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# 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 colourless, tabular crystals up to 140  $\mu\text{m}$  in length, associated with dittmanite and nitratine. Witzkeite is colorless and transparent, with a white streak and a vitreous lustre. It is brittle, with Mohs hardness 2 and distinct cleavage on  $\{001\}$ . Measured density is 2.40(2)  $\text{g cm}^{-3}$ , calculated density is 2.403  $\text{g cm}^{-3}$ . 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 5 analyses,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{N}_2\text{O}_5$  by gas chromatography; wt.%):  $\text{Na}_2\text{O}$  12.83,  $\text{K}_2\text{O}$  22.64,  $\text{CaO}$  7.57,  $\text{FeO}$  0.44,  $\text{SO}_3$  39.96,  $\text{N}_2\text{O}_5$  12.7,  $\text{H}_2\text{O}$  4.5, total 100.63;  $\text{CO}_2$  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:  $a = 24.902(2)$  Å,  $b = 5.3323(4)$  Å,  $c = 17.246(1)$  Å,  $\beta = 94.281(7)^\circ$ ,  $V = 2283.6(3)$  Å<sup>3</sup> ( $Z = 4$ ). 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 sulphate 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) (-8 0 2), 2.85 (6) (8 0 2), 2.69 (9) (-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  $\text{cm}^{-1}$ . The spectrum shows the typical bands of  $\text{SO}_4^{2-}$  ions (1192, 1154, 1116, 1101, 1084, 993, 634, 617  $\text{cm}^{-1}$ ) and of  $\text{NO}_3^-$  ions (1385, 1354, 830, 716, 2775  $\text{cm}^{-1}$ ). Moreover, a complex pattern of bands relatively to the  $\text{H}_2\text{O}$  is visible (bands at 3565, 3419, 3260, 2405, 2110, 1638, 499  $\text{cm}^{-1}$ ). The IR spectrum will be discussed in detail.

**Key-words:** witzkeite, new mineral, guano, crystal structure, sulphate, nitrate, IR spectroscopy.

## Introduction

Minerals simultaneously containing sulphate 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  $P2_1/m$  (Sabelli 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 sulphate 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 sulphate-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 catalogue number MMP M10009. The name is in honour 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  $\mu\text{m}$  in length (Figure 1) and is associated with dittmarite 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 at 20°C and more rapidly at 50°C). The measured density (by flotation in heavy liquids) is 2.40(2)  $\text{g cm}^{-3}$ , which is in excellent agreement with the calculated density, 2.403  $\text{g cm}^{-3}$ , 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:  $n_x = b$ ,  $n_y = a$ ,  $n_z = c$

The Gladstone-Dale compatibility index calculated from the empirical formula is  $1 - (K_p/K_c) = -0.018$  (*superior*).

## **Methods**

### *Chemical data*

Chemical analyses (5) 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  $\mu\text{m}$  beam diameter, 70 seconds live count time).  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{N}_2\text{O}_5$  were determined by gas chromatography (CHN analysis of gaseous products obtained by heating of the mineral at 1400°C). No  $\text{CO}_2$  was detected (detection limit  $\cong$  0.05 wt.%).

Analytical data are given in Table 1. The empirical formula (based on 24 anions) is  $\text{Na}_{3.40}\text{K}_{3.95}\text{Ca}_{1.11}\text{Fe}_{0.05}(\text{NO}_3)_{1.93}(\text{SO}_4)_{4.10}(\text{H}_{4.10}\text{O}_{1.81})$ . The idealized formula is

$\text{Na}_4\text{K}_4\text{Ca}(\text{NO}_3)_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , which requires  $\text{Na}_2\text{O} = 14.89$ ;  $\text{K}_2\text{O} = 22.62$ ;  $\text{CaO} = 6.73$ ;  $\text{N}_2\text{O}_5 = 12.97$ ;  $\text{SO}_3 = 38.46$ ;  $\text{H}_2\text{O} = 4.33$ ; total 100.00 wt%.

