Thermessaite-(NH_4), $(NH_4)_2AlF_3(SO_4)$, a new fumarole mineral from La Fossa crater at Vulcano, Aeolian Islands, Italy

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Running title: Thermessaite-(NH_4), a new mineral

Abstract

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Thermessaite-(NH_4), ideally $(NH_4)_2AlF_3(SO_4)$, is a new mineral found as a medium- to high-temperature (about 250-300°C) fumarole encrustation at the rim of La Fossa crater, Vulcano, Aeolian Islands, Italy. The mineral deposited as aggregates of micrometer-sized sharp prismatic crystals on the surface of a pyroclastic breccia in association with thermessaite, sulfur, arcanite, mascagnite, and intermediate members of the arcanite-mascagnite series.

The new mineral is colorless to white, transparent, non-fluorescent, has a vitreous luster, and a white streak. The calculated density is 2.185 g/cm^3. Thermessaite-(NH_4) is orthorhombic, space group *Pbcn*, with a = 11.3005(3) Å, b = 8.6125(3) Å, c = 6.8501(2) Å, V = 666.69(4) Å^3, Z = 4. The eight strongest reflections in the X-ray powder-diffraction data [d in Å (I) (hkl)] are: 5.65 (100) (200), 4.84 (89) (111), 6.85 (74) (110), 3.06 (56) (112), 3.06 (53) (221), 3.08 (47) (311), 2.68 (28) (022), 2.78 (26) (130). The average chemical composition, determined by quantitative SEM-EDS (N by difference), is (wt%): K_2O 3.38, Al_2O_3 25.35, SO_3 36.58, F 26.12, $(NH_4)_2O$ 22.47, O = F -11.00, total 102.90. The empirical chemical formula, calculated on the basis of 7 anions *pfu*, is $[(NH_4)_{1.85}K_{0.15}]_{\Sigma 2.00}Al_{106}F_{2.94}S_{0.98}O_{3.06}$. The crystal structure, determined from single-crystal X-ray diffraction data [$R(F)$ = 0.0367], is characterized by corner-sharing AlF_4O_2 octahedra which form [001] octahedral chains by sharing two *trans* fluoride atoms [Al–F2 = 1.8394(6) Å]. Non-bridging Al–F1 distances are shorter [1.756(1) Å]. The two *trans* oxygen atoms [Al–O = 1.920(2) Å] are from SO_4 tetrahedra. NH_4^+ ions occur in layers parallel to (100) which alternate regularly with (100) layers containing ribbons of corner-sharing AlF_4O_2 octahedra and associated SO_4 groups. The NH_4^+ ions are surrounded by five oxygen atoms and by four fluorine atoms. The mineral is named as the (NH_4)-analogue of thermessaite, $K_2AlF_3(SO_4)$, and corresponds to an anthropogenic phase found in the burning Anna I coal dump of the Anna mine, Aachen, Germany. Both mineral and mineral name have been approved by the IMA-CNMNC commission (IMA 2011-077).

Keywords: thermessaite-(NH_4), new mineral, sublimates, fumaroles, crystal structure, Vulcano, Aeolian Islands, Italy.

Introduction

The last thermal crisis, which started at Vulcano (Aeolian Island, Italy) in 1988 and reached a maximum in 1993, was characterized by an intense deposition of interesting and rare sublimate minerals. With the aim of investigating the correlation between the deposition of the mineralogical phases and the fumarole temperature, composition of the gas phase and the volcanic activity, our team began a systematic mineralogical investigation which led, since 1994, to the discovery of a large variety of rare phases and new minerals (Garavelli, 1994; Garavelli and Vurro, 1994; Ferrara *et al*., 1995; Coradossi *et al*., 1996; Borodaev *et al*., 1998, 2000, 2001, 2003; Vurro *et al*., 1999; Cheynet *et al*., 2000; Garavelli *et al*., 1997, 2003, 2005, 2013, 2014; Pinto *et al*., 2006a, b, c, 2008, 2011, 2014, 2015a, b; Mitolo *et al*., 2009, 2011, 2013; Balić-Žunić *et al*., 2016). The abundance and variety of minerals described for the La Fossa crater fumaroles attracted worldwide interest in the mineralogy of the area.Within a few years La Fossa crater became a mineralogical attraction for researchers and collectors. The large number of minerals described for the locality, about thirty of which have been discovered only in the last 20 years, makes the La Fossa crater of Vulcano one of the most prolific type localities in the world, in Italy second only to Vesuvius.

Attracted by this “mineralogical paradise”, the Italian mineral collector G. Scavo visited the locality in 2005 and returned home with a number of interesting mineralogical samples, subsequently given to us for examination. In these samples, some minute, sharp prismatic crystals directly growing on the surface of a pyroclastic breccia focused our attention and resulted in the recognition of the new mineral thermessaite-(NH_4) described herein.

Thermessaite-(NH_4) is the NH_4 analogue of thermessaite, $K_2AlF_3(SO_4)$ (Demartin *et al*., 2008; type locality also La Fossa crater), and is identical to an anthropogenic phase from the burning Anna I coal dump at the Anna mine, near Aachen, North Rhine-Westphalia, Germany (Witzke *et al*., 2015). The IMA Commission on on New Minerals, Nomenclature and Classification approved both the new mineral and its name (IMA No. 2011-077, Garavelli *et al*., 2012). The holotype is deposited in the mineral collections of the Museum "C.L. Garavelli" in the "Dipartimento di Scienze della Terra e Geoambientali", Università degli Studi di Bari "Aldo Moro", Italy, sample number 15/nm-V28.

