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Article

Russoite, $NH_4ClAs_2^{3+}O_3(H_2O)_{0.5}$, a new phylloarsenite mineral from Solfatara Di Pozzuoli, Napoli, Italy

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Abstract

The new mineral russoite (IMA2015-105), $NH_4ClAs_2^{3+}O_3(H_2O)_{0.5}$, was found at the Solfatara di Pozzuoli, Pozzuoli, Napoli, Italy, as a fumarolic phase associated with alacránite, dimorphite, realgar, mascagnite, salammoniac and an amorphous arsenic sulfide. It occurs as hexagonal plates up to ~300 μm in diameter and 15 μm thick, in rosette-like intergrowths. On the basis of powder X-ray diffraction measurements and chemical analysis, the mineral was recognised to be identical to the corresponding synthetic phase $NH_4ClAs_2O_3$ $(H_2O)_{0.5}$. Crystals are transparent and colourless, with vitreous lustre and white streak. Tenacity is brittle and fracture is irregular. Cleavage is perfect on {001}. The measured density is 2.89(1) g/cm³; the calculated density is 2.911 g/cm³. The empirical formula, (based on 4.5 anions per formula unit) is $[(NH_4)_{0.94},K_{0.06}]_{\Sigma1.00}(Cl_{0.91},Br_{0.01})_{\Sigma0.92}As_{2.02}O_3(H_2O)_{0.5}$. Russoite is hexagonal, space group $P622$, with $a = 5.2411(7)$, $c = 12.5948(25)$ Å, $V = 299.62(8)$ Å³ and $Z = 2$. The eight strongest X-ray powder diffraction lines are $[d_{obs} Å(I)(hkl)]$: 12.63(19)(001), 6.32(100)(002), 4.547(75)(100), 4.218(47)(003), 3.094(45)(103), 2.627(46)(110), 2.428(31)(112) and 1.820(28)(115). The structure, was refined to $R = 0.0518$ for 311 reflections with $I > 2\sigma(I)$ and shows a different location of the ammonium cation and water molecules with respect to that reported for the synthetic analogue. The mineral belongs to a small group of phylloarsenite minerals (lucabindiite, torrecillasite and gajardoite). It contains electrically neutral As_2O_3 layers, topologically identical to those found in lucabindiite and gajardoite between which are ammonium cations and outside of which Cl^- anions. Water molecules and additional ammonium cations are located in a layer between two levels of chloride anions.

Introduction

The Solfatara di Pozzuoli is one of ~40 volcanoes in the Campi Flegrei area and is located three kilometres from the centre of the town of Pozzuoli, Napoli, Italy. Solfatara formed during the third Flegrean eruptive period and dates to ~3700–3900 years ago. Inside the Solfatara some active fumaroles are present, the most important of which is called 'Bocca Grande' and has a temperature of ~160°C. During a research campaign carried out in 2011, a few samples of the new mineral russoite, $NH_4ClAs_2^{3+}O_3(H_2O)_{0.5}$, were collected at the 'Bocca Grande' fumarole, where this phase formed as a sublimate product. Powder X-ray diffraction (PXRD) measurements and chemical analysis showed the mineral to be identical to the corresponding synthetic phase $NH_4ClAs_2O_3(H_2O)_{0.5}$ (Edstrand and Blomqvist, 1955). A suitable single crystal of the natural product could not be found for an accurate X-ray structure refinement, however the PXRD data and the analytical results perfectly matched those of the synthetic phase and so were considered to be sufficient for a positive identification of the new mineral species for approval by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA2015-105).

The name russoite was chosen to honour Dr. Massimo Russo (b. 1960), researcher at Osservatorio Vesuviano, Istituto Nazionale di Geofisica e Vulcanologia, Napoli. His work has been devoted mainly to the mineralogy of Italian volcanoes and he is author of several books and articles on this topic. Holotype material is deposited in the Reference Collection of the DCSSI, Università degli Studi di Milano, catalogue number 2015–01.

The recent availability of new material allowed us to obtain more accurate single-crystal intensity data for structure refinement. These data showed the location of the ammonium cation and water molecule different to that proposed by Edstrand and Blomqvist (1955).

