

Campostriniite, $(\text{Bi}^{3+}, \text{Na})_3(\text{NH}_4, \text{K})_2\text{Na}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$, a new sulfate isostructural with görgeyite, from La Fossa Crater, Vulcano, Aeolian Islands, Italy

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ABSTRACT

The new mineral campostriniite, $(\text{Bi}^{3+}, \text{Na})_3(\text{NH}_4, \text{K})_2\text{Na}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$, was found in an active fumarole (fumarole FA, temperature $\sim 350^\circ\text{C}$) at La Fossa Crater, Vulcano, Aeolian Islands, Sicily, Italy. It occurs on a pyroclastic breccia as white prismatic crystals up to 0.2 mm long, in association with adranosite, demicheleite-(Br), demicheleite-(I), argesite and sassolite. The mineral is monoclinic, space group: $C2/c$ (no. 15) with $a = 17.748(3)$, $b = 6.982(1)$, $c = 18.221(3)$ Å, $\beta = 113.97(1)^\circ$, $V = 2063(1)$ Å³ and $Z = 4$. The six strongest reflections in the powder X-ray diffraction pattern are: [d_{obs} in Å ($I(hkl)$)] 6.396(100)(110), 7.507(75)($\bar{2}02$), 2.766(60)($\bar{3}16$), 3.380(57)(312), 5.677(55)(111), 3.166(50)(4 0 2). The empirical formula (based on 25 anions p.f.u.) is $\text{Bi}_{2.41}\text{N}_{1.52}\text{Na}_{2.41}\text{K}_{0.48}\text{S}_{6.07}\text{H}_{8.08}\text{O}_{25}$. The calculated density is 3.87 g cm^{-3} . Using single-crystal diffraction data, the structure was refined to a final $R(F) = 0.051$ for 3025 independent observed reflections [$I > 2\sigma(I)$]. Campostriniite is isostructural with görgeyite and belongs to the 7.CD group of the Strunz classification system. The structure contains two independent nine-fold coordinated sites, one of them located on a two-fold axis (M1) and the other one in general position (M2) essentially occupied by Bi^{3+} atoms and minor amounts of Na^+ ions, an eight-fold coordinated site fully occupied by Na^+ ions and another eight-fold coordinated site occupied by NH_4^+ and K^+ ions; three independent sulfate anions in a general position and a water molecule coordinated to M1 and located on a two-fold axis are also present.

KEYWORDS: campostriniite, new mineral species, crystal structure, bismuth sulfate, Vulcano island, Italy.

Introduction

SULFATES containing bismuth are quite rare (see for instance ruff.info/ima/), the only examples known up to now are: atlasovite $\text{Cu}_6\text{Fe}^{3+}\text{Bi}^{3+}\text{O}_4(\text{SO}_4)_5 \cdot \text{KCl}$ (Popova *et al.*, 1987) and markhininite $\text{TlBi}(\text{SO}_4)_2$ (Filatov *et al.*, 2013) found as sublimates from the Great Fissure, Tolbachik volcano, Kamchatka, cannonite $\text{Bi}_2\text{O}(\text{SO}_4)\text{O}(\text{OH})_2$, originally found at Marysvale, Piute Co. Utah, USA (Stanley *et al.*, 1992), riomarinaite $\text{BiSO}_4\text{OH} \cdot \text{H}_2\text{O}$ originally found at Falcacci stope, Rio Marina, Elba

Island, Italy (Rögner, 2005) and aiolosite $\text{Na}_2(\text{Na}_2\text{Bi})(\text{SO}_4)_3\text{Cl}$, occurring as sublimate at La Fossa Crater, Vulcano, Aeolian Islands, Sicily, Italy (Demartin *et al.*, 2010a; Campostrini *et al.*, 2011). Only recently two additional new species were discovered at La Fossa crater, i.e. baliczunite $\text{Bi}_2\text{O}(\text{SO}_4)_2$ (Pinto *et al.*, 2014) and leguernite $\text{Bi}_{38}\text{O}_{42}(\text{SO}_4)_{15}$ (Garavelli *et al.*, 2013).

Campostriniite, $(\text{Bi}^{3+}, \text{Na})_3(\text{NH}_4, \text{K})_2\text{Na}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$ is another new bismuth sulfate recently found at La Fossa Crater. The name is to honour Italo Campostrini (b. 1959), a very active mineralogist especially in the study of volcanic sublimates. His particular interest in this field led him to discover several new mineral species at Vulcano and Vesuvius. This mineral has been approved as a new species by the

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International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA CNMNC; No. 2013-086) with the simplified formula $(\text{Bi}^{3+}, \text{Na})_3(\text{Na}, \text{K})_4(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$. However subsequent investigations by Fourier transform infrared spectroscopy (FTIR) measurements and improved crystal-structure refinement showed that the previously overlooked ammonium is an essential constituent of this mineral; therefore, the proposed chemical formula needed to be slightly revised and approved by the IMA CNMNC (No. 2013-086a).

This paper deals with the description of the new mineral, together with its crystal-structure determination.