Occurrence and physical properties

Thermessaite-(NH_4) is a volcanic sublimate found on the surface of an altered sample of pyroclastic breccia collected in 2005 in close proximity to the active, medium- to high-temperature fumarole F11 (*T* about 250-300°C at the time of sampling), located at the rim of La Fossa crater at Vulcano, Aeolian islands, Italy (Fig. 1). Geological and metallogenic data for the La Fossa crater area are given in previous papers (Garavelli *et al*., 1997; Campostrini *et al*., 2011; Balić-Žunić *et al*., 2016, and references therein).

Individual single crystals of thermessaite-(NH_4) are very rare. Generally the mineral occurs as aggregates of radiating elongated needles in which the individual maximum crystal dimensions are always less than 0.2 mm. The vitreous crust on which the thermessaite-(NH_4) crystals are directly grown, consists of amorphous silica and aluminum silicon fluorides. Sulfur, thermessaite [$K_2AlF_3(SO_4)$], arcanite [$K_2(SO_4)$], mascagnite [$(NH_4)_2(SO_4)$], and intermediate members of the arcanite-mascagnite series have been identified in the sample rock in which thermessaite-(NH_4) was found.

Thermessaite-(NH_4) is colorless to white in color, with a white streak and a vitreous luster. The minute acicular crystals are transparent to translucent. No twinning was observed. Thermessaite-(NH_4) is brittle and no cleavage, parting, or fracture were observed.

The very small dimensions, as well as the softness and friability of the crystals, precluded direct measurements of the refractive indices and physical properties such us density and micro-hardness. The calculation of the mean refractive index was done using the Gladstone-Dale constants of Mandarino (1976, 1981). Taking into account the empirical formula, the mean refractive index of thermessaite-(NH_4) is 1.54. The calculated density from single-crystal X-ray data and empirical formula is 2.185 gcm^{-3}.

Chemical data

Quantitative chemical analyses were obtained by SEM-EDS methods. The electron microscope used for these analyses was a S360 Cambridge Scanning Electron Microscope coupled with an Oxford-Link Ge ISIS Energy Dispersive Spectrometer equipped with a Super Atmosphere Thin Window©, since this allows better detection of light elements. An energy-dispersive spectrometer (EDS) was chosen for quantitative analyses of the tiny crystals instead of a wavelength-dispersive spectrometer (WDS), because it allows analyses at a non-critical working distance (Ruste, 1979; Acquafredda and Paglionico, 2004; Balić-Žunić *et al.*, 2016) and using a lower probe current. The non-critical working distance permits quantitative EDS analyses even directly on crystal surfaces not totally flat, that is when it lacks the necessary focusing WDS geometry. Moreover, the micrometer-sized crystals of thermessaite-(NH_4) quickly decompose at a probe current exceeding 3 nA, which generates few X-ray photons easily detectable only by an EDS detector.

The investigated subsample, which consisted of an aggregate of radiating crystals 100 μm in size, was sputtered with a 30 nm-thick carbon film to perform SEM-EDS observations and microanalysis. Operating conditions of the SEM were: 15 kV accelerating voltage, 500 pA probe current, 2500 cps as average count rate on the whole spectrum, typical counting time 100 s. X-ray intensities were converted to wt% by the ZAF-4/FLS quantitative analysis software support of Oxford-Link Analytical (UK) that allows to match the peaks of the standards with the ones of the analyzed mineral, taking into account the relative contribution of the matrix and also when there are partial or complete overlaps among peaks of different elements. The standards employed were: orthoclase (K), corundum (Al), barite (S), and synthetic LiF (F). The analytical results (mean of 11 analyses) are reported in Table 1. The empirical chemical formula, calculated on the basis of 7 anions per formula unit (*pfu*), is $[(NH_4)_{1.85}K_{0.15}]_{\Sigma 2.00}Al_{106}F_{2.94}S_{0.98}O_{3.06}$. The ammonium content was calculated from the K content, taking into account the $(NH_4,K)_2AlF_3(SO_4)$ stoichiometry ($NH_4 + K = 2$ *pfu*).

The simplified formula of thermessaite-(NH_4) is $(NH_4)_2AlF_3(SO_4)$ which ideally requires $(NH_4)_2O$ 24.10, Al_2O_3 23.59, SO_3 37.05, F 26.36, and O = F -11.10 wt%.

Crystallography

Single-crystal X-ray diffraction data were collected from a selected crystal fragment (0.110 × 0.040 × 0.035 mm) from the holotype using a Bruker AXS X8 APEX2 CCD automated diffractometer equipped with a kappa-geometry goniometer and graphite-monochromatized Mo*K*α radiation (50 kV and 30 mA operating conditions). A Miracol fiber optics capillary collimator (0.3 mm diameter) was used to enhance the beam intensity and to reduce beam divergence. Five sets of 19 frames were used for initial unit-cell determination, whereas complete data collection was accomplished by several ϕ and ω scans with a 0.5° frame width, 120 s exposure time per frame, and a crystal-to-detector distance of 40 mm. The collection strategy was optimized by the Apex suite program (Bruker, 2003a). Details about data collection and refinement are summarized in Table 2. Data reduction, including intensity integration, correction for Lorentz, polarization, background effects, and scale variation, was done using the package SAINT-IRIX (Bruker, 2003b). A semi-empirical absorption correction (Blessing, 1995) was applied using the SADABS program (Sheldrick, 2008). The approximate minimum and maximum X-ray transmission-factors were 0.6535 and 0.7461, respectively.

