
M−O5 ×2	2.073(5)	2.0721(16)	2.066(2)
M−O6 ×2	2.083(5)	2.0734(16)	2.067(2)
M−O7 ×2	2.051(5)	2.0396(15)	2.041(2)
S1−O1	1.476(5)	1.4765(16)	1.481(2)
S1−O2	1.459(5)	1.4536(17)	1.461(2)
S1−O3	1.481(5)	1.4764(15)	1.481(2)
S1−O4	1.474(5)	1.4758(16)	1.480(2)

[a] The table was created using publCIF software (Westrip 2010). [b] References: [1] Margulis and Templeton (1962); [2] This work; [3] Tahirov et al. (1994).

Table 4. Band assignments in the infrared transmission spectrum of nickeloan boussingaultite from Orgueil.

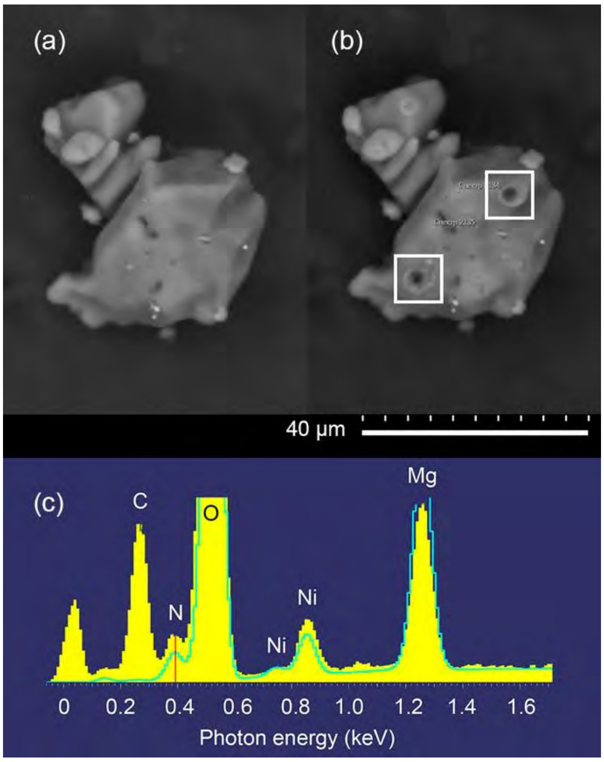
Wavenumber (cm^{-1}) [a]	Wavelength (µm)	Assignment [b]
3260 s	3.07 s	$\nu(H_2O)$
3066 s	3.26 s	$\nu(H_2O)$
2925 m sh	3.42 m sh	$\nu(NH_4)$
2850 m sh	3.51 m sh	$\nu(NH_4)$
1676 m	5.97 m	$\nu_2(NH_4)+\delta(H_2O)$
1470 m	6.8 m	$\nu_4(NH_4)$
1431 s	6.99 s	$\nu_4(NH_4)$
1148 s	8.71 s	$\nu_3(SO_4)$
1086 s	9.21 s	$\nu_3(SO_4)$
982 m	10.18 m	$\nu_1(SO_4)$
816 m sh	12.25 m sh	$\nu_T(H_2O)$
722 m	13.85 m	$\nu_T(H_2O)$
626 m	15.97 m	$\nu_4(SO_4)$
615 m sh	16.26 m sh	$\nu_4(SO_4)$

[a] Intensity and shape abbreviations: s – strong; m – medium; sh – shoulder.
[b] Band assignments according to Culka et al. (2009).

Table 5. Ammonium- and hydroxyl-stretching vibrations (the 3.2 µm feature) in the infrared spectra of nickeloan boussingaultite and Comet 67P.

Orgueil		Comet 67P	Assignment [a]
Transmittance	Reflectance	Reflectance	
3.07	3.13	3.11	$\nu(H_2O)$
3.26	3.29	3.26	$\nu(H_2O)$
3.42	3.46	3.38	$\nu(NH_4)$
3.51	3.53	3.48	$\nu(NH_4)$

[a] Band assignments according to Culka et al. (2009).