Occurrence, chemical data and physical properties

Four samples of campostriniite were collected in April 2008 at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy, in an active fumarole [fumarole FA, reported in Borodaev *et al.* (2000) and Pinto *et al.* (2006)]. At that time the temperature of the fumarole reached a peak of $\sim 350^\circ\text{C}$. The mineral occurs on a pyroclastic breccia as white prismatic crystals up to 0.2 mm long, in association with adranosite $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, demicheleite-(Br) BiSBr , demicheleite-(I) BISI , argesite $(\text{NH}_4)_7\text{Bi}_3\text{Cl}_{16}$ and sassolite $\text{B}(\text{OH})_3$ (Fig. 1). The most commonly observed forms are: $\{20\bar{1}\}$, $\{\bar{2}21\}$, $\{102\}$, $\{112\}$; such an indexing has been obtained by comparison of computer-generated drawings of the crystals in the point group $2/m$.

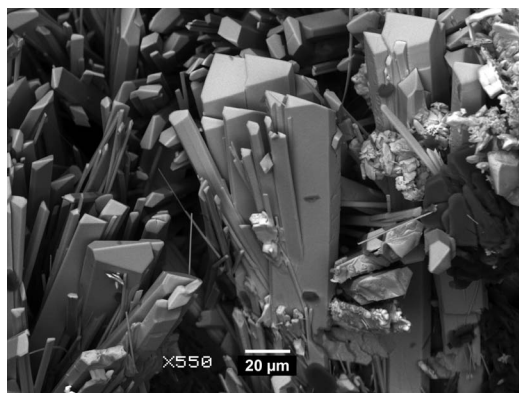


FIG. 1. Backscattered electron image of crystals of campostriniite.

No twinning is apparent. The streak is white and the lustre is vitreous. Cleavage and fracture were not observed. No fluorescence was observed under SW or LW ultraviolet radiation. The $a:b:c$ ratio calculated from the unit-cell parameters is 2.542:1:2.610 (single-crystal data). Density could not be measured because the mineral is soluble in the Clerici solution and no other liquids with appropriate density were available. The density calculated using the empirical formula and single-crystal unit-cell data is 3.87 g cm^{-3} .

Campostriniite is biaxial (sign undetermined). Only an approximate value of the refractive indexes could be measured ($n > 1.68$, 589 nm) because the mineral reacts in a few minutes with liquids having a refractive index close to 1.70. Taking into account the empirical chemical formula and the density based on it, the calculated mean refractive index is 1.680, using the Gladstone-Dale constants of Mandarino (1976, 1981).

Quantitative chemical analyses (18) were carried out in energy dispersive spectroscopy (EDS) mode using a JEOL JSM 5500 LV scanning electron microscope equipped with an IXRF EDS 2000 microprobe (20 kV excitation voltage, 10 pA beam current, 2 μm beam diameter). This analytical method was chosen because the sample is severely damaged by using the wavelength dispersive spectroscopy technique, even with a low voltage and current and a large diameter of the electron beam. Element concentrations were measured using the $K\alpha$ lines for S, K and Na, and the $M\alpha$ line for Bi. No amounts of other elements $>0.1 \text{ wt.}\%$ were detected. The presence of ammonium was established from crystal-structure analysis and confirmed by the FTIR spectrum, recorded on a Jasco IRT-3000 spectrometer, that shows absorption bands at 3071 and 1418 cm^{-1} , consistent with the presence of an NH_4^+ ion (Farmer, 1974; Busigny *et al.*, 2003) (Fig. 2), together with absorptions due to the presence of sulfates and water. The $(\text{NH}_4)_2\text{O}$ content was calculated by stoichiometry, taking into account its partial replacement by K (see later). Because of the small amount of material available no direct determination of the water content by thermal methods was possible and the H_2O content was calculated by stoichiometry after the structure determination. The mean analytical results are reported in Table 1. The empirical formula (based on 25 anions per formula unit) is $\text{Bi}_{2.41}\text{N}_{1.52}\text{Na}_{2.41}\text{K}_{0.48}\text{S}_{6.07}\text{H}_{8.08}\text{O}_{25}$. Also taking into account the