The structure of thermessaite-(NH_4) was refined in the space group *Pbcn* using the full-matrix least-squares program SHELXL-97 (Sheldrick, 2008), and starting from the atomic coordinates of thermessaite (Demartin *et al.*, 2008) and by placing N on the K site. All the hydrogen atoms of the ammonium ion showed up clearly in the difference-Fourier map and were included in the final refinement by restraining N–H distances to the value of 1.00(2) and using isotropic atomic displacement parameters. The site occupation factor for the ammonium site was refined taking into account the substitution $K^+ \leftrightarrow NH_4^+$; the obtained occupancy results [NH_4 = 0.86(1), K = 0.14(1)] lead to the structural formula $[(NH_4)_{1.72}K_{0.28}]AlF_3(SO_4)$, in good agreement with the results of the chemical analyses (Table 1).

The refinement converged to the agreement $R(F)$ value of 0.0367 for 672 observed reflections [$I > 2\sigma(I)$]. Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography (Ibers and Hamilton, 1974). In the final refinement anisotropic displacement factors were used for all the atoms with the exception of hydrogens of the ammonium group.

Single-crystal X-ray diffraction data were also obtained from a crystal (0.02 × 0.02 × 0.36 mm) of the anthropogenic material recovered from the burning Anna I coal dump of the Anna mine (Aaachen, Germany) using a Bruker ApexII diffractometer (equipped with a CCD detector) with Mo*K*α radiation (for details see again Table 2). The measured intensity data were processed with the Bruker program suite APEX2, including a multi-scan absorption correction with SADABS (Sheldrick, 2002). A full-matrix least-squares refinement on F^2

(SHELXL-97, Sheldrick, 2008), with scattering factors for neutral atoms, was performed starting from atomic coordinates of thermessaite, leading to a final *R*(*F*) of 0.0372, and the structural formula $[(NH_4)_{1.70}K_{0.30}]AlF_3(SO_4)$, very similar to that of the type material. Although all H atoms of the NH_4 group could be located on the difference-Fourier map, their N–H bond lengths had to be restrained as described for the Vulcano sample and their isotropic displacement parameters fixed to 0.08 Å^2, in agreement with the observation that at least two of them seemed to be involved in bifurcated hydrogen bonds.

Fractional atomic coordinates, occupancies, and displacement parameters for the natural thermessaite-(NH_4) from Vulcano and the corresponding anthropogenic material from the Anna mine are presented in Table 3, while selected interatomic distances are listed in Table 4. The CIF-files with crystal-structure data of both samples, as well as tables of structure factors, have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below). The X-ray powder-diffraction pattern calculated from the single-crystal structure model of the holotype is given in Table 5.

Description of crystal structure

A polyhedral representation of the crystal structure of thermessaite-(NH_4) from Vulcano is given in Figures 2a, b. It consists of chains of corner-sharing AlF_4O_2 octahedra running along [001] and joined to each other by sharing two fluorine atoms at opposite vertices. The bridging Al–F2 distances are longer than the non-bridging Al–F1 distances (Table 4). Similar features are observed in the structure of thermessaite (Demartin *et al*., 2008). The two oxygen atoms at the remaining equatorial corners are shared with SO_4 tetrahedra (Fig. 2b), which ensure further connection of adjacent AlF_4O_2 octahedra, so forming ribbons which extend infinitively along [001]. The S–O distances are longer for bridging oxygens than for non-bridging oxygen atoms (Table 4). Isolated NH_4^+ ions occur in layers parallel to (100) which alternate regularly with (100) layers containing ribbons of corner-sharing AlF_4O_2 octahedra and associated SO_4 groups. The general scheme of the structure as well as bond-distances within the AlF_4O_2 octahedra and the sulfate groups are very similar to those in thermessaite (Demartin *et al*., 2008). NH_4^+ ions represent significantly distorted tetrahedra with N–H bond lengths ranging from 0.97(2) to 0.99(2) Å in the structure of the holotype sample from Vulcano. In both the holotype and the Anna mine samples, the NH_4^+ ions are partially replaced by K^+ ions. Interestingly, but probably a simple coincidence, the refined N:K ratios are very similar [0.86(1):0.14 *vs* 0.848(4):0.152]. The NH_4^+/K^+ ions are located in nine-coordinate sites where they are bonded to five oxygen atoms (O1, O2) and four fluorine atoms (F1, F2) and thereby provide an important linkage between the chains. The donour-acceptor distances N···O/F range between 2.789(2) and 3.272(3) Å (type material; values for the Anna mine crystal are very similar; Table 4) and reflect weak to very weak hydrogen bonding. The local orientation of the NH_4^+ ions in these nine-coordinate sites will be controlled by the significant hydrogen bonding present and probably also indirectly by the (NH_4):K ratio.

Genetic features

Thermessaite-(NH_4) is a new anhydrous fluoride sulfate from a medium- high-temperature fumarole at La Fossa crater volcano. Its discovery is a remarkable event, not just because of the simultaneous presence in it of ammonium, aluminum, and fluorine as essential constituents, which occurs only in thermessaite-(NH_4), but also because it permits us to discuss once more the conditions of mineral deposition at La Fossa crater fumaroles.

