

Witzkeite: A new rare nitrate-sulphate mineral from a guano deposit at Punta de Lobos, Chile

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ABSTRACT

Witzkeite, ideally $\text{Na}_4\text{K}_4\text{Ca}(\text{NO}_3)_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, is a new mineral found in the oxidation zone of the guano mining field at Punta de Lobos, Tarapacá region, Chile. It occurs as colorless, tabular crystals up to 140 μm in length, associated with ditmanite and nitratine. Witzkeite is colorless and transparent, with a white streak and a vitreous luster. It is brittle, with Mohs hardness 2 and distinct cleavage on $\{001\}$. Measured density is 2.40(2) g/cm^3 , calculated density is 2.403 g/cm^3 . Witzkeite is biaxial (–) with refractive indexes $\alpha = 1.470(5)$, $\beta = 1.495(5)$, $\gamma = 1.510(5)$, measured $2V = 50\text{--}70^\circ$. The empirical composition is (electron microprobe, mean of five analyses, H_2O , CO_2 , and N_2O_5 by gas chromatography; wt%): Na_2O 12.83, K_2O 22.64, CaO 7.57, FeO 0.44, SO_3 39.96, N_2O_5 12.7, H_2O 4.5, total 100.64; CO_2 was not detected. The chemical formula, calculated based on 24 O, is: $\text{Na}_{3.40}\text{K}_{3.95}\text{Ca}_{1.11}\text{Fe}_{0.05}(\text{NO}_3)_{1.93}(\text{SO}_4)_{4.10}(\text{H}_{4.10}\text{O}_{1.81})$. Witzkeite is monoclinic, space group $C2/c$, with unit-cell parameters: $a = 24.902(2)$, $b = 5.3323(4)$, $c = 17.246(1)$ Å, $\beta = 94.281(7)^\circ$, $V = 2283.6(3)$ Å³ ($Z = 4$). The crystal structure was solved using single-crystal X-ray diffraction data and refined to $R_1(F) = 0.043$. Witzkeite belongs to a new structure type and is noteworthy for the very rare simultaneous presence of sulfate and nitrate groups. The eight strongest X-ray powder-diffraction lines [d in Å (I in %) ($h k l$)] are: 12.38 (100) (2 0 0), 4.13 (19) (6 0 0), 3.10 (24) (8 0 0), 2.99 (7) ($\bar{8}$ 0 2), 2.85 (6) (8 0 2), 2.69 (9) ($\bar{7}$ 1 3), 2.48 (12) (10 0 0), and 2.07 (54) (12 0 0). The IR spectrum of witzkeite was collected in the range 390–4000 cm^{-1} . The spectrum shows the typical bands of SO_4^{2-} ions (1192, 1154, 1116, 1101, 1084, 993, 634, and 617 cm^{-1}) and of NO_3^- ions (1385, 1354, 830, 716, and 2775 cm^{-1}). Moreover, a complex pattern of bands related to H_2O is visible (bands at 3565, 3419, 3260, 2405, 2110, 1638, and 499 cm^{-1}). The IR spectrum is discussed in detail.

Keywords: Witzkeite, new mineral, guano, crystal structure, sulfate, nitrate, IR spectroscopy

INTRODUCTION

Minerals simultaneously containing sulfate and nitrate groups as species-defining components are extremely rare. Only three such mineral species were previously known: darapskite, $\text{Na}_3(\text{SO}_4)(\text{NO}_3) \cdot \text{H}_2\text{O}$, space group $P2_1/m$ (Sabbelli 1967), ungemachite, $\text{K}_3\text{Na}_8\text{Fe}^{3+}(\text{SO}_4)_6(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, space group $R\bar{3}$ (Groat and Hawthorne 1986) and humberstonite, $\text{K}_3\text{Na}_7\text{Mg}_2(\text{SO}_4)_6(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, space group $R\bar{3}$ (Burns and Hawthorne 1994). Ungemachite and humberstonite are structurally similar to one another, whereas darapskite has a markedly different structural arrangement. These minerals all have similar origin and provenance as they are found in sulfate and nitre deposits situated in Chile (even if in different regions), all occurring in areas with very arid climates.