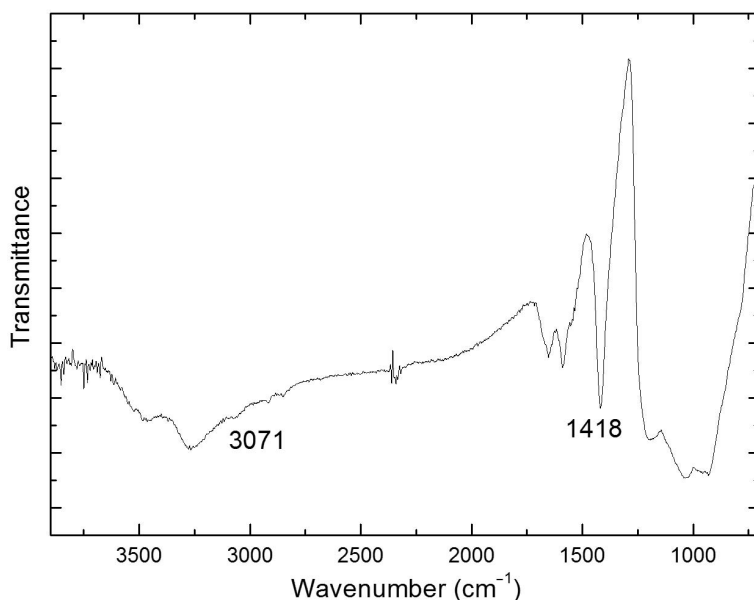


FIG. 2. FTIR spectrum of campostriniite

distribution of the cations in the sites, as derived from structure refinement (see below) the chemical formula can be written as $(\text{Bi}_{2.41}^{3+}, \text{Na}_{0.41})_{\Sigma=2.82}[(\text{NH}_4)_{1.52}, \text{K}_{0.48}]_{\Sigma=2} \text{Na}_2(\text{SO}_4)_{6.06} \cdot \text{H}_2\text{O}$. The ideal formula is $(\text{Bi}_{2.5}^{3+}\text{Na}_{0.5})(\text{NH}_4, \text{K})_2\text{Na}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$, the end-member formula is $(\text{Bi}_{2.5}^{3+}\text{Na}_{0.5})(\text{NH}_4)_2\text{Na}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$. The sum of the Bi and Na molar amounts is slightly smaller than the theoretical value of 3 because either volatilization of Na under the microprobe beam or partial overlap of the $\text{SK}\alpha$ and $\text{BiM}\alpha$ lines in the EDS spectrum result in an overestimation of the S content and

underestimation of the Bi content. Holotype material is deposited in the Reference Collection of the Dipartimento di Chimica, Università degli Studi di Milano, specimen number 2013-03.

X-ray data

Powder X-ray diffraction data (Table 2) have been obtained using a Rigaku DMAX II diffractometer, with graphite monochromated $\text{CuK}\alpha$ radiation. The indexing of the powder-diffraction pattern was made by comparison with the pattern calculated after the structure

TABLE 1. Analytical data for campostriniite (average of 18 analyses).

Constituent	Wt.%	Range	SD	Probe standard
Bi_2O_3	46.65	46.23–46.90	0.41	Metallic Bi
SO_3	40.33	40.01–40.88	0.31	Anhydrite
Na_2O	6.21	6.10–6.60	0.42	Albite
K_2O	1.88	1.75–1.91	0.04	Orthoclase
$(\text{NH}_4)_2^*$	3.28			
H_2O^*	1.50			
Total	99.85			

* by stoichiometry (see text).

The empirical formula (based on 25 anions per formula unit) is $\text{Bi}_{2.41}\text{N}_{1.52}\text{Na}_{2.41}\text{K}_{0.48}\text{S}_{6.06}\text{H}_{8.08}\text{O}_{25}$.

TABLE 2. Powder X-ray diffraction data for campostriniite.

<i>hkl</i>	<i>I</i> _{rel}	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)*
002	21	8.292	8.323
202	75	7.507	7.529
110	100	6.396	6.396
111	55	5.677	5.673
202	8	4.878	4.895
113	18	4.569	4.570
204	12	4.522	4.522
402	47	4.410	4.413
310	12	4.259	4.266
004	22	4.156	4.162
313	12	4.065	4.072
404	30	3.763	3.765
020	19	3.495	3.481
312	57	3.380	3.381
114	17	3.254	3.258
220	11	3.182	3.198
402	50	3.166	3.169
221	75	3.048	3.051
206	25	3.026	3.029
406	21	2.900	2.903
604	42	2.856	2.854
316	60	2.766	2.767
511	20	2.729	2.725
421	20	2.719	2.721
223	3	2.600	2.596
116	28	2.409	2.408
206	19	2.347	2.348
226	10	2.285	2.285
131	20	2.259	2.258
423	30	2.170	2.171
625	18	2.135	2.134
608	19	2.114	2.115
333	18	2.104	2.106
227	22	2.078	2.074
913	24	1.889	1.887
916	26	1.836	1.836
2010	17	1.780	1.780
516	18	1.724	1.724
318	20	1.671	1.671
9110	15	1.544	1.544

* Calculated from the unit cell $a = 17.718(2)$, $b = 6.962(1)$, $c = 18.216(2)$ Å, $\beta = 113.96(1)^\circ$ obtained from least-squares refinement of the above data using the program *UNITCELL* (Holland and Redfern, 1997).

determination. The following unit-cell parameters $a = 17.718(2)$, $b = 6.962(1)$, $c = 18.216(2)$ Å, $\beta = 113.96(1)^\circ$ were derived from least-squares refinement from the above data using the program *UNITCELL* (Holland and Redfern,