Occurrence, chemical data and physical properties

The new mineral russoite was found as a fumarolic phase associated with alacránite, dimorphite, mascagnite, realgar, salammoniac and an amorphous arsenic sulfide. In the same fumarole other interesting and rare minerals are found: adranosite, adranosite-(Fe), efremovite, huizingite-(Al) and godovikovite. Russoite occurs as rosette-like intergrowths or subparallel aggregates formed by hexagonal plates flattened on {001} and bounded by {100} up to ~300 μm in diameter and 15 μm thick, (Figs 1,2). These aggregates are sometimes yellowish due to admixed amorphous arsenic sulfide. Crystals are colourless to white, transparent or translucent, with vitreous lustre and white streak. Tenacity is brittle and fracture is irregular. Cleavage is perfect
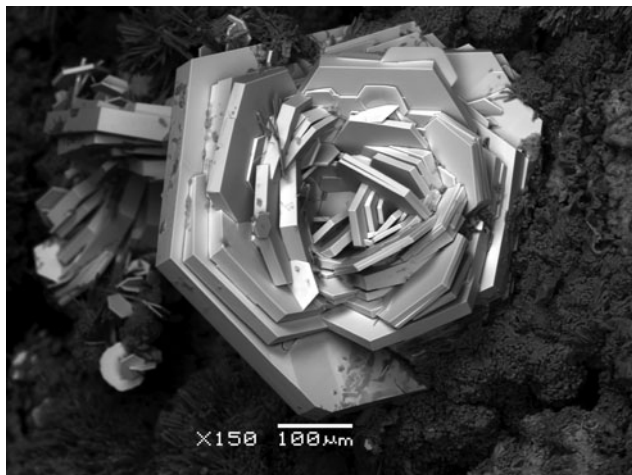
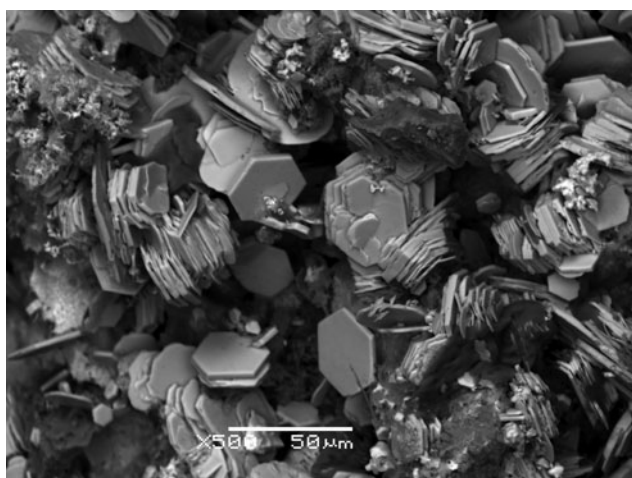Fig. 1. Back-scatter electron image of rosette-like aggregates of russoite.

Fig. 2. Back-scatter electron image of subparallel crystal aggregates of russoite.

on {001}. The mineral does not fluoresce in longwave or short-wave ultraviolet light. No twinning is apparent. The measured density by flotation in a diiodomethane/benzene solution is 2.89(1) g/cm^3, the calculated density using the empirical formula and unit-cell data is 2.911 g/cm^3. Due to the minute size of the crystals the Mohs hardness could not be determined. Optically russoite is uniaxial (–), with $\omega = 1.810(6)$ and $\varepsilon = 1.650(5)$ (measured in white light). The calculated mean refractive index using the Gladstone-Dale constants of Mandarino (1976, 1981) is 1.757.

The infrared spectrum of russoite (Fig. 3) was recorded in a KBr disk, in the range 4000–400 cm^{-1}, using a Jasco FTIR-470 Plus spectrometer. It is consistent with the presence of ammonium [bands at (cm^{-1}): 3254, ν_3; 3145, $2\nu_2$ and 1403, ν_4], H_2O [bands at (cm^{-1}): 3454, ν_3; 3398, ν_1 and 1625, ν_2] and arsenite (bands at 604 and 670 cm^{-1}) (Farmer, 1974; Busigny *et al.*, 2003). The weak absorption at ∼2400 cm^{-1} is due to atmospheric CO_2, that at 1110 cm^{-1} might be attributed to minor OH^- partially replacing the chloride ion.