The new mineral witzkeite, the fourth sulfate-nitrate compound discovered in nature, is characterized by a new crystal structure type. It was found in the oxidation zone of an outcrop $1 \times 1 \text{ m}^2$ in size located in a guano mining area ($400 \times 200 \text{ m}$ across) on the southeast slope of Punta de Lobos, Tarapacá

region (Chile), approximately 90 km south of Iquique ($21^\circ 12' \text{S}$ $70^\circ 05' \text{W}$). Witzkeite appears to be extremely rare as only two small samples have been found.

Witzkeite has been approved by the Commission on New Minerals, Nomenclature and Classification, IMA no. 2011-084. Holotype material is deposited in the mineralogical collection of the Museum of Mineralogy of the Department of Geosciences at the University of Padova (Italy), under catalog number MMP M10009. The name is in honor of Thomas Witzke (b. 1963), a well-known German mineralogist whose study of alteration processes and products has resulted in the discovery and description of several new minerals.

APPEARANCE, MINERAL ASSOCIATION, PHYSICAL AND OPTICAL PROPERTIES

Witzkeite forms elongated, tabular crystals up to 140 μm in length (Fig. 1) and is associated with ditmanite and nitratine. It is colorless and transparent, with a white streak and a vitreous lustre. Witzkeite is brittle, with Mohs hardness 2 and distinct cleavage on $\{001\}$. No parting is observed and fracture is uneven. Twinning was not observed. Witzkeite dissolves in water (slowly

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FIGURE 1. SEM image of witzkeite.

at 20 °C and more rapidly at 50 °C). The measured density (by flotation in heavy liquids) is 2.40(2) g/cm³, which is in excellent agreement with the calculated density, 2.403 g/cm³, using the empirical formula.

Witzkeite is biaxial (–) with refractive indices $\alpha = 1.470(5)$, $\beta = 1.495(5)$, $\gamma = 1.510(5)$ (for white light); the measured $2V_x$ is in the range 50–70°, the measured $2V_x$ with a spindle stage is 52°, $2V_x$ calculated is 74.4°, dispersion is weak, $r > v$, optical orientation: $n_x \parallel b$, $n_y \sim a$, $n_z \parallel c$. The Gladstone-Dale compatibility index calculated from the empirical formula is $1 - (K_p/K_c) = -0.018$ (superior).

METHODS

Chemical data

Chemical analyses (five) were carried out by means of an electron microprobe (VEGA TS 5130 MM SEM, standardized EDS mode, INCA analyzer, 15.7 kV, 0.5 nA, 16 µm beam diameter, 70 s live count time). H₂O, CO₂, and N₂O₅ were determined by gas chromatography (CHN analysis of gaseous products obtained by heating of the mineral at 1400 °C). No CO₂ was detected (detection limit ~0.05 wt%).

Analytical data are given in Table 1. The empirical formula (based on 24 anions) is Na_{3.40}K_{3.95}Ca_{1.11}Fe_{0.05}(NO₃)_{1.93}(SO₄)_{4.10}(H_{4.10}O_{1.81}). The idealized formula is Na₄K₄Ca(NO₃)₂(SO₄)₄·2H₂O, which requires Na₂O = 14.89; K₂O = 22.62; CaO = 6.73; N₂O₅ = 12.97; SO₃ = 38.46; H₂O = 4.33; total 100.00 wt%.

Single-crystal X-ray diffraction

All the experimental details concerning the single-crystal X-ray study are reported in Table 2.