1997). The unit-cell parameters reported in Table 3 were obtained from 7197 single-crystal reflections with $I > 5\sigma(I)$. In the same Table single-crystal diffraction data and refinement parameters are also reported. A total of 10,415 intensities corresponding to a complete scan of the reciprocal lattice up to $2\theta = 63.16^\circ$ were collected from a crystal (0.052 mm × 0.120 mm × 0.164 mm) using a Bruker Apex II diffractometer equipped with a 2K CCD detector and MoK α radiation ($\lambda = 0.71073$ Å). A one-minute measuring time and a 0.5° frame width were used. The intensity data were reduced using the program *SAINTE* (Bruker, 2001), and corrected for Lorentz, polarization as well as for background. An absorption correction ($\mu = 22.2$ mm⁻¹, $T_{\min} = 0.509$, $T_{\max} = 1.000$) was applied using the *SADABS* program (Sheldrick, 2000). After averaging the symmetry-related reflections ($R_{\text{int}} = 0.0505$), 3237 independent data were obtained. The crystal structure was solved by direct methods and refined using the *SHELXL97* program (Sheldrick, 2008) implemented in the *WinGX* suite (Farrugia, 1999). A refinement of the occupancy at the M1 and M2 sites revealed a significant substitution of the Bi³⁺ ions by Na⁺ ions (the two ions have virtually the same ionic radius) and partial replacement of NH₄⁺ by K⁺ in the N site, as shown in Table 4. The refinement of the occupancy at the M3 site showed it to be exclusively occupied by Na⁺ and therefore it was kept fixed to unity during the subsequent cycles of the refinement. The formula resulting from the structure refinement is (Bi_{2.50}Na_{0.50})_{Σ=3} [(NH₄)_{1.43}K_{0.57}]_{Σ=2}Na₂(SO₄)₆·H₂O, where a perfect match in the charge balance between the cations and the anions is achieved. The hydrogen atoms of the water molecule and of the ammonium ions were detected in a difference Fourier map. They were included with no restraints and with appropriate occupancy in the final cycles of the structure refinement and gave no convergence problems (max shift/sigma 0.027). The final *R* value is 0.051 for 3025 observed reflections [$I > 2\sigma(I)$]. The coordinates and displacement parameters of the atoms are reported in Table 4; selected interatomic distances are listed in Table 5. A table with the observed and calculated structure-factors tables has been deposited with the Principal Editor of *Mineralogical Magazine* and is available at http://www.minersoc.org/pages/e_journals/dep_mat_mm.html.

TABLE 3. Single-crystal diffraction data and refinement parameters for campostriniite.

Crystal system	Monoclinic
Space group	C2/c (no. 15)
<i>a</i> (Å)	17.748(3)
<i>b</i> (Å)	6.982(1)
<i>c</i> (Å)	18.221(3)
β (°)	113.97(1)
<i>V</i> (Å ³)	2063(1)
<i>Z</i>	4
Radiation	MoK α
μ (mm ⁻¹)	22.2
<i>D</i> _{calc} (g cm ⁻³)	3.935
Measured reflections	10,415
Independent reflections	3237
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	3025
Parameters refined	196
Final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)] and <i>wR2</i> (all data)	0.051, 0.117
<i>S</i>	1.27

Notes: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$;
 $w = 1 / [\sigma^2(F_o^2) + (0.0159q)^2 + 117.7q]$ where $q = [\max(0, F_o^2 + 2F_c^2)] / 3$;
 $S = \{ \sum [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$ where *n* is the number of reflections and *p* is the number of refined parameters.

Description of the crystal structure

Campostriniite has a simplified $M_7(SO_4)_6 \cdot H_2O$ stoichiometry, analogous to that of görgeyite $K_2Ca_5(SO_4)_6 \cdot H_2O$ (Smith and Walls, 1980), the same space group and similar unit-cell parameters (for görgeyite $a = 17.51(1)$, $b = 6.822(5)$, $c = 18.21(1)$ Å, $\beta = 113.3(1)^\circ$). The structure refinement confirms that the two minerals are isostructural. Therefore campostriniite fits into the 7.CD.20. group of the Strunz classification system: subgroup of sulfates with only large cations (Strunz and Nickel, 2001). Campostriniite is also isotypic to the synthetic mixed-valence cerium sulfate $K_5Ce_2(SO_4)_6 \cdot H_2O$ (Casari and Langer, 2007). Projections of the crystal structure are shown in Figs 3–5. There are two independent nine-fold coordinated sites, one of them (M1) located on a two-fold axis (4*e* Wyckoff position) and the other one (M2) in the 8*f* general position that are occupied by Ca²⁺ ions in görgeyite; here both sites are essentially occupied by Bi³⁺ ions with minor substitution by Na⁺ ions (Table 4). The other two cation sites are eight-fold coordinated, the one occupied by Ca²⁺ ions in görgeyite is here exclusively occupied by Na⁺ ions (M3 site), the other one occupied by K⁺ ions in görgeyite is here occupied by NH₄⁺ ions with a minor amount of K⁺ ions. There are also three independent sulfate anions in general positions

and a water molecule, located on a two-fold axis and belonging to the M1 coordination polyhedron. In the polyhedra, where the Bi³⁺ cations prevail, the average M1–O and M2–O distances compare well (2.524 and 2.537 Å, respectively) in spite of different amounts of Na⁺ replacing Bi³⁺ in the two sites. This feature is a consequence of the ionic radius of both cations being virtually the same. It is worth noting that a significant Na⁺ → Bi³⁺ replacement has been already observed in aiolosite, Na₂(Na₂Bi)(SO₄)₃Cl (Demartin *et al.*, 2010*a*) where the content of Na⁺ ions prevails upon Bi³⁺ ions in the 6*h* site of the apatite-type structure, but the average M–O distance is comparable to that of campostriniite (2.516 Å). The simultaneous presence of Bi³⁺ and Na⁺ ions in the same crystallographic site has also been observed in some other synthetic lead apatites where Pb²⁺ ions are partly replaced by minor amounts of Bi³⁺ and Na⁺ cations (Hamdi *et al.*, 2007), in fluoratromicrolite (Na,Ca,Bi)₂Ta₂O₆F (Witzke *et al.*, 2011) and in cesstibantite (Ercit *et al.*, 1993; Gorogotskaya *et al.*, 1996), where bismuth is, however, a minor constituent. In the K₅Ce₂(SO₄)₆·H₂O compound the M1 site is on average larger than in campostriniite (2.878 vs. 2.524 Å) due to the larger size of the K⁺ ion with respect to the Bi³⁺ or Na⁺ ions, whereas the M2 site occupied by Ce³⁺/Ce⁴⁺ ions has dimensions

TABLE 4. Atomic coordinates and displacement parameters [$U_{eq}/U_{(i,j)}$, Å²] for camptostriinite.