Quantitative chemical analyses (six) were carried out in energy-dispersive spectroscopy (EDS) mode using a JEOL JSM 5500 LV scanning electron microscope equipped with an IXRF
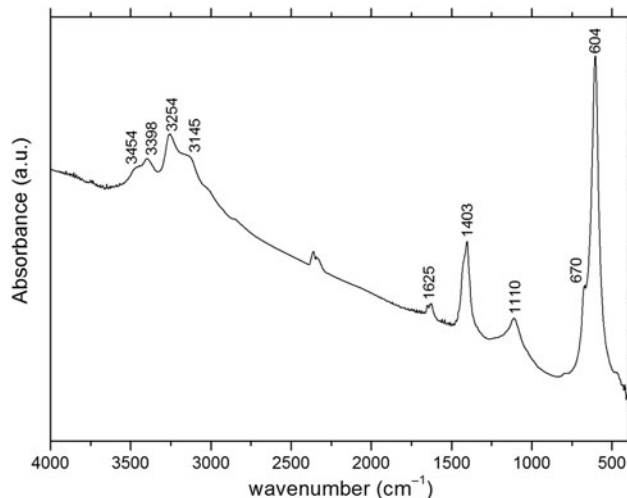

Fig. 3. Fourier-transform infrared spectrum of russoite.

EDS 2000 microprobe (20 kV excitation voltage, 10 pA beam current and 2 μm beam diameter). This analytical method was chosen because the crystal intergrowths did not take a good polish and it was impossible to prepare a flat polished sample; moreover the crystals are severely damaged by using the wavelength-dispersive spectroscopy technique, even with a low voltage and current and a large diameter of the electron beam. In this case, as reported by Ruste (1979) and Acquafredda and Paglionico (2004), the EDS detector gives more accurate analyses of small volumes of sample with a probe current <1 nA and gives good results when collecting X-rays from a non-perfect flat surface of the specimen. X-ray intensities were converted to wt.% by *ZAF* quantitative analysis software. The standards employed were: synthetic InAs (As); halite (Cl); and synthetic KBr (K and Br). Element concentrations were measured using the $K\alpha$ lines for Cl and K, and the $L\alpha$ line for As and Br. The mean analytical results are reported in Table 1. No amounts of other elements above 0.1 wt.% were detected. Water and ammonium contents were not analysed because the mineral is intimately mixed with mascagnite and realgar and is not possible to obtain a sufficient amount of pure sample suitable for this kind of analysis. The presence of N was also evident in the EDS spectrum for some crystals, however the uncertainties of the measurements were considered too large for a quantitative estimation of this element. Therefore, the ammonium and water contents were deduced from the $NH_4ClAs_2O_3(H_2O)_{0.5}$ stoichiometry, taking into account the K content, which partly replaces the ammonium ion ($K + NH_4 = 1$ atoms per formula unit [apfu]). The empirical formula (based on 4.5 anions pfu) is: $[(NH_4)_{0.94}K_{0.06}]_{\Sigma1.00}(Cl_{0.91}, Br_{0.01})_{\Sigma0.92}As_{2.02}O_3(H_2O)_{0.5}$. The simplified formula is $NH_4ClAs_2O_3(H_2O)_{0.5}$.

The PXRD pattern (Table 2), obtained using a conventional Rigaku DMAX II diffractometer, with graphite monochromatised Cu$K\alpha$ radiation, is in good agreement with that calculated for the synthetic phase (PDF2 – entry 00-076-1366, powder diffraction files from the International Centre for Diffraction Data, http://www.icdd.com/), for which the structure was solved by Edstrand and Blomqvist (1955) on the basis of Weissenberg film measurements. Using the same indexing of the synthetic phase and the program *UNITCELL* (Holland and Redfern, 1997) the following unit-cell parameters $a = 5.259(2)$, $c = 12.590(5)$ Å and $V = 301.55(2)$ Å^3 were refined for russoite. They are in good

Table 1. Analytical data for russoite (average of six analyses)*.