### *Single-crystal X-ray diffraction*

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

The analysis of the data gave unit-cell parameters  $a = 24.902(2) \text{ \AA}$ ,  $b = 5.3323(4) \text{ \AA}$ ,  $c = 17.246(1) \text{ \AA}$ ,  $\beta = 94.281(7)^\circ$ ,  $V = 2283.6(3) \text{ \AA}^3$ . Statistics of intensity showed the presence of a *C*-centred lattice while systematic absences of reflections were compatible with *c*-glide. The Sheldrick's criterion observed for the reflections was  $|E^2 - 1| = 0.873$ , which led us to solve the structure in a 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). Structure was completed by locating light atoms (oxygens) 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  $\text{ \AA}$  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 O<sub>w</sub>, which has a low bond valence incidence (being thus a plausible candidate for H<sub>2</sub>O 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 set free to vary. The observed values were kept stable during the refinement leading the model to convergence. A further maximum was observed at 1 Å of the O<sub>8</sub> atom and 2.21 Å of the O<sub>1</sub> 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<sup>-1</sup> in the IR spectrum indicate that a minor part of SO<sub>4</sub> groups is protonated being [HSO<sub>4</sub>] groups (see below), which could explain the presence of a maximum near O<sub>8</sub>. Moreover, the empirical formula shows some excess of hydrogen that might be ascribed to acid sulphate groups.

At the last refinement stage, with anisotropic atomic displacement parameters for all atoms (except for hydrogens) 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 at  $R_1(F) = 0.072$  for all 2484 independent reflections.

Refinement parameters and  $R$  indices for witzkeite are given in Table 2. Fractional atom coordinates and anisotropic-displacement  $U_{eq}$  (all the anisotropic displacement parameters are provided in the CIF file submitted to the journal) 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 a  $\text{CuK}\alpha$  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 Å) are reported in Table 5. Unit cell parameters refined from the powder data are as follows:  $a = 24.88(1)$  Å,  $b = 5.323(2)$  Å,  $c = 17.23(1)$  Å,  $\beta = 94.22(1)^\circ$ ,  $V = 2275.7(5)$  Å<sup>3</sup>.

### *IR spectroscopy*

Witzkeite was mixed with anhydrous KBr, pelletized, and analysed using ALPHA FT-IR spectrometer (Bruker Optics) with the resolution of 4 cm<sup>-1</sup>. 16 scans were obtained in the range of 390 - 4000 cm<sup>-1</sup>. 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 sulphate and nitrate slabs parallel to the (100) plane alternating along [100] (Figure 3a). The sulphate slab is constituted by 3 independent cation sites and two independent SO<sub>4</sub> anion groups. The inner part of the slab is formed by one 8-fold coordinated cation site occupied by Ca (*Ca* site; average <Ca-O> distance of 2.491 Å), and a (7+1)-fold coordinated site occupied by Na (Na2 site, <Na2-O> = 2.565 Å; Table 4). This inner part of the slab is decorated with one 6-fold coordinated cationic site and by SO<sub>4</sub> groups. The cation site is occupied by Na (*Na* site), and coordinates with 5 oxygen atoms and one H<sub>2</sub>O group (<Na1 - O> = 2.379 Å; Table 4). The SO<sub>4</sub> groups are symmetrically independent (S1 and S2 sites; both with <S-O> =

1.471 Å). The described amount 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  $(\text{NO}_3)$  group with the *N* site in 3-fold coordination ( $\langle \text{N-O} \rangle = 1.247$  Å), and by K ions in two symmetrically independent sites (the K1, K2 sites), which are 9-fold coordinated by the oxygen atoms of the nitrate groups and by the  $\text{O}_w$  site [bonded to the K1, K2 and Na1 sites] show bond valence value of 0.385 v.u., thus confirming it as a  $\text{H}_2\text{O}$  group. One oxygen coordinating the *N* site is forming hydrogen bond from the  $\text{O}_w$  site ( $\text{O11} \dots \text{O}_w = 2.855$  Å). Observed deformation of the  $(\text{NO}_3)$  planar group could be due to the strong hydrogen bond between one oxygen atom of the  $\text{NO}_3$  group and the hydrogen atoms of the  $\text{H}_2\text{O}$  groups. The K1 and K2 sites show occupancies at 0.99 and 0.97.