The analysis of the data gave unit-cell parameters $a = 24.902(2)$ Å, $b = 5.3323(4)$ Å, $c = 17.246(1)$ Å, $\beta = 94.281(7)^\circ$, $V = 2283.6(3)$ Å³. Statistics of intensity showed the presence of a C-centered lattice while systematic absences of reflections were compatible with *c*-glide. The Sheldrick's criterion observed for the reflections was $|\mathbf{E}^2 - 1| = 0.873$, which led us to solve the structure in a

TABLE 1. Chemical data for witzkeite

Oxides	wt%	Range	Probe standard
Na ₂ O	12.83	12.64–12.96	albite
K ₂ O	22.64	22.27–22.92	orthoclase
CaO	7.57	7.35–7.72	diopside
FeO	0.44	0–0.67	Fe
SO ₃	39.96	39.41–40.29	BaSO ₄
N ₂ O ₅	12.7		
H ₂ O	4.5		
Total	100.64		

TABLE 2. Crystal parameters, data collection, and structure-refinement details

Crystal system	Monoclinic
Cell determination	
Unit-cell parameters	
<i>a</i>	24.902(2) Å
<i>b</i>	5.3323(4) Å
<i>c</i>	17.246(1) Å
β	94.281(7) (°)
Unit-cell volume	2283.6(3) Å ³
Space group	C2/c
Z	4
Crystal size (mm)	0.080 × 0.060 × 0.030
Software	CrysAlis (Oxford Diffraction)
Data collection	
Diffractometer	STOE STADI IV (CCD detector, Oxford Diffraction)
Temperature (K)	298(2)
Radiation, wavelength (Å)	MoK α , 0.71073
Θ range for data collection (°)	2.98–27.87
<i>h</i> , <i>k</i> , <i>l</i> ranges	–31 +31, –6 +6, –22 +22
Omega scan width (°), exposure time (s)	1, 60
Total reflections collected	22565
Unique reflections (<i>R</i> _{int} %)	2484 (6.78)
Unique reflections <i>F</i> > 4 Σ (<i>F</i>)	1847
Absorption correction method	XRED, XSHAPE (Stoe and Cie 1999, 2001)
Structure refinement	
Structure solution and Refinement software	SHELXS-SHELXL-97 (Sheldrick 1997; Farrugia 1999)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2484/0/190
<i>R</i> ₁ [<i>F</i> > 4 σ (<i>F</i>)]	0.043
<i>R</i> ₁ all	0.072
w <i>R</i> ²	0.101
Goodness-of-fit on <i>F</i> ²	1.09
Highest peak, deepest hole (<i>e</i> /Å ^{–3})	0.62, –0.60
Weighting scheme	1/[$\sigma^2(F_o^2) + (0.0481P)^2 + 0.00P$] where $P = (F_o^2 + 2F_c^2)/3$ (SHELXL-97)

Notes: $R_{int} = (n/n - 1)^{1/2} [F_o^2 - F_c(\text{mean})^2] / \Sigma F_o^2$.

$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

Goof = $\{ \Sigma [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$.

non-centrosymmetric space group (i.e., *Cc*). The positions of the atoms were determined by direct methods using the SHELXS software in the WINGX package (Sheldrick 2008; Farrugia 1999). The structure was completed by locating light atoms (O atoms) in Fourier difference maps. The full-matrix least-squares program SHELXL-97 (Sheldrick 2008) was used for the refinement of the structure. The occupancies of all atom sites were left free to vary and all sites were found to be fully occupied. We used neutral scattering curves for all the atoms, taken from *The International Tables of X-ray Crystallography* (Ibers and Hamilton 1974). However, a test on the final model for the presence of a center of symmetry by refining the inversion twin matrix led to a rather inconclusive value of 0.4(1). Therefore, we tried the solution with the *C2/c* space group, which led to a stable model with a similar *R*-value, lower error on bond lengths and well-behaved anisotropic-displacement parameters. A satellite site was observed at 0.85 Å from a Ca-occupied site and was added to the model as being partially occupied by Fe. Moreover, the Fourier difference maps showed clearly the presence of two maxima close to the oxygen atom Ow, which has a low bond-valence sum (being thus a plausible candidate for H₂O group). These two maxima were at the right distance from oxygen (ca. 0.8 Å) and at a reasonable H-O-H angle (105°). Therefore, two hydrogen atoms were added to the model and both coordinates and isotropic displacement were set free to vary. The observed values were stable during the refinement, leading the model to convergence. A further maximum was observed at 1 Å of the O8 atom and 2.21 Å of the O1 atom. This maximum is close to the Ca site (1.83 Å) but farther from the Fe site (2.26 Å). However, due to the probable low occupancy it could not be added to the model. Nevertheless, weak bands at 2110 and 2405 cm^{–1} in the IR spectrum indicate that a minor part of SO₄ groups is protonated, being [HSO₄] groups (see below), which could explain the presence of a maximum near O8. Moreover, the empirical formula shows some excess of hydrogen that might be ascribed to acid sulfate groups.