Atom	Occupancy	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
M1	Bi 0.7947(5) Na 0.2053(5)	0	0.90486(2)	¼	0.01609(4)
M2	Bi 0.8546(4) Na 0.1454(4)	0.155686(7)	0.92458(2)	−0.011139(6)	0.02056(3)
M3	Na 1.000	0.22214(7)	0.6326(2)	0.29333(6)	0.0205(3)
N	N 0.716(3) K 0.284(3)	0.07118(10)	0.3967(2)	0.10039(12)	0.0413(5)
S1	1	0.36941(3)	1.08331(8)	0.08612(3)	0.0105(1)
S2	1	0.29113(3)	0.61622(8)	0.15734(3)	0.0111(1)
S3	1	0.07605(3)	0.90203(9)	0.11782(3)	0.0123(1)
O1	1	0.37997(12)	1.2248(3)	0.03136(11)	0.0230(5)
O2	1	0.39613(12)	0.8927(3)	0.07106(11)	0.0199(5)
O3	1	0.42001(14)	1.1341(3)	0.17049(11)	0.0237(6)
O4	1	0.28201(10)	1.0816(3)	0.07503(11)	0.0177(4)
O5	1	0.24489(12)	0.6750(3)	0.07029(10)	0.0181(5)
O6	1	0.36653(11)	0.5233(3)	0.15560(10)	0.0172(5)
O7	1	0.31293(13)	0.7824(3)	0.21095(12)	0.0257(6)
O8	1	0.24273(12)	0.4764(3)	0.17860(11)	0.0241(5)
O9	1	0.14264(11)	1.0283(3)	0.11921(11)	0.0193(5)
O10	1	0.05059(12)	0.7866(3)	0.04342(10)	0.0198(5)
O11	1	0.10062(12)	0.7794(3)	0.18857(11)	0.0253(6)
O12	1	0.00523(12)	1.0201(3)	0.11757(11)	0.0213(5)
Ow	1	0	1.2691(6)	¼	0.044(1)
H	1	0.041(2)	1.369(5)	0.265(2)	0.024(10)
H1	0.716	0.064(4)	0.387(9)	0.047(3)	0.041(18)
H2	0.716	0.073(3)	0.533(9)	0.112(3)	0.035(17)
H3	0.716	0.123(4)	0.341(9)	0.139(3)	0.043(18)
H4	0.716	0.026(4)	0.349(9)	0.103(3)	0.036(17)

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
M1	0.02002(6)	0.01419(6)	0.01853(5)	0	0.01242(4)	0
M2	0.02857(4)	0.02012(5)	0.01925(3)	−0.00371(4)	0.01616(3)	−0.00750(4)
M3	0.0174(4)	0.0263(5)	0.0138(4)	−0.0013(4)	0.0022(3)	−0.0022(4)
N	0.0292(7)	0.0253(7)	0.0644(10)	−0.0090(7)	0.0138(7)	−0.0028(6)
S1	0.0113(2)	0.0102(2)	0.0103(2)	−0.0013(2)	0.0047(1)	0.0002(2)
S2	0.0106(2)	0.0132(2)	0.0103(2)	0.0015(2)	0.0050(1)	0.0017(2)
S3	0.0134(2)	0.0142(2)	0.0120(2)	0.0006(2)	0.0079(1)	0.0001(2)
O1	0.0231(7)	0.0277(10)	0.0232(7)	0.0055(7)	0.0144(5)	−0.0038(7)
O2	0.0184(7)	0.0156(8)	0.0257(8)	−0.0079(7)	0.0088(6)	0.0023(6)
O3	0.0322(10)	0.0192(9)	0.0109(7)	0.0007(7)	−0.0002(7)	0.0023(8)
O4	0.0138(6)	0.0196(8)	0.0254(7)	0.0019(7)	0.0138(5)	0.0013(6)
O5	0.0248(8)	0.0165(8)	0.0119(6)	0.0034(6)	0.0064(5)	0.0030(7)
O6	0.0167(7)	0.0206(8)	0.0133(6)	0.0037(6)	0.0052(5)	0.0086(6)
O7	0.0357(9)	0.0196(9)	0.0233(7)	−0.0030(7)	0.0135(6)	0.0083(8)
O8	0.0264(8)	0.0263(10)	0.0252(7)	0.0065(7)	0.0161(5)	0.0009(7)
O9	0.0172(7)	0.0223(9)	0.0201(7)	0.0003(7)	0.0093(5)	−0.0043(7)
O10	0.0228(8)	0.0238(9)	0.0114(6)	−0.0083(6)	0.0054(5)	−0.0064(7)
O11	0.0255(8)	0.0330(11)	0.0189(7)	0.0093(7)	0.0104(6)	−0.0012(8)
O12	0.0203(8)	0.0223(9)	0.0237(7)	0.0002(7)	0.0114(6)	0.0002(7)
Ow	0.032(2)	0.041(2)	0.042(2)	0	−0.003(2)	0

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2(U^{11}h^2(a^*)^2 + \dots + 2U^{12}hka^*b^* + \dots); U_{eq} = 1/3[U^{22} + 1/\sin^2\beta(U^{11} + U^{33} + 2U^{13}\cos\beta)]$$

CAMPOSTRINIITE, A NEW MINERAL

TABLE 5. Selected interatomic distances (Å) and hydrogen bonds in campostriniite.