On the sulphate layer, the Ca site has a split site position at 0.85 Å along [100], which is occupied by Fe in 4-fold 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 chemistry. The two Na-dominant sites show populations having 1 a.p.f.u 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 disorder in the model. Moreover, the amount of Na observed from site occupancy is higher than the one obtained by chemical analyses (4.00 vs. 3.40 a.p.f.u.). 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 a.p.f.u. 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 (Figure 2) and their assignments (in  $\text{cm}^{-1}$ ; s – strong band, w – weak band, sh – shoulder) are 3565sh, 3419 (O-H stretching vibrations of  $\text{H}_2\text{O}$  molecules, medium strength hydrogen bonds), 3260w (O-H stretching vibrations of  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  molecules), 1385, 1354s (asymmetric stretching vibrations of  $\text{NO}_3^-$  ions), 1192s, 1154s, 1116s, 1101s, 1084s (asymmetric stretching vibrations of  $\text{SO}_4^{2-}$  ions), 993 (symmetric stretching vibrations of  $\text{SO}_4^{2-}$  ions), 830 (out-of-plane bending vibrations of  $\text{NO}_3^-$  ions), 716 (in-plane plane bending vibrations of  $\text{NO}_3^-$  ions), 634, 617 (bending vibrations of  $\text{SO}_4^{2-}$  ions), 499 (libration vibrations of  $\text{H}_2\text{O}$  molecules). The splitting of the bands of asymmetric N-O and S-O stretching vibrations and relatively high intensity of the symmetric S-O stretching vibrations at  $993 \text{ cm}^{-1}$  show relatively strong distortion of both  $\text{SO}_4$  tetrahedra and  $\text{NO}_3^-$  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  $\text{HSO}_4^{2-}$  ions in witzkeite. In fact, a maximum was observed at  $1 \text{ \AA}$  of the O8 site, which is bond to the S2 site, perhaps explaining the slight excess of H observed in the chemical formula.

### *Relations with other structures*

In addition to witzkeite, as described in the Introduction section, three further minerals have been previously described in the literature having in common species-defining sulfate and nitrate groups and among these, only darapskite shows structural similarities to witzkeite. Darapskite, which was found in the same region as witzkeite, also shows alternation of layers containing  $\text{SO}_4$  and  $\text{NO}_3$  groups . However, in

darapskite there is only one independent  $\text{SO}_4$  group and one  $\text{NO}_3$  group versus the two independent  $\text{SO}_4$  groups and one  $\text{NO}_3$  group of witzkeite (see Fig. 3b). Moreover, in darapskite the Na-Ca-Na cation layer in between the  $\text{SO}_4$  groups is missing. In darapskite the oxygen atoms of the  $\text{NO}_3$  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  $\text{NO}_3$  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  $\text{NO}_3$  groups for the darapskite are perpendicular to the sulfate layers and parallel to a plane which is oriented at almost  $45^\circ$  from that formed by the  $\text{NO}_3$  in witzkeite.. Concerning the other two phases bearing both ( $\text{SO}_4$ ) and ( $\text{NO}_3$ ) 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,  $\text{K}_6(\text{Na},\text{K})_4\text{Na}_6\text{Mg}_{10}(\text{SO}_4)_{12}(\text{IO}_3)_{12}\cdot 12(\text{H}_2\text{O})$ , and carlosruizite  $\text{K}_6(\text{Na},\text{K})_4\text{Na}_6\text{Mg}_{10}(\text{SeO}_4)_{12}(\text{IO}_3)_{12}\cdot 12(\text{H}_2\text{O})$  (Konnert et al. 1994), which have layers of cations coordinated by  $\text{SeO}_4$  and  $\text{SO}_4$  tetrahedra, respectively, alternating with layers of planar  $\text{IO}_3$  groups.

A further structure similar to witzkeite could be hypothesized for hectorfloresite (Ericksen et al. 1989), which shows a similar but anhydrous stoichiometry,  $\text{Na}_9(\text{IO}_3)(\text{SO}_4)_4$  (considering one planar  $\text{IO}_3$  group of instead of two  $\text{NO}_3$  groups). However, there are no available structural data for hectorfloresite to allow us to verify its degree of crystallographic similarity with witzkeite.

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## Table and figure captions.