At the last refinement stage, with anisotropic atomic displacement parameters for all atoms (except for H atoms) and no constraints, the residual value was *R*₁(*F*)

= 0.043 for 1847 observed reflections [$F_o > 4\sigma(F_o)$] and 190 parameters and $R_i(F)$ = 0.072 for all 2484 independent reflections.

Refinement parameters and R indices for witzkeite are given in Table 2. Fractional atom coordinates and anisotropic displacement U_{eq} are shown in Table 3. Selected bond distances are reported in Table 4. Structure factors for witzkeite and the CIF file, including anisotropic displacement parameter values, are provided as deposited material.

Powder X-ray diffraction

X-ray powder diffraction data were obtained on a Siemens D5000 diffractometer using $\text{CuK}\alpha$ radiation and a zero-background silicon sample holder. Indexing was performed using the Rietveld method according to the crystal structure of witzkeite. X-ray powder diffraction data (in angstroms) are reported in Table 5. Unit-cell parameters refined from the powder data are as follows: $a = 24.88(1)$, $b = 5.323(2)$, $c = 17.23(1)$ Å, $\beta = 94.22(1)^\circ$, $V = 2275.7(5)$ Å³.

¹ Deposit item AM-12-070, CIF and structure factors. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 3. Atom coordinates and U_{eq} (Å²) values for witzkeite

Atom	x/a	y/b	z/c	U_{eq}
Ca	½	0.1735(3)	¼	0.0163(3)
Fe	½	0.333(5)	¼	0.0152(7)
K1	0.15202(3)	0.25031(14)	0.10623(4)	0.0247(3)
K2	0.32417(3)	0.24292(14)	0.23240(5)	0.0275(3)
S1	0.56605(3)	-0.75113(15)	0.07266(4)	0.0153(2)
S2	0.41680(3)	-0.27020(15)	0.22437(5)	0.0157(2)
Na1	0.41977(5)	0.24195(22)	0.07588(7)	0.0214(3)
Na2	0.50009(6)	-0.26669(23)	0.08618(7)	0.0241(3)
N1	0.75732(13)	0.2462(6)	0.12315(21)	0.0323(8)
O1	0.43161(10)	0.4724(4)	0.20028(13)	0.0258(6)
O2	0.35931(9)	-0.2587(4)	0.23440(14)	0.0226(6)
O3	0.43758(10)	-0.0133(4)	-0.02829(13)	0.0239(6)
O4	0.43613(10)	0.5377(4)	-0.01849(13)	0.0227(6)
O5	0.55222(10)	-0.2044(4)	0.20292(13)	0.0238(6)
O6	0.38488(9)	0.2567(4)	0.37627(14)	0.0250(6)
O7	0.51776(9)	0.2672(4)	0.11856(13)	0.0210(5)
O8	0.43192(10)	-0.0888(4)	0.16526(13)	0.0259(6)
O9	0.25780(11)	0.0436(5)	0.34995(17)	0.0413(8)
O10	0.25789(11)	0.4491(5)	0.34928(17)	0.0417(8)
O11	0.78891(14)	0.2472(5)	0.07049(19)	0.0504(9)
H1	0.3102(17)	0.377(7)	0.059(2)	0.037(14)
H2	0.308(2)	0.134(8)	0.060(3)	0.07(2)
Ow	0.32731(13)	0.2459(7)	0.05085(18)	0.0383(7)