M1–O3 ^a	2.453(2)	M2–O1 ^g	2.518(2)
M1–O3 ^b	2.453(2)	M2–O2 ^h	2.476(2)
M1–O6 ^c	2.438(2)	M2–O4	2.415(2)
M1–O6 ^d	2.438(2)	M2–O5	2.416(2)
M1–O11	2.614(3)	M2–O5 ^h	2.511(2)
M1–O11 ^c	2.614(3)	M2–O6 ^h	2.525(2)
M1–O12	2.581(2)	M2–O9	2.582(2)
M1–O12 ^f	2.581(2)	M2–O10	2.627(2)
M1–Ow	2.544(4)	M2–O12 ⁱ	2.751(2)
<M1–O>	2.524	<M2–O>	2.537
M3–O3 ^b	2.855(3)	N···O1 ^h	2.987(3)
M3–O4 ^b	2.455(2)	N···O2 ^a	2.931(3)
M3–O7 ^b	2.516(2)	N···O8	2.844(3)
M3–O7	2.812(3)	N···O9 ^j	2.826(3)
M3–O8 ^d	2.481(3)	N···O10	2.884(3)
M3–O8	2.513(3)	N···O10 ^k	2.927(3)
M3–O9 ^b	2.392(2)	N···O11	3.053(3)
M3–O11	2.450(2)	N···O12 ^j	2.945(3)
<M3–O>	2.560	<N···O>	2.925
S1–O1	1.469(2)	S2–O5	1.517(2)
S1–O2	1.476(2)	S2–O6	1.499(2)
S1–O3	1.474(2)	S2–O7	1.464(2)
S1–O4	1.481(2)	S2–O8	1.453(2)
<S1–O>	1.475	<S2–O>	1.483
S3–O9	1.466(2)	N–H1	0.93(7)
S3–O10	1.481(2)	N–H2	0.98(6)
S3–O11	1.459(2)	N–H3	0.98(5)
S3–O12	1.501(2)	N–H4	0.89(7)
<S3–O>	1.477	Ow–H	0.97(4)
Hydrogen bonds			
<i>D</i> ··· <i>A</i> (Å)		H··· <i>A</i> (Å)	<i>D</i> –H··· <i>A</i> (°)
N···O10	2.884(3)	H2···O10	2.10(6)
N···O11	3.053(3)	H2···O11	2.14(6)
N···O8	2.844(3)	H3···O8	2.16(6)
N···O1 ^h	2.987(3)	H1···O1 ^h	2.19(7)
N···O9 ^j	2.826(3)	H3···O9 ^j	2.26(7)
N···O12 ^j	2.945(3)	H4···O12 ^j	2.36(6)
N···O10 ^k	2.927(3)	H1···O10 ^k	2.37(6)
N···O2 ^a	2.931(3)	H4···O2 ^a	2.15(6)
N···Ow ^j	3.552(3)	H4···Ow ^j	2.94(7)
Ow···O2 ^d	3.145(2)	H···O2 ^d	2.73(4)
Ow···O3 ^d	2.990(4)	H···O3 ^d	2.15(4)
Ow···O7 ^d	3.101(2)	H···O7 ^d	2.52(4)
			N–H2···O10
			136(5)
			N–H2···O11
			154(4)
			N–H3···O8
			125(5)
			N–H1···O1 ^h
			144(5)
			N–H3···O9 ^j
			115(4)
			N–H4···O12 ^j
			123(5)
			N–H1···O10 ^k
			118(5)
			N–H4···O2 ^a
			145(5)
			N–H4···Ow ^j
			127(4)
			Ow–H···O2 ^d
			107(3)
			Ow–H···O3 ^d
			145(4)
			Ow–H···O7 ^d
			119(3)

Symmetry codes: a = $x - \frac{1}{2}, y - \frac{1}{2}, z$; b = $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; c = $x - \frac{1}{2}, y + \frac{1}{2}, z$; d = $\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$; e = $-x, y, \frac{1}{2} - z$; f = $-x, y, \frac{1}{2} - z$; g = $\frac{1}{2} - x, \frac{5}{2} - y, -z$; h = $\frac{1}{2} - x, \frac{3}{2} - y, -z$; i = $-x, 2 - y, -z$; j = $x, y - 1, z$; k = $-x, 1 - y, -z$.

more similar to those observed in campostriniite (2.537 vs. 2.472 Å). The two remaining eight-fold sites have different average sizes: the M3O₈ site has an average M3–O distance of 2.560 Å,

consistent with the occupation of this site by Na⁺, whereas the other occupied by the ammonium and K⁺ ions is larger (average distance 2.925 Å) and more similar to a zeolitic cavity rather than to a