Constituent	Mean	Range	S.D.	Probe standard
As_2O_3	74.16	73.25–75.80	0.65	synthetic InAs
Cl	11.96	11.73–12.94	0.44	halite
Br	0.44	0.25–0.80	0.31	synthetic KBr
K_2O	1.05	0.65–1.22	0.12	synthetic KBr
$(NH_4)_2O^†$	9.04	–		
$H_2O^†$	3.35	–		
Total	100.00			
–O = Cl, Br	−2.75			
Total	97.25			

[†]Calculated by stoichiometry; S.D. – standard deviation.

Table 2. Powder X-ray diffraction data for russoite and a comparison with the $NH_4ClAs_2O_3(H_2O)_{0.5}$ synthetic analogue (PDF2 – entry 00-076-1366)[†].

	Russoite			PDF2 00-076-1366[$]		
I_{calc}**	I_{obs}	d_{obs}(Å)	d_{calc}(Å)*	d(Å)	I_{obs}	h k l
58	19	12.63	12.590	12.574	63	0 0 1
100	100	6.32	6.295	6.287	100	0 0 2
22	75	4.547	4.554	4.550	18	1 0 0
18	8	4.283	4.283	4.279	10	1 0 1
23	47	4.218	4.197	4.191	21	0 0 3
20	11	3.695	3.690	3.686	15	1 0 2
57	45	3.094	3.086	3.083	55	1 0 3
50	46	2.627	2.629	2.627	42	1 1 0
2	13	2.522	2.518	2.515	2	0 0 5
55	31	2.428	2.427	2.424	29	1 1 2
1	12	2.273	2.278	2.275	1	2 0 0
4	4	2.229	2.229	2.226	4	1 1 3
12	10	2.211	2.204	2.201	6	1 0 5
1	4	2.096	2.098	2.096	1	0 0 6
10	8	2.021	2.018	2.016	10	1 1 4
1	4	1.902	1.906	1.904	1	1 0 6
6	4	1.847	1.845	1.843	5	2 0 4
12	28	1.820	1.819	1.817	7	1 1 5
3	6	1.794	1.799	1.796	1	0 0 7
2	4	1.718	1.722	1.720	2	2 1 0
1	7	1.706	1.706	1.704	1	2 1 1
2	4	1.671	1.673	1.671	2	1 0 7
4	5	1.594	1.593	1.591	6	2 1 3
1	5	1.574	1.574	1.572	1	0 0 8

[†]ICDD database (powder diffraction files from the International Centre for Diffraction Data, http://www.icdd.com/)
[$]Pattern calculated from ICSD (Inorganic Crystal Structure Database http://www2.fiz-karlsruhe.de/icsd_home.html) using POWD-12++
*Calculated from the unit cell ($a = 5.259(2)$ Å; $c = 12.590(5)$ Å) obtained from least-squares refinement from the above data using the program UNITCELL (Holland and Redfern, 1997).
**Calculated from our structure data.

agreement with those reported for the synthetic phase $a = 5.254$ and $c = 12.574$ Å.

Single-crystal structure determination

A new sampling, carried out in April 2016, after the approval of russoite as a new mineral by the IMA-CNMNC, gave the us opportunity to collect additional specimens with larger aggregates of crystals (up to 0.3 mm), from which an attempt was made to obtain fragments suitable for single-crystal structure determination. In fact, the fragments are not perfect single crystals, as they are made of several small platelets stacked almost parallel to each other, but slightly misaligned. After many attempts, one fragment was found to be composed by only two different

Table 3. Single-crystal diffraction data and refinement parameters for russoite.