Aluminum phases, mainly hydrous sulfates (i.e. alunogen, alunite, etc.) and/or fluorides (i.e. ralstonite), are relatively common among volcanic fumarole minerals and their occurrence is generally interpreted as a secondary deposition during the final stage of the process of interaction between volcanic fumarole fluids and wall rocks crossed by the fluids rising to the surface (fumarole encrustations). The cooling and oxidation of high-temperature volcanic gases result in: (i) the formation in proximity of the surface of acidic condensates that react with the wall rocks; (ii) a differential leaching from the rocks of the elements, according to their different mobility; (iii) The precipitation of secondary minerals. Unlike these phases, thermessaite-(NH_4) cannot be considered a secondary mineral, but a primary phase formed by direct deposition from the fumarole steam moving through the rocks to the surface (volcanic sublimate). This is confirmed not only by the temperature values measured at fumaroles where the new mineral was collected, which prevent the existence of a condensed aqueous phase reacting with the rocks, but also by the morphology and the condition of growth of the mineral. As a matter of fact, thermessaite-(NH_4) appears directly growing from the rocks sometimes covered by crusts of vitreous amorphous silica and ammonium silico-fluorides, in small radiating aggregates of acicular and elongated individual crystals, without any signs of dissolution and recrystallization.

Ammonium mineral phases are relatively abundant among sublimate minerals from the La Fossa crater fumaroles, and their occurrence is due to the relatively high ammonia content in the volcanic fluids discharging from the area. NH_4 minerals generally occurs around vents with medium-high temperature values (300-200°C) and generally consist of chlorides (containing traces of Br and I) (i.e. salammoniac) and complex chloride-sulfates and sulfates. This assemblage is indicative of a chlorine-rich environment, in which the elements known to form volatile metal chlorides (Me = Na, Pb, Bi, Sn, Fe) can be easily transported in the fumarolic steam as $MeCl_x$ complexes. The chlorine complexes act as carriers for the metals and, in the generally reducing, H_2S rich conditions registered at Vulcano fumaroles at the end of last century, form sulfochloride complexes which act as catalysts for the reactions leading to the formation of the high-temperature sulfide and sulfosalt assemblage (Balić-Žunić *et al*., 2016, and references therein). In that context, the anoxic conditions of the environment and the fumarole gas composition existing prevented at that time the formation of high-temperature metal sulfates, which are generally abundant in high-temperature fumarole environments around other volcanoes in the world.

Since the beginning of the 2000s, the thermodynamic conditions at fumaroles at the La Fossa crater of Vulcano gradually changed. Temperature values remained high, but the percentage of deposited sulfides and sulfosalts was gradually reduced, and new phases began to form and were subsequently described as new minerals. They mainly consist of metal chlorides, complex chloride-sulfates and sulfates, whose occurrence is indicative of more oxidizing conditions than the previous ones, probably favored by a reduction of the gas fluxes connected to the volcanic activity, and the consequent increased mixing process of the volcanic fumarole steam with the atmosphere in proximity of the surface (Fig. 3). This order of deposition is consistent also with the finding at Vulcano fumaroles of the Bi-sulfates leguernite and balićžunicite (Garavelli *et al*., 2014; Pinto *et al*., 2014, 2015a, b), as well as with the remarkable formation of the complex chloride-sulfates which could represent the intermediate stage of the transition from halide to sulfate assemblage after the intrusion of atmospheric oxygen into the system.

The simple ammonium chloride salammoniac, which is very abundant around La Fossa crater fumaroles with temperature values up to 300°C, as well as the new ammonium tin-, ammonium lead-, and ammonium bismuth-chlorides, panichiite (Demartin *et al*., 2009a), brontesite (Demartin *et al*., 2009b), and argesite (Demartin *et al*., 2012), respectively, could be interpreted as the last stage of the transition from halide to sulfate assemblage in a chlorine-rich environment.

In spite of the abundance of simple or complex chlorides among the La Fossa crater sublimates, minerals containing fluorine are here relatively rare and their finding is always a remarkable event connected to local increase of the F/Cl ratio in the fumarolic steam.

Although fluorides have been reported in many studies of volcanic encrustations (Jacobsen *et al*., 2014, and references therein, Balić-Žunić *et al*., 2016, 2018), the geochemistry and mineralogy of fluorine in the fumarolic environment is poorly known. Fumarole emanations are especially enriched in fluorine because of the condensation of HF gas. As a matter of fact, HF reacts strongly with rock-forming silicates, so its role in the alteration of rocks crossed by volcanic gases rising to the surface is important (Africano and Bernard, 2000 and references therein). The leaching of the rocks by HF enriches the volcanic fluids by supplying them with complexes like SiF_4, BF_3, or AlF_3, which reach the surface and contribute to the sublimate deposition around and in the inner areas of fumaroles. At Vulcano, BF_4^- ions participate in the formation of the sublimate barberiite, NH_4BF_4; SiF_4^- ions determine the formation of Na and K silicofluoride minerals such as malladrite, hieratite, and demartinite, but to the best of our knowledge, the ammonium silicofluorides cryptohalite and bararite [both $(NH_4)SiF_6$] have never been found there. Either way, the thin crust of vitreous and amorphous ammonium silicofluorides covering the rocks of the fumarole in which thermessaite-(NH_4) was found, simultaneously prove the existence of ammonium silicofluorides in Vulcano fumaroles and a possible potential finding of cryptohalite and bararite among sublimates from the area. In this context, thermessaite-(NH_4) represents a very interesting finding of another mineral at Vulcano, to this day second only to barberiite, containing both ammonium and fluorine as essential constituents. In addition, thermessaite-(NH_4) represents the first ammonium sublimate of Vulcano in which Al is one of the major species-forming elements, presumably formed at Vulcano due to the presence of AlF_3 complexes in the fumarole steam. The transport of aluminum in volcanic emissions in the form of fluoride complexes is commonly reported in the literature, and the finding of the new mineral oskarssonite, AlF_3, among volcanic sublimates from Mt. Hekla, Iceland (Jakobsen *et al*., 2014) even more confirms the presence of this compound in fumarole environments. Oskarsson (1981) and Rosenberg