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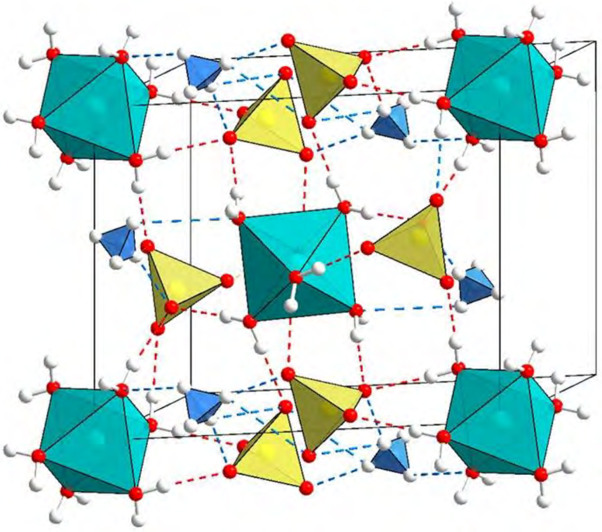

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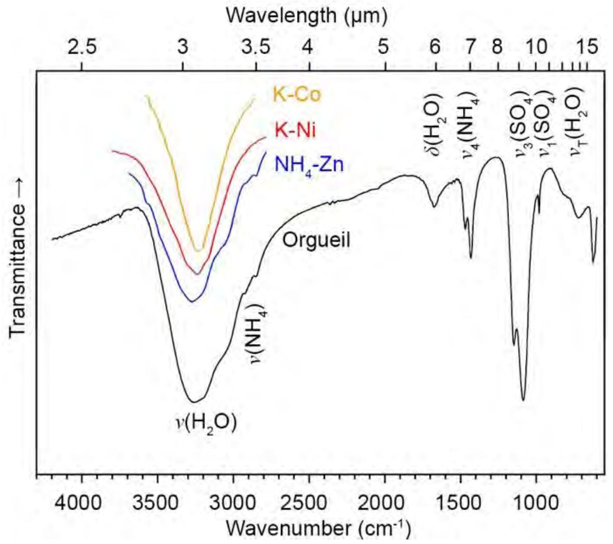

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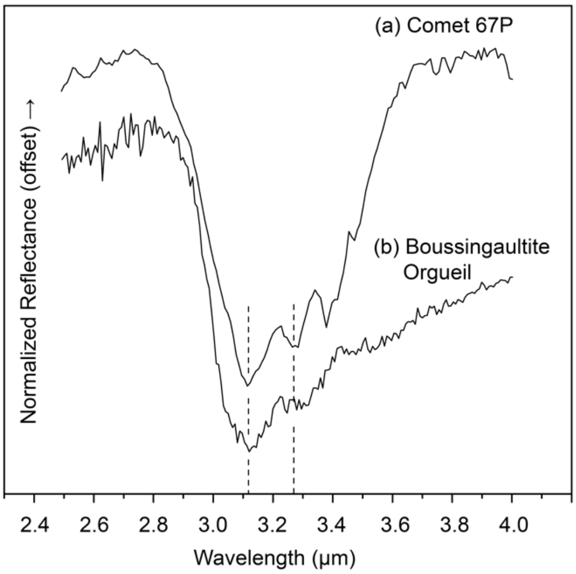

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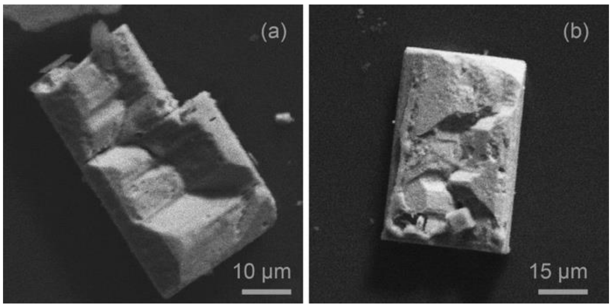

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