Crystal data	
Crystal system	Hexagonal
Space group	$P622$ (no. 177)
Temperature (K)	294
a (Å)	5.2411(7)
c (Å)	12.5948(25)
V (Å^3)	299.62(8)
Z	2
D_{calc} (g cm^{-3})	2.911
Data collection	
Radiation wavelength (Å)	Mo$K\alpha$, 0.71073
μ (mm^{-1})	11.39
Instrument	APEX II CCD diffractometer
Absorption correction	Empirical (SADABS, Sheldrick, 2000)
T_{min}, T_{max}	0.465, 1.000
Reflections measured	3196
Independent reflections	354
Observed reflections [$I > 2\sigma(I)$]	311
Refinement	
Parameters refined	21
Final R [$I > 2\sigma(I)$] and $wR2$ (all data)	0.0518, 0.1010
GoF	1.211
$\Delta\rho$max, $\Delta\rho$min (e^- Å^{-3})	1.63, −1.23

Notes: $R = \Sigma||Fo|-|Fc||/ \Sigma|Fo|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(Fo^2)+(0.0625q)^2]$ where $q = [max(0, F_o^2) + 2F_c^2]/3$; Gof $=\{\Sigma[w(F_o^2-F_c^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

individuals, sufficiently misaligned to allow the collection of a complete set of reflections, suitable for a new structure refinement. The diffracted intensities, corresponding to a complete scan of the reciprocal lattice up to $2\theta = 63.60°$, were collected at room temperature using a Bruker Apex II diffractometer equipped with a 2 K CCD detector and Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). A frame-time of 1 min and a 0.5° frame width were used. The intensity data were reduced using the program SAINT (Bruker, 2001), and corrected for Lorentz, polarization and background factors. An absorption correction ($\mu = 11.39$ mm^{-1}, $T_{min} = 0.465$) was applied using the SADABS program (Sheldrick, 2000). Details about the data collection and refinement are summarised in Table 3. The crystallographic information file and structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below)

Starting from the atomic coordinates reported by Edstrand and Blomqvist (1955) we refined the structure in the $P622$ space group, using the SHELXL97 program (Sheldrick, 2008) implemented in the WinGX suite (Farrugia, 1999). This refinement apparently confirmed the atomic positions found by these authors for all the atoms, with the only exception of the location of the ammonium ion on the $2d$ Wyckoff position [⅓, ⅔, ½]. It should be noted that the ammonium position was chosen by Edstrand and Blomqvist (1955) between two possible residuals in the electron density map, as it was the only one which assured reasonable ammonium–chloride distances, and the correct charge balance, if fully occupied. In our difference-Fourier map we found instead no significant electron density at the $2d$ Wyckoff position, but an electron density residual of ~4.4 e^-/ Å^3 at the $3g$ Wyckoff position [½, 0, ½], which was thought at first to be compatible with the possible presence of the ammonium ion at this site. With this assumption, because the multiplicity of the ammonium site is 3 and that of the chloride site is 2, the occupation of the ammonium ion should have been fixed to the value of ⅔ to maintain the charge balance between the ammonium and the chloride ions. However, even with partial occupation of this site, the ammonium

Table 4. Atomic coordinates and displacement parameters [$U_{eq}/U^{(i,j)}$, Å²] for russoite*.