(1988) suggested that AlF_3 is one of the principal high-temperature volcanogenic salts that form incrustations by fractional condensation of volcanic gases. Its presence in the volcanic steam is due to to the leaching of the rocks by HF contained in volcanic steams, according to the reaction $Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O$. Silicates of the affected rocks are also involved in the reactions, and the equilibrium $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$ shifts progressively to the right, SiF_4 becoming a significant F-bearing molecular species below 300°C (Rosenberg, 1992). The finding of vitreous ammonium-silicofluoride crusts associated whith thermessaite-(NH_4) strengthens the hypothesis of the simultaneous leaching from the rocks as the source of Si and Al in fumarole fluids of Vulcano, and provides further clue of the transport of both these elements as fluorine complexes. Laboratory investigation in the system AlF_3–Al_2O_3–H_2O–HF permitted to synthesize AlF_3 as one of the phases at 450-700ºC and demonstrated that, in this system, the AlF_3 hydration grade increases with increasing temperature (Rosenberg, 2006). Thermochemical calculations applied to the cooling of volcanic gases discharging from Mount St. Augustine volcano fumaroles (Getahun *et al.*, 1996) indicated that solid AlF_3 starts forming as sublimate around 300°C, which is about the same value as measured in the fumarole from which thermessaite-(NH_4) was collected. It could be speculated that the presence of ammonium in the volcanic steam somehow prevented at Vulcano the formation of oskarssonite, AlF_3, favouring the thermessaite-(NH_4) deposition. As in the case of the aforementioned AlF_3 laboratory experiments (Rosenberg, 2006), the absence of hydration in thermessaite-(NH_4) could be interpreted as due to a deposition at relatively low temperature. A possible reaction explaining the condensation of the new mineral is the following: $2NH_3 + AlF_3 + H_2S + 2O_2 \rightarrow (NH_4)_2AlF_3(SO_4)$ or $2(NH_4)^+ + AlF_3 + SO_2 + O_2 \rightarrow (NH_4)_2AlF_3(SO_4)$, which requires the incorporation of oxygen in the system. Similar reactions not involving AlF_3 could lead to the deposition of mascagnite, which has been found associated to thermessaite-(NH_4). Mascagnite deposition presumably immediately follows, or happens simultaneously, to the thermessaite-(NH_4) formation, according to the following reaction $2NH_3 + H_2S + 2O_2 \rightarrow (NH_4)_2(SO_4)$ or $2(NH_4)^+ + SO_2 + O_2 \rightarrow (NH_4)_2(SO_4)$.

This mineralogical assemblage represents a remarkable intermediate stage of the transition from halide to sulfate in a fluorine-rich, oxidized environment, and the thermessaite-(NH_4) formation is interpreted as the end stage of the fluoride/sulfate conversion. Possible processes explaining the mineralogy observed are shown schematically in Figure 3. The high-temperature volcanic gases interact with the wall rocks and cool during their uprising through the fumarole vent. Due to the lowering of the flow rate and the pronounced fracturation of the near-surface rocks, atmospheric O_2 enters into the fumarole vent leading to the oxidation of the gas phase. The presence of native sulfur in the mineral assemblage is also consistent with this process as it can be produced by the reaction $SO_2 + 2H_2S \rightarrow 3S + 2H_2O$ (Mizutani and Sugiura, 1996).

The finding of thermessaite-(NH_4) in the burning Anna I dump of the Anna coal mine in Aldsdorf (Germany), although remarkable, it is not surprising due to: (i) the similarity of the burning-coal steams with volcanic exhalations (the vent which yielded the anthropogenic thermessaite-(NH_4) samples had a temperature of 170°C); (ii) the strong analogies in the mineralogy of the La Fossa crater fumaroles and the burning dump at Anna mine (Witzke *et al.*, 2015). Solid condensed phases known both from the La Fossa crater and the Anna I mine dump include sulfur, selenium, salammoniac, metal chlorides, (NH_4)-metal-sulfate chlorides, metal-sulfate fluorides, anhydrous and hydrous metal-sulfates. The absence of sulfides and sulfosalts at the Anna Mine is probably due to the negligible Pb and Bi concentrations of both coal and associated (sedimentary) country rocks. Also the burning dump may feature more oxidizing near-surface conditions, which would prevent the deposition of these reduced sulfide and sulfosalt phases and, conversely, favour the high-temperature anhydrous sulfate formation.

In both the mentioned environments, the gas composition and the temperatures in the depths are enough to permit the mobilization of volatile elements by the leaching of selected elements from the rocks crossed by the acidic fluids rising to the surface. At fumaroles and on the surface of the dump the processes leading to mineral deposition are the same, except water condensation which is surely more abundant in the dump than in fumaroles, as testified by the abundance of hydrous sulfates at Anna I if compared with the Vulcano medium-high temperature fumaroles.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/xxxx

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FIGURE CAPTIONS

Fig. 1. La Fossa crater at Vulcano Island (Italy) and location of fumarole F11, the sampling site of thermessaite-(NH_4).