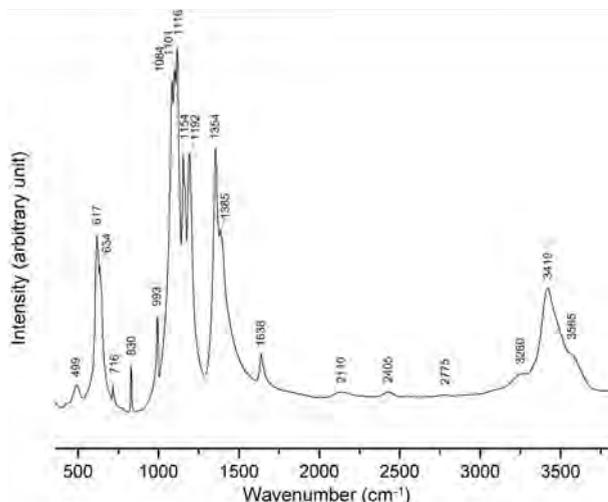


FIGURE 2. Infrared spectrum of witzkeite.

IR spectroscopy

Witzkeite was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) with the resolution of 4 cm⁻¹. Sixteen scans were obtained in the range of 390–4000 cm⁻¹. The spectrum of a pure KBr pellet was used as reference. The spectrum of witzkeite is shown in Figure 2.

RESULTS AND DISCUSSIONS

Crystal structure

The crystal structure of witzkeite represents a new crystal structure topology; it can be described in terms of sulfate and nitrate slabs parallel to the (100) plane alternating along [100] (Fig. 3, left side). The sulfate slab consists of three independent cation sites and two independent SO₄ anion groups. The inner part of the slab is formed by one eightfold-coordinated cation

TABLE 4. Selected bond lengths (Å) and angles (°) for witzkeite

Ca-O1 ×2	2.441(2)	K1-O2	2.784(2)	K2-O1	3.030(3)
Ca-O5 ×2	2.562(2)	K1-O3	2.882(2)	K2-O2	2.797(2)
Ca-O7 ×2	2.394(2)	K1-O4	2.995(2)	K2-O2	2.814(2)
Ca-O8 ×2	2.568(2)	K1-O5	3.104(3)	K2-O6	2.808(2)
<Ca-O>	2.491	K1-O6	2.876(2)	K2-O9	2.884(3)
		K1-O6	2.811(2)	K2-O9	2.911(3)
Fe-O1 ×2	1.993(11)	K1-O9	2.794(3)	K2-O10	2.861(3)
Fe-O7 ×2	2.368(5)	K1-O10	2.819(3)	K2-O10	2.914(3)
<Fe-O>	2.181	K1-Ow	2.795(3)	K2-Ow	3.138(3)
		<K1-O>	2.873	<K2-O>	2.906
Na2-O3	2.422(3)				
Na2-O3	2.772(2)	Na1-O1	2.471(2)	S1-O3	1.470(2)
Na2-O4	2.500(3)	Na1-O3	2.323(2)	S1-O4	1.471(2)
Na2-O4	2.540(3)	Na1-O4	2.324(2)	S1-O6	1.452(2)
Na2-O5	2.336(2)	Na1-O7	2.499(3)	S1-O7	1.492(2)
Na2-O7	2.578(2)	Na1-O8	2.347(2)	<S1-O>	1.471
Na2-O7	2.928(2)	Na1-Ow	2.311(3)	TAV*	2.416
Na2-O8	2.447(3)	<Na1-O>	2.379		
<Na2-O>	2.565			S2-O1	1.488(2)
		Ow-H1	0.84(4)	S2-O2	1.456(2)
N1-O9	1.245(4)	Ow-H2	0.79(5)	S2-O5	1.465(2)
N1-O10	1.252(4)	Ow-O11	2.855	S2-O8	1.474(2)
N1-O11	1.245(5)	H1-Ow-H2	105.05°	<S2-O>	1.471
<N1-O>	1.247	O11...Ow-H	152.6°	TAV	2.066

*TAV = tetrahedral angle variance (Robinson et al. 1971).