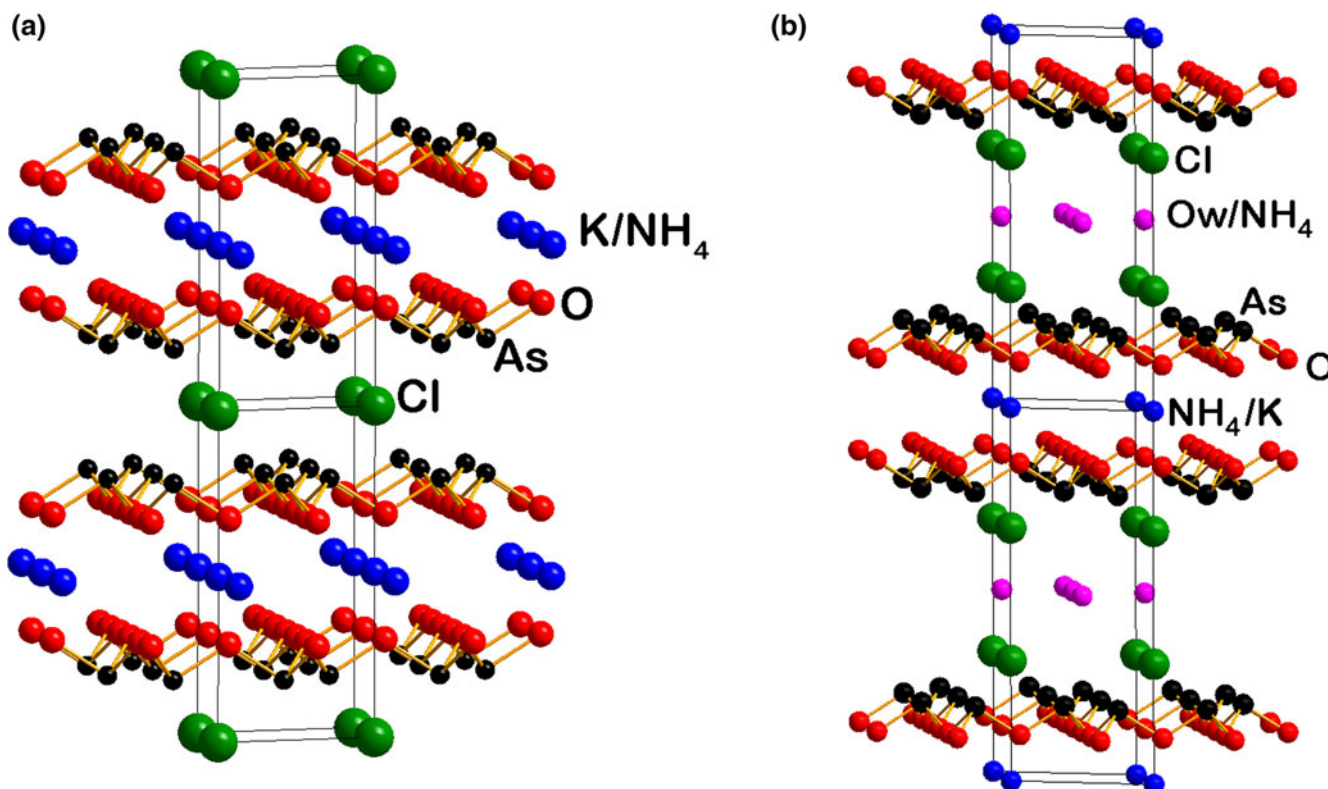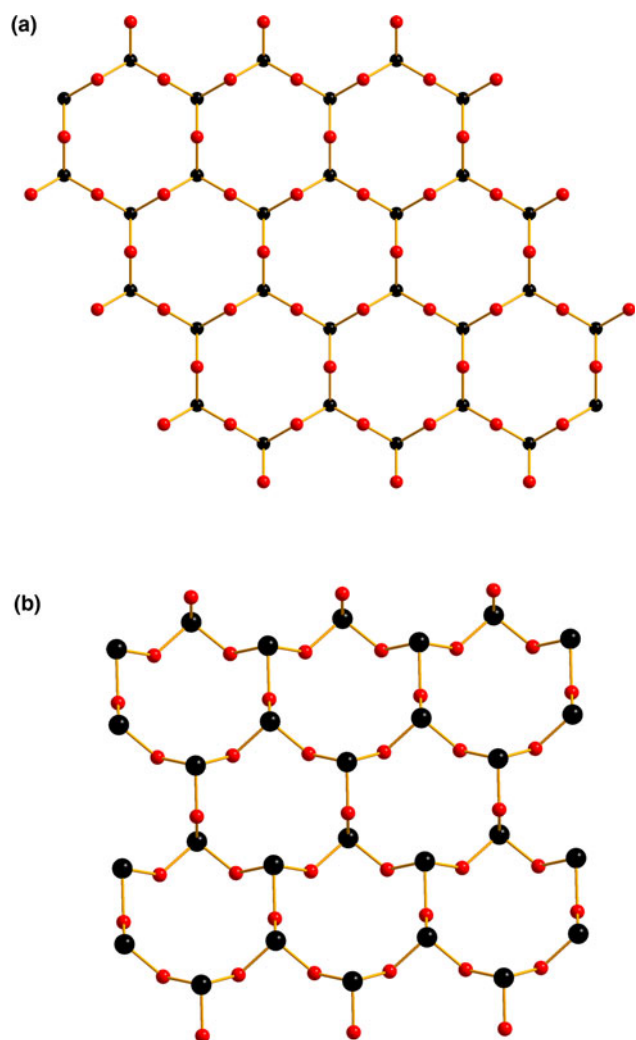| Atom	Wyck.	Occupancy	x/a	y/b	z/c	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
As	4h	1	1/3	2/3	0.21224(2)	0.01708(6)	0.01357(7)	0.01357(7)	0.02411(13)	0	0	0.0678(3)
O	6i	1	0	1/2	0.13607(13)	0.0202(4)	0.0121(5)	0.0168(4)	0.0281(7)	0	0	0.0046(5)
Cl	2e	1	0	0	0.32220(10)	0.0340(2)	0.0313(3)	0.0313(3)	0.0395(5)	0	0	0.0156(1)
N(1)	1a	0.936(6)	0	0	0	0.0323(11)	0.0277(11)	0.0277(11)	0.041(2)	0	0	0.0138(6)
K(1)	1a	0.064(6)	0	0	0	0.0323(11)	0.0277(11)	0.0277(11)	0.041(2)	0	0	0.0138(6)
N(2)	3g	0.341(12)	1/2	0	1/2	0.098(3)	0.145(7)	0.067(5)	0.057(4)	0	0	0.33(2)
Ow	3g	0.340(10)	1/2	0	1/2	0.098(3)	0.145(7)	0.067(5)	0.057(4)	0	0	0.33(2)