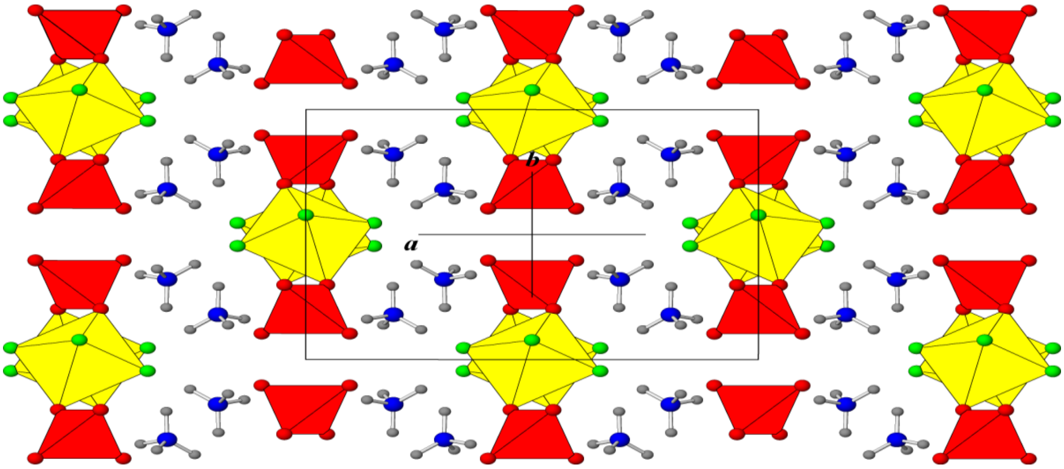

Fig. 2a. The crystal structure of thermessaite-(NH_4) in a view along the *c*-axis (yellow = AlO_4F_2 octahedra, red = SO_4 tetrahedra, blue spheres = N atoms, gray spheres = H atoms, red spheres= O atoms, green spheres = F atoms). The unit cell is outlined and N–H bonds are shown.

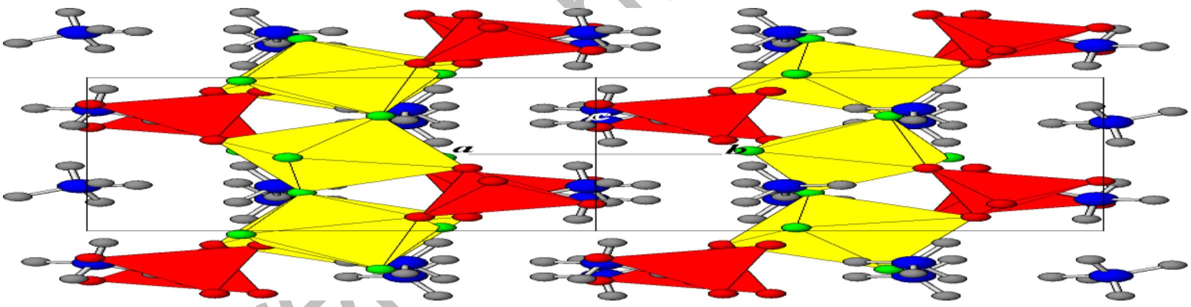

Fig. 2b. The crystal structure of thermessaite-(NH_4) in a view along the [110] axis, perpendicular to the octahedral-tetrahedral chains. Legend as in Fig. 2a.

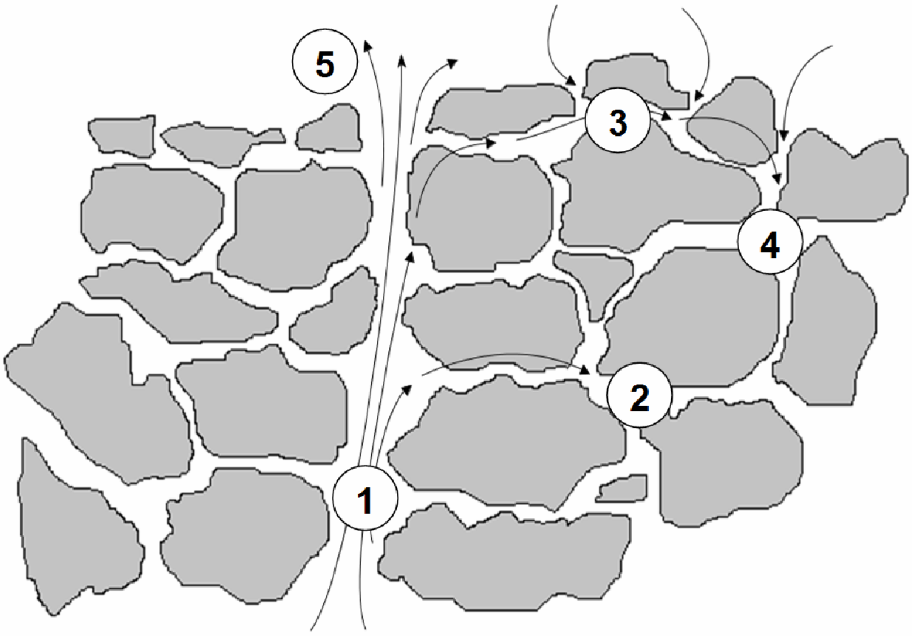

Fig. 3. Scheme of the processes occurring at medium- to high-temperature fumaroles of the La Fossa crater. 1. Volcanic gases rise to the surface interacting with wall rocks and leaching selected elements (Si, Al); 2. Deposition of high-temperature sublimates in reducing conditions (no interaction with the atmosphere); 3. Dilution of volcanic gases with the atmosphere and deposition of phases (halides to sulfates) in oxidizing conditions (medium-high temperature zone); 4. Condensation of the fumarole steam far from the vent and deposition of fumarolic encrustations (hydrous sulfates), in oxidizing conditions at about 100°C or less, after the mixing of the volcanic fluid phase with the atmospheric fluids entering the system, and interaction with the rocks; 5. Deposition of medium-high temperature sublimates in reducing conditions. The high fluxes of the gases prevented the incorporation of atmospheric oxygen in the system and the formation of oxidizing conditions. High temperature values at the vent are also due to the high fluxes of gases.