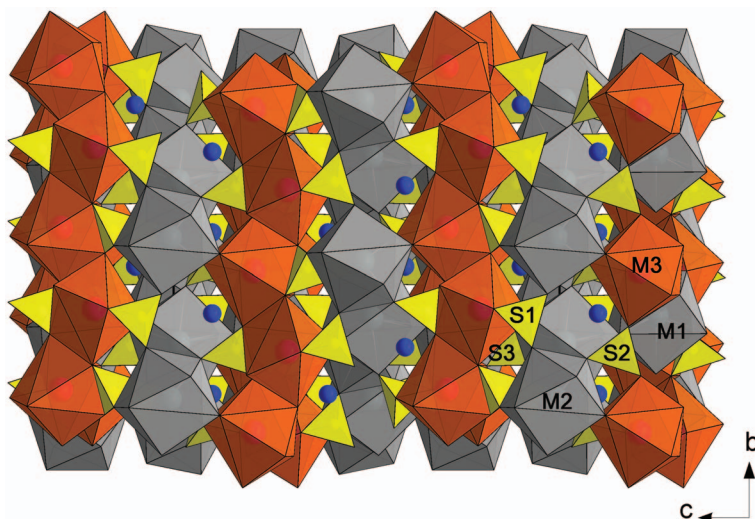


FIG. 3. Projection of the structure of campostriniite along [100]. The positions of the NH_4^+/K^+ ions are shown as blue spheres. Hydrogen atoms of the ammonium ions are omitted for clarity.

framework building block (Table 5). The corresponding average distance in the $\text{K}_5\text{Ce}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$ compound for the two eight-fold sites are 2.793 and 2.893 Å, the former being significantly larger than the corresponding M3 site in campostriniite due to the size of the K^+ ion being larger than that of Na^+ , the latter instead is

about of the same size. The site occupied by cerium in $\text{K}_5\text{Ce}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$ is therefore the only site having average dimensions comparable to that of the M1O_9 , M2O_9 , M3O_8 sites, in campostriniite. Due to the different size of these nine-fold and eight-fold sites, in spite of the isostructural relationships between these phases,

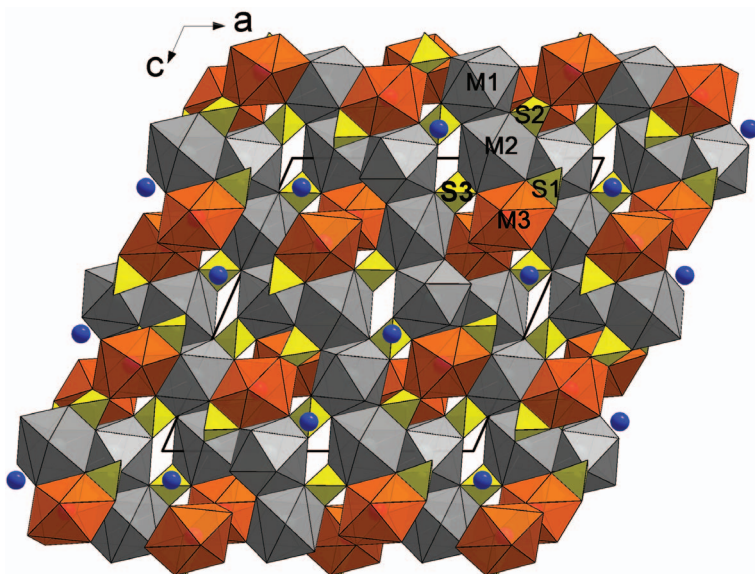


FIG. 4. Projection of the structure of campostriniite along [010]

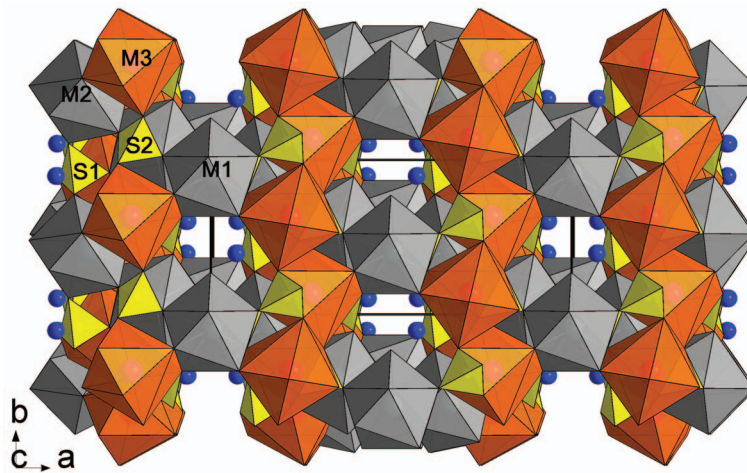


FIG. 5. Projection of the structure of campostriniite along [001].

the structure of $K_5Ce_2(SO_4)_6 \cdot H_2O$ can be described as containing layers in the ab plane with composition $[Ce_2(SO_4)_6]^{5n-}$, stacked in the c direction (Casari and Langer, 2007). On the other hand the structure of campostriniite can be better

described as formed by: (1) $M1O_9$ and $M2O_9$ edge-sharing polyhedra arranged in a zig-zag way parallel to [101] (Fig. 6a); (2) edge-sharing $M3O_8$ polyhedra and sulfate anions (Fig. 6b); (3) a linear arrangement of $M1O_9$, $M2O_9$, $M3O_8$, and SO_4