TABLE 5. X-ray powder-diffraction data for witzkeite

l_{rel}	d_{meas} (Å)	d_{calc} (Å)	h	k	l
100	12.377	12.408	2	0	0
3	8.587	8.592	0	0	2
2	7.315	7.320	2	0	2
1	5.198	5.205	1	1	0
19	4.134	4.136	6	0	0
1	3.881	3.882	1	1	3
3	3.837	3.839	6	0	2
5	3.510	3.514	5	1	1
4	3.410	3.416	4	0	4
3	3.143	3.144	5	1	3
24	3.100	3.102	8	0	0
7	2.989	2.989	8	0	2
6	2.851	2.852	8	0	2
9	2.689	2.691	7	1	3
2	2.609	2.608	8	0	4
12	2.482	2.482	10	0	0
4	2.431	2.432	8	0	4
2	2.335	2.335	10	0	2
2	2.278	2.278	6	0	6
1	2.241	2.238	6	2	0
54	2.068	2.068	12	0	0
4	2.045	2.046	11	1	1
1	1.950	1.949	0	2	6
2	1.834	1.834	11	1	5

Note: Uncertainties in measured d -spacings are estimated to be around 0.001 Å. * Indexed with $a = 24.88(1)$, $b = 5.323(2)$, $c = 17.23(1)$ Å, $\beta = 94.22(1)^\circ$. All lines were used for unit-cell refinement.

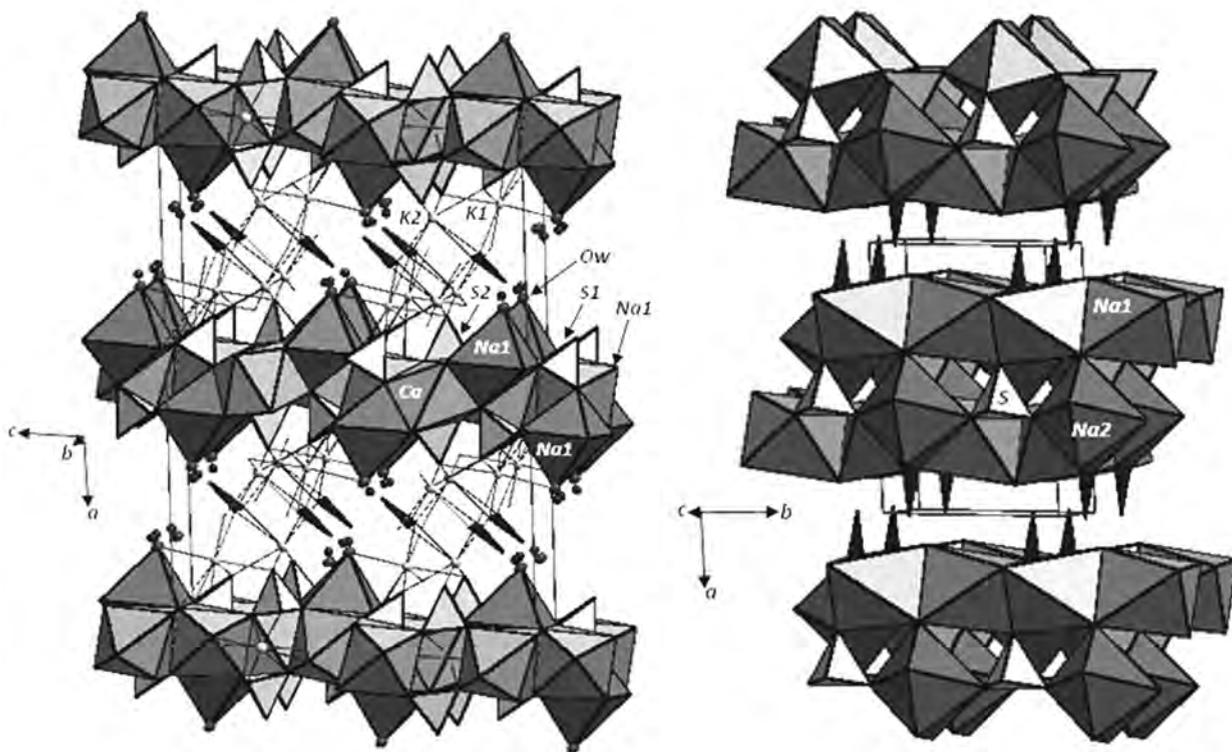


FIGURE 3. (left) Crystal structure of witzkeite viewed along a direction close to the **b** (the shortest axis in figure) axis to better show the NO_3 groups. For simplicity the **a** (the longest) and **c** (the intermediate) axes are not reported in perspective; (right) crystal structure of darapskite. Atom labels are reported on the figure.