Table 1. SEM-EDS chemical-analytical data for thermessaite-(NH_4) (average of eleven point analyses).

CONSTITUENT	WT%	RANGE	SD
K_2O	3.38	2.77 – 4.02	0.42
Al_2O_3	25.35	24.67 – 26.35	0.57
SO_3	36.58	35.48 – 37.86	0.73
F	26.12	24.77 – 26.65	0.55
$(NH_4)_2O$*	22.47	20.83 – 22.03	0.33
	113.90		
O = F	-11.00		
Total	102.90		

*The ammonium content was deduced for each point analysis from the K content, taking into account the $(NH_4,K)_2AlF_3(SO_4)$ stoichiometry (i.e. $NH_4 + K = 2$ *apfu*).

Table 2. Summary of parameters describing data collection and refinement for thermessaite-(NH_4) and for the anthropogenic phase from the Anna mine.

	New mineral from Vulcano	anthropogenic phase
Crystal-structural formula	$[(NH_4)_{1.72}K_{0.28}]AlF_3(SO_4)$	$[(NH_4)_{1.70}K_{0.30}]AlF_3(SO_4)$
Crystal dimensions (mm)	0.035 × 0.040 × 0.110	0.02 x 0.03 x 0.12
Crystal system, space group	Orthorhombic, *Pbcn*	Orthorhombic, *Pbcn*
a (Å)	11.3005(3)	11.289(2)
b (Å)	8.6125(3)	8.598(2)
c (Å)	6.8501(2)	6.851(1)
V (Å^3)	666.69(4)	665.0(2)
Z	4	4
Temperature (K)	293	293
D_x (g/cm^3)	2.224	2.208
X-ray conditions (kV, mA)	50, 30	50, 30
Wavelength of radiation (Å)	0.71073	0.71073
Detector to sample distance (mm)	40	35
Number of frames	695	425
Rotation width per frame (°)	0.5	2
Measuring time (s)	120	400
$2\theta_{max}$ (°)	61.04 (d = 0.70 Å)	70.56 (d = 0.615 Å)
Independent reflections	959	1478
Reflections with $Fo > 4\sigma(Fo)$	672	916
R_{int}	0.0445	0.0650
R_σ	0.0422	0.0496
Ranges of h, k, l	$-16 \leq h \leq 13$	$-17 \leq h \leq 18$
	$-12 \leq k \leq 11$	$-10 \leq k \leq 13$
	$-9 \leq l \leq 7$	$-10 \leq l \leq 11$
R [$F_o > 4\ \sigma\ (F_o)$]	0.0367	0.0386
R (all data)	0.0685	0.0902
wR [$F_o > 4\ \sigma\ (F_o)$]	0.0752	0.0815
wR (all data)	0.0868	0.0977
Goof	1.028	1.009
Refined parameters	70	67
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.038P)^2+0.4443P]$ where $P = [max(F_o)^2+2(Fc)^2]/3$	$w=1/[\sigma^2(F_o^2)+(0.041P)^2+0.49P]$ where $P = [max(F_o)^2+2(Fc)^2]/3$
$D\rho_{min}$, $D\rho_{max}$ (e/Å^3)	-0.39, 0.32	-0.63, 0.38

Table 3. Atomic coordinates, occupancies (s.o.f.) and displacement factors (Å^2) for thermessaite-(NH_4) and for the anthropogenic phase from the Anna mine.

Atom	*x*	*y*	*z*	*Occupancy*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}/U_{iso}
Thermessaite-(NH_4)											
Al	1/2	0	0	1	0.0169(4)	0.0128(4)	0.0086(5)	-0.0001(3)	0.0011(4)	-0.0013(4)	0.0128(2)
F1	0.8493(1)	0.4539(2)	0.4779(2)	1	0.0176(6)	0.0238(7)	0.0232(9)	-0.0024(6)	-0.0020(6)	-0.0036(5)	0.0216(3)
F2	1/2	0.0779(2)	1/4	1	0.029(1)	0.0154(9)	0.0099(9)	0	0.0015(8)	0	0.0182(4)
S	0	0.19620(8)	1/4	1	0.0218(4)	0.0115(3)	0.0133(4)	0	0.0007(3)	0	0.0155(2)
O1	-0.0972(2)	0.1039(2)	0.3242(3)	1	0.036(1)	0.0248(9)	0.026(1)	0.0055(8)	0.0026(8)	-0.0135(8)	0.0290(4)
O2	-0.0471(2)	0.2985(2)	0.0914(2)	1	0.0261(8)	0.0150(7)	0.014(1)	0.0024(7)	-0.0046(7)	-0.0025(6)	0.0185(4)
N	0.6939(2)	0.3206(2)	0.2079(3)	0.86(1)	0.0311(9)	0.0307(9)	0.036(1)	-0.009(8)	-0.007(8)	0.0021(7)	0.0327(4)
K	0.6939(2)	0.3206(2)	0.2079(3)	0.14(1)	0.0311(9)	0.0307(9)	0.036(1)	-0.009(8)	-0.007(8)	0.0021(7)	0.0327(4)
H1	0.667(6)	0.357(8)	0.078(5)	0.86(1)							0.16(3)
H2	0.755(5)	0.379(7)	0.28(1)	0.86(1)							0.17(3)
H3	0.693(5)	0.208(2)	0.197(9)	0.86(1)							0.11(2)
H4	0.637(5)	0.329(8)	0.314(8)	0.86(1)							0.15(3)
Anthropogenic phase											
Al	1/2	0	0	1	0.0171(3)	0.0147(4)	0.0089(3)	-0.0001(3)	0.0007(3)	-0.0010(3)	0.0136(2)
F1	0.84925(10)	0.45388(13)	0.47814(17)	1	0.0195(6)	0.0257(6)	0.0218(6)	-0.0021(5)	-0.0025(5)	-0.0032(5)	0.0223(3)
F2	1/2	0.07776(17)	1/4	1	0.0313(8)	0.0166(7)	0.0094(6)	0	0.0012(7)	0	0.0191(3)
S	0	0.19621(7)	1/4	1	0.0220(3)	0.0131(3)	0.0127(3)	0	0.0005(3)	0	0.0159(2)
O1	-0.09724(15)	0.10380(17)	0.3239(2)	1	0.0372(9)	0.0258(8)	0.0271(8)	0.0054(7)	0.0019(7)	-0.0126(7)	0.0300(4)
O2	-0.04722(14)	0.29892(15)	0.09130(19)	1	0.0272(7)	0.0166(7)	0.0150(6)	0.0017(5)	-0.0051(6)	-0.0024(6)	0.0196(3)
N	0.69395(14)	0.32039(17)	0.2072(2)	0.845(4)	0.0341(9)	0.0334(9)	0.0316(9)	-0.0089(6)	-0.0067(6)	0.0012(6)	0.0334(6)