Wyck. – Wyckoff letter
*The anisotropic displacement factor exponent takes the form: $-2\pi^2(U^{11}h^2(a^*)^2+\ldots+2U^{12}hka^*b^*+\ldots)$;
U_{eq} according to Fischer and Tillmanns (1988).

Table 5. Selected interatomic distances (Å) and angles (°) in russoite.

As–O (×3)	1.7995(9)	Cl···O (×6)	3.532(1)
As···Cl (×3)	3.3422(7)	N(2)···Ow	2.6315(4)
As···As (×3)	3.0386(4)	Ow/N(2)···Cl (×4)	3.4628(9)
O–As–O (×3)	93.97(6)	N(1)···O (×12)	3.145(1)
As–O–As	115.19(9)	N(1)···Cl (×2)	4.079(1)

ions are too close one another at a distance of 2.6315(4) Å, which is unrealistic. To obtain a correct set of interatomic contacts among the ammonium ions, the occupancy of the site should have been ⅓ only, but this does not fulfil charge balance. At this point we began to doubt that other atoms in the model proposed by Edstrand and Blomqvist were correctly assigned, even if they apparently refined correctly, in particular the location of the water molecules between two As₂O₃ layers. Our doubts have also been supported by the evidence that the large cations are located

between the As₂O₃ layers in the structure of the other phylloarsenites (see later). Therefore we replaced the water molecule at the 1a Wyckoff position by an ammonium ion, and we considered the 3g Wyckoff position to be ⅓ occupied by an additional ammonium and ⅓ occupied by a H₂O molecule. This model is confirmed by the values of the refined occupancies (see Table 4) of the site and by the correct interatomic contacts between symmetry-related and hydrogen-bonded ammonium cations and water molecules. Replacement of ammonium with minor K, as suggested by the chemical analysis, was also taken into account. The value of the refined occupancy of the N(1) site is in good agreement with the K content obtained from the chemical analysis. The H atoms of the H₂O molecule and of the ammonium ion at 3g could not be located in a difference-Fourier map, where residual peaks around O and N indicate a situation of disorder. The same happens for the hydrogen atoms of the ammonium N(1), which is located inside a regular hexagonal

Fig. 4. A comparison between the structure of lucabindiite (*a*) and that of russoite (*b*).

Fig. 5. As_2O_3 sheets in russoite, lucabindiite, gajardoite (*a*) and torrecillasite (*b*); As = black spheres and O = red spheres.

Table 6. Bond-valence analysis for russoite (non-disordered atoms). Values are expressed in valence units (vu)*.