site occupied by Ca (Ca site; average $\langle\text{Ca-O}\rangle$ distance of 2.491 Å), and a (7+1)-fold-coordinated site occupied by Na (Na2 site, $\langle\text{Na2-O}\rangle = 2.565$ Å; Table 4). This inner part of the slab is decorated with one sixfold coordinated cationic site and by SO_4 groups. The cation site is occupied by Na (Na1 site), and coordinates with five oxygen atoms and one H_2O group ($\langle\text{Na1-O}\rangle = 2.379$ Å; Table 4). The SO_4 groups are symmetrically independent (S1 and S2 sites; both with $\langle\text{S-O}\rangle = 1.471$ Å). The number of sites accounts for the chemistry of the slab being $\text{Na}_4\text{Ca}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, with an overall charge of -2 .

The $\text{Na}_4\text{Ca}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ slab alternates along [100] with potassium nitrate slabs $[\text{K}_4(\text{NO}_3)_2]^{2+}$; this slab is built by a planar (NO_3) group with the N site in threefold coordination ($\langle\text{N-O}\rangle = 1.247$ Å), and by K ions in two symmetrically independent sites (the K1, K2 sites), which are ninefold coordinated by the oxygen atoms of the nitrate groups and by the Ow site [bonded to the K1, K2, and Na1 sites]. This Ow atom shows a bond valence value of 0.385 v.u., thus confirming it as a H_2O group. One oxygen coordinating the N site is forming a hydrogen bond from the Ow site ($\text{O11}\cdots\text{Ow} = 2.855$ Å). The observed deformation of the (NO_3) planar group could be due to the strong hydrogen bond between one oxygen atom of the NO_3 group and the hydrogen atoms of the H_2O groups. The K1 and K2 sites show occupancies of 0.99 and 0.97, respectively.

In the sulfate layer, the Ca site has a split site position at 0.85 Å along [100], which is occupied by Fe in fourfold coordination (Fe-site, $\langle\text{Fe-O}\rangle = 2.181$ Å; Table 4); observed occupancy factors

for Ca and the Fe split position are 0.89 and 0.04, respectively, in good agreement with the chemical analysis. The two Na-dominant sites show populations having 1 apfu of Na. The excess Ca found in the empirical formula, might disorder eventually into the Na2 site. However, we have not found evidences for such a disorder in the model. Moreover, the amount of Na observed from site occupancy refinement is higher than the one obtained by chemical analyses (4.00 vs. 3.40 apfu). This discrepancy may reflect some chemical zoning, with the crystal studied by single-crystal diffraction being richer in Na. Still, Na + Ca + Fe in the chemical formula (see above section) do not account for 5 apfu. Therefore, provided the nature of the mineral, the lower Na found by EMP analyses might be due to Na migration under the electron beam.

IR spectroscopy

Absorption bands in the IR spectrum of witzkeite (Fig. 2) and their assignments (in cm^{-1} ; s = strong band, w = weak band, sh = shoulder) are as follows: 3565sh, 3419 (O-H stretching vibrations of H_2O molecules, medium strength hydrogen bonds), 3260w (O-H stretching vibrations of H_2O molecules, strong hydrogen bonds), 2775w (overtone of N-O stretching mode), 2405w, 2110w (combination modes and/or O-H stretching vibrations of acid OH groups), 1638 (bending vibrations of H_2O molecules), 1385, 1354s (asymmetric stretching vibrations of NO_3^- ions), 1192s, 1154s, 1116s, 1101s, 1084s (asymmetric stretching vibrations of SO_4^{2-} ions), 993 (symmetric stretching vibrations of