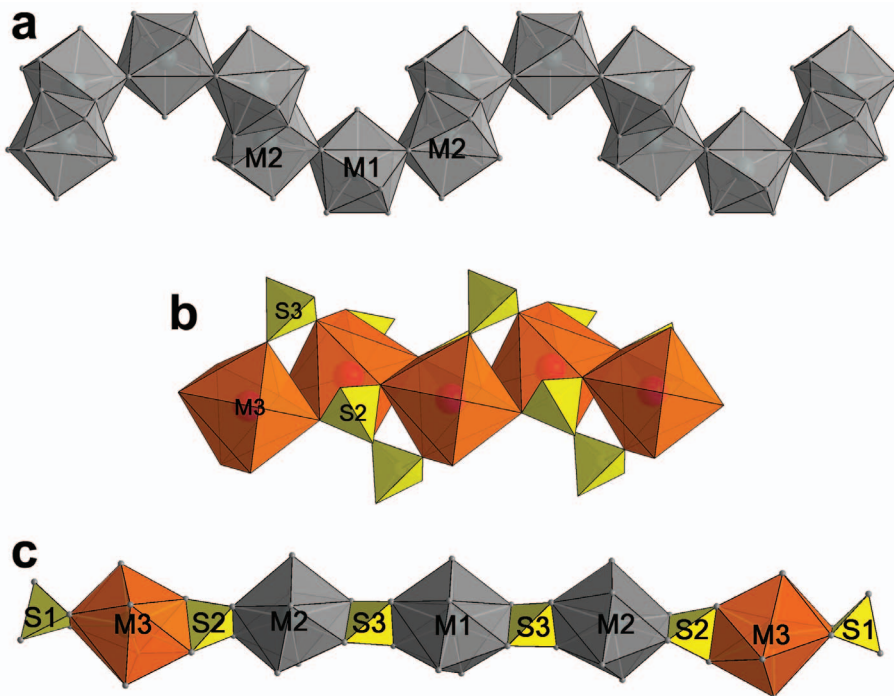


FIG. 6. Structural motives observed in the crystal structure of campostriniite.

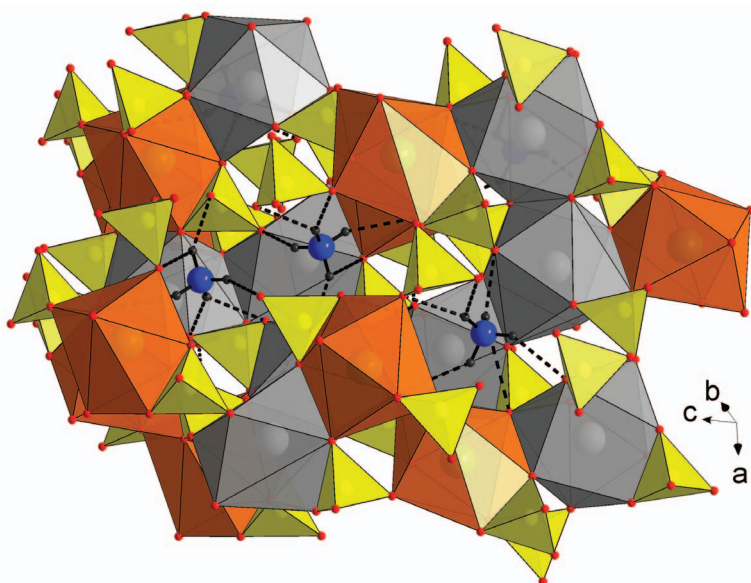


Fig. 7. The hydrogen bonds involving the NH_4^+ cations.

edge-sharing polyhedra (Fig. 6c). Condensation of the above motives gives rise to a three-dimensional framework, having interstitial sites occupied by NH_4^+ and K^+ ions (blue spheres in Figs 3–5).

The average S–O distance computed on all the three sulfate anions is 1.478 Å, not significantly different from the value of 1.473 Å reported by Hawthorne *et al.* (2000); the minimum and maximum values observed here are 1.453(2) and 1.517(2) Å. The O–S–O angles are within the 107.7(1)–111.4(1)° range.

The ammonium ion is involved in hydrogen bonds with the sulfate oxygen atoms (Fig. 7) and its interactions are reported in Table 5. In the same Table the hydrogen bonds involving the water molecule are also reported.

Conclusions

The discovery of campostriniite is an additional example of the presence of ammonium-containing minerals in the intracrater fumarole FA at Vulcano, along with the recently discovered brontesite $(\text{NH}_4)_3\text{PbCl}_5$, panichiite $(\text{NH}_4)_2\text{SnCl}_6$, argesite $(\text{NH}_4)_7\text{Bi}_3\text{Cl}_{16}$, adranosite $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, pyracmonite $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$, aluminopyracmonite $(\text{NH}_4)_3\text{Al}(\text{SO}_4)_3$ and thersiaite $(\text{NH}_4)_3\text{KNa}_2\text{Fe}^{2+}\text{Fe}^{3+}(\text{SO}_4)_3\text{Cl}_5$ (Demartin *et al.*, 2009a,b; 2010b,c; 2012; 2013; 2014).

As ammonium compounds tend to dissociate even at moderate temperatures, it is very probable that all these species formed only in the last few years when the temperature of the fumarole decreased from ~700°C measured in 1993 to the present value of 250°C.

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