	O	Cl	Σ_c
As	0.97 × 3→	0.04 × 3	3.15
	0.97 × 2↓		
N(1) H_4^+	0.08 × 12→	0.02 × 2→	1.00
	0.08 × 1↓	0.02 × 2↓	
Σ_a	2.05	0.16	

*As^{3+}–O, As^{3+}–Cl and NH_4^+–Cl bond-valence parameters from Brown and Altermatt (1985), Brese and O'Keeffe (1991) and Brown (2009), respectively.

et al., 2016), forms a small group of phylloarsenite minerals. All these phases contain electrically neutral As_2O_3 sheets consisting of $As^{3+}O_3$ pyramids that share O atoms to form six-membered rings. The large cations are located between the sheets and the halide anions are outside them.

Russoite has closer structural relationships with lucabindiite, $(K,NH_4)As_4O_6(Cl,Br)$ (*a* = 5.2386(7) and *c* = 9.014(2) Å), a complex arsenite chloride first found at La Fossa crater, Vulcano Island, Sicily, and with gajardoite $KCa_{0.5}As_4^{3+}O_6Cl_2 \cdot 5H_2O$ (*a* = 5.2558(8) and *c* = 16.9666(18) Å). These minerals display similarity in their hexagonal unit-cell parameter *a*, whereas the *c* parameter is variable due to the different stacking sequence of the large cations, chloride ions and H_2O molecules (Fig. 4). In russoite, lucabindiite and gajardoite, the conformation of the As_2O_3 layers (Fig. 5*a*) is the same, with all the As apices, and therefore the stereoactive lone pair of each As^{3+} atom, pointing in the same direction normal to the layer (planar layers). In the orthorhombic torrecillasite (Fig. 5*b*) one of the As apices points in the opposite direction (wavy layers). Planar As_2O_3 layers with interlayer regions containing *M* large cations, alternating with interlayer regions containing halogen anions, are also present in a group of synthetic compounds isostructural with lucabindiite, studied by Pertlik (1988), with the general formula MAs_4O_6X (*M* = K or NH_4; *X* = Cl, Br or I).

The peculiarity of russoite is that we have, in the region between two levels of chloride ions, a disordered layer of water molecules and ammonium cations, interacting with each other via hydrogen bonds. The bond-valence analysis (Table 6) shows reasonable values with only one striking anomaly: the bond-valence sums for the Cl site is only 0.16 valence units (vu). Low values of the bond-valence sums for the Cl site have also been observed in lucabindiite (0.31 vu), torrecillasite (0.49 vu) and gajardoite (0.24 vu) and were interpreted by Kampf et al. (2016) to be possibly related to the strong repulsive effect of the As^{3+} lone pair, which is directed towards the Cl sites. The coordination of the As atoms is therefore characterised by the presence of three short As–O distances (1.7995(9) Å and three As···Cl longer interactions (3.3422(7) Å).

prismatic cavity, because the site symmetry is higher than the symmetry of the ammonium ion and each hydrogen is therefore distributed over a number of symmetry-related sites. The final *R* index is 0.0518 for 311 independent data having $I > 2\sigma(I)$ and 21 parameters. The *MISSIM* algorithm in the *PLATON* program (Spek, 2003) suggests a possible $P6/mmm$ (pseudo) symmetry for the non-disordered atoms of the structure. The statistical test ($|E^2-1| = 0.876$) does not indicate unequivocally the centrosymmetric/non-centrosymmetric nature of russoite (expected values: centrosymmetric = 0.968, non-centrosymmetric = 0.736). As the refinement in the space group $P6/mmm$ gives a significantly higher final *R* = 0.0606 for 232 independent data with $I > 2\sigma(I)$, the correct space group for russoite seems to be $P622$. Fractional atomic coordinates, occupancies, and anisotropic displacement parameters are presented in Table 4. Selected interatomic distances are reported in Table 5.

Crystal structure of russoite

The mineral, together with lucabindiite $(K,NH_4)As_4O_6(Cl,Br)$ (Garavelli et al., 2013), torrecillasite Na $(As,Sb)_4^{3+}O_6Cl$ (Kampf et al., 2014) and gajardoite $KCa_{0.5}As_4^{3+}O_6Cl_2 \cdot 5H_2O$ (Kampf

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