K	0.69395(14)	0.32039(17)	0.2072(2)	0.155(4)	0.0341(9)	0.0334(9)	0.0316(9)	-0.0089(6)	-0.0067(6)	0.0012(6)	0.0334(6)
H1	0.670(4)	0.348(5)	0.073(4)	0.848							0.08
H2	0.764(3)	0.375(4)	0.252(6)	0.848							0.08
H3	0.700(4)	0.214(3)	0.165(6)	0.848							0.08
H4	0.643(3)	0.318(4)	0.322(5)	0.848							0.08

Table 4. Selected interatomic distances (Å) for thermessaite-(NH_4) and the anthropogenic phase from the Anna mine.

		Holotype	Anthropogenic phase
Al–	F1	1.756(1) x 2	1.754(1) x 2
	F2	1.839(1) x 2	1.839(1) x 2
	O2	1.920(1) x 2	1.914(1) x 2
S–	O1	1.448(2) x 2	1.447(2) x 2
	O2	1.497(2) x 2	1.499(1) x 2
N–	H1*	0.99(2)	0.97(2)
	H2	0.98(2)	0.97(2)
	H3	0.97(2)	0.99(2)
	H4	0.98(2)	0.97(2)
N···	O1	2.789(2)	2.787(2)
	F1	2.796(2)	2.7992(19)
	F1’	2.883(2)	2.8744(19)
	O1’	2.920(3)	2.918(2)
	F2	3.042(2)	3.0384(19)
	O2	3.039(2)	3.034(2)
	F1’’	3.055(2)	3.050(2)
	O1’	3.113(3)	3.109(2)
	O2’	3.272(3)	3.274(2)

* N–H bond lengths were restrained to 1.00(2) Å (see text).

Table 5. Calculated X-ray powder diffraction pattern (*d* in Å) for thermessaite-(NH_4) holotype.

h	***k***	***l***	***d*(*hkl*)**	I/I_o
1	1	0	6.850	74
2	0	0	5.650	100
1	1	1	4.844	89
2	1	1	3.889	3
0	2	1	3.646	6
3	1	0	3.451	6
0	0	2	3.425	4
3	1	1	3.082	47
1	1	2	3.063	56
2	2	1	3.063	53
4	0	0	2.825	5
1	3	0	2.782	26
2	1	2	2.773	1
0	2	2	2.681	28
3	2	1	2.620	2
1	2	2	2.608	7
1	3	1	2.578	3
3	0	2	2.534	1
4	1	1	2.499	9
3	1	2	2.431	4
2	3	1	2.398	15
4	2	0	2.362	3
3	3	0	2.283	1
4	2	1	2.233	1
5	1	0	2.186	5
3	2	2	2.184	2
4	0	2	2.179	4
1	1	3	2.166	1
3	3	1	2.166	17
1	3	2	2.160	1
4	1	2	2.113	5
5	1	1	2.083	2
2	1	3	2.056	1
0	4	1	2.054	3
2	3	2	2.050	1
1	4	1	2.021	5
0	2	3	2.017	5
2	4	0	2.012	1
1	2	3	1.986	7
4	2	2	1.945	1
2	4	1	1.930	1
5	2	1	1.921	3
3	1	3	1.904	2
2	2	3	1.900	11
5	0	2	1.886	1
6	0	0	1.883	6
5	1	2	1.843	1
0	4	2	1.823	5
3	4	1	1.803	1
3	2	3	1.778	1
6	1	1	1.777	2
5	3	0	1.776	6
1	3	3	1.765	1
4	3	2	1.736	2
2	4	2	1.735	2
6	2	0	1.726	1
5	3	1	1.719	5
0	0	4	1.713	4
4	4	0	1.713	1
1	5	0	1.703	1
1	1	4	1.661	4
4	2	3	1.642	1
3	4	2	1.641	1
2	0	4	1.639	1
3	3	3	1.615	1
2	1	4	1.610	1
2	5	1	1.602	1
0	2	4	1.591	1
7	1	0	1.587	4
3	0	4	1.559	1
7	1	1	1.546	1
6	2	2	1.541	8
2	2	4	1.532	1
3	5	1	1.527	1
1	5	2	1.525	8
4	3	3	1.510	1
2	4	3	1.510	3