SO_4^{2-} ions), 830 (out-of-plane bending vibrations of NO_3^- ions), 716 (in-plane bending vibrations of NO_3^- ions), 634, 617 (bending vibrations of SO_4^{2-} ions), 499 (libration vibrations of H_2O molecules). The splitting of the bands of asymmetric N-O and S-O stretching vibrations and the relatively high intensity of the symmetric S-O stretching vibrations at 993 cm^{-1} indicate strong distortion of both SO_4 tetrahedra and NO_3^- groups. Taking into account weak IR bands in the range $2100\text{--}2500\text{ cm}^{-1}$, one cannot exclude the presence of trace amounts of HSO_4^- ions in witzkeite. In fact, a maximum was observed at 1 \AA of the O8 site, which is bonded to the S2 site, perhaps explaining the slight excess of H observed in the chemical formula.

Relations with other structures

As described in the Introduction section, three other minerals have been previously described in the literature that have species-defining sulfate and nitrate groups in common with witzkeite. Among these, only darapskite shows structural similarities to witzkeite. Darapskite, which was found in the same region as witzkeite, also shows alternating layers containing SO_4 and NO_3 groups. However, in darapskite there is only one independent SO_4 group and one NO_3 group vs. the two independent SO_4 groups and one NO_3 group of witzkeite (see Fig. 3b). Moreover, in darapskite the Na-Ca-Na cation layer in between the SO_4 groups is missing. In darapskite, the oxygen atoms of the NO_3 groups coordinate Na atoms instead of K atoms like in witzkeite and show a significantly different arrangement with respect to that of witzkeite: in witzkeite, the planar NO_3 groups are nearly parallel to the (102) plane. Assuming a similar orientation between witzkeite and darapskite unit cells so that the sulfate layers are parallel in both structures, the NO_3 groups for the darapskite are perpendicular to the sulfate layers and parallel to a plane, which is oriented at almost 45° from that formed by the NO_3 in witzkeite. Concerning the other two phases bearing both (SO_4) and (NO_3) groups, ungemachite and humberstonite, they do not show any structural similarities with witzkeite.

Among sulfate and selenate minerals, some structural similarities with witzkeite can be also found for example in fuenzalidaite, $\text{K}_6(\text{Na,K})_4\text{Na}_6\text{Mg}_{10}(\text{SO}_4)_{12}(\text{IO}_3)_{12}\cdot 12(\text{H}_2\text{O})$, and carlosruizite $\text{K}_6(\text{Na,K})_4\text{Na}_6\text{Mg}_{10}(\text{SeO}_4)_{12}(\text{IO}_3)_{12}\cdot 12(\text{H}_2\text{O})$ (Konert et al. 1994), which have layers of cations coordinated by SeO_4 and SO_4 tetrahedra, respectively, alternating with layers of planar IO_3 groups.

A further structure similar to witzkeite could be hypothesized for hectorfloresite (Erickson et al. 1989), which shows a similar but anhydrous stoichiometry, $\text{Na}_6(\text{IO}_3)(\text{SO}_4)_4$ (considering one planar IO_3 group instead of two NO_3 groups). However, there are no structural data available for hectorfloresite to allow us to verify its degree of crystallographic similarity with witzkeite.

ACKNOWLEDGMENTS

The research was funded by “ex-60%” funds from University of Padova to F. Nestola. This work was supported by the Russian Foundation for Basic Research (grants nos. 11-05-00407-a and 11-05-00397-a) and FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo), Process 2009/09125-5, for financial support; the members of the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC-IMA) for their helpful suggestions and comments, which were all considered in writing the work. The two referees A. Kampf and R.L. Frost are thanked together with the Associate Editor for their very helpful revisions, which strongly improved the manuscript.

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MANUSCRIPT RECEIVED JANUARY 16, 2012

MANUSCRIPT ACCEPTED JUNE 5, 2012

MANUSCRIPT HANDLED BY FERNANDO COLOMBO