**Table 1.** Chemical data for witzkeite.

**Table 2.** Crystal parameters, data collection and structure refinement details.

**Table 3.** Atom coordinates and  $U_{\text{eq}}$  ( $\text{\AA}^2$ ) values (with exception of oxygens, Fe, O2 and O10 sites for which  $U_{\text{iso}}$  is reported) for witzkeite.

**Table 4.** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for witzkeite.

**Table 5.** X-ray powder-diffraction data for witzkeite.\*

**Figure 1.** SEM image of witzkeite.

**Figure 2.** Infrared spectrum of witzkeite.

**Figure 3.** Crystal structure of a) witzkeite viewed along a direction close to the  $b$  (the shortest axis in figure) axis in order to better show the  $\text{NO}_3$  groups. For simplicity the two  $a$  (the longest axis in figure) and  $c$  (the intermediate axis in figure) axes are not reported in perspective; b) crystal structure of darapskite

**Table 1**

Oxides	wt%	Range	Probe standard
Na <sub>2</sub> O	12.83	12.64-12.96	Albite
K <sub>2</sub> O	22.64	22.27-22.92	Orthoclase
CaO	7.57	7.35-7.72	Diopside
FeO	0.44	0-0.67	Fe
SO <sub>3</sub>	39.96	39.41-40.29	BaSO <sub>4</sub>
N <sub>2</sub> O <sub>5</sub>	12.7		
H <sub>2</sub> O	4.5		
Total	100.64		



**Table 2**

<b>Cell determination</b>	
Crystal system	Monoclinic
Unit cell parameters <i>a</i> , <i>b</i> , <i>c</i> , $\beta$	24.902(2) Å
	5.3323(4) Å
	17.246(1) Å
	94.281(7) (°)
Unit cell volume	2283.6(3) Å <sup>3</sup>
Space group	<i>C2/c</i>
<i>Z</i>	4
Crystal size (mm)	0.080x0.060x0.030
Software	Crysalis (Oxford Diffraction)
<b>Data collection</b>	
Diffractometer	STOE STADI IV (CCD detector, Oxford diffraction)
Temperature (K)	298(2)
Radiation, wavelength (Å)	Mo <sub>K<math>\alpha</math></sub> , 0.71073
$\theta$ 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> <sub>int</sub> %)	2484 (6.78)
Unique reflections <i>F</i> > 4 $\sigma$ ( <i>F</i> )	1847
Absorption correction method	XRED, XSHAPE (Stoe and Cie 2000; 2001)
<b>Structure refinement</b>	
Structure solution and Refinement software	SHELXS-SHELXL-97 (Sheldrick 1997, Farrugia, 1999)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	2484/0/190
<i>R</i> <sub>1</sub> [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	0.043
<i>R</i> <sub>1</sub> all	0.072
<i>wR</i> <sup>2</sup>	0.101
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.09
Highest peak, deepest hole (e Å <sup>-3</sup> )	0.62, -0.60
Weighting scheme	$1 / [\sigma^2(F_o^2) + (0.0481P)^2 + 0.00P]$ where $P = (F_o^2 + 2 \times F_c^2) / 3$ (SHELXL-97)
<p>Notes: <math>R_{int} = (n / n - 1)^{1/2} [F_o^2 - F_o(\text{mean})^2] / \sum F_o^2</math></p> $R_1 = \sum    F_o   -   F_c    / \sum   F_o  $ $\text{Goof} = \{ \sum [ w ( F_o^2 - F_c^2 )^2 ] / (n - p) \}^{1/2}$	

**Table 3**

<b>Atom</b>	<b><i>x/a</i></b>	<b><i>y/b</i></b>	<b><i>z/c</i></b>	<b><i>U<sub>eq</sub></i></b>
<b>Ca</b>	½	0.1735(3)	¼	0.0163(3)
<b>Fe</b>	½	0.333(5)	¼	0.0152(7)
<b>K(1)</b>	0.15202(3)	0.25031(14)	0.10623(4)	0.0247(3)
<b>K(2)</b>	0.32417(3)	0.24292(14)	0.23240(5)	0.0275(3)
<b>S(1)</b>	0.56605(3)	-0.75113(15)	0.07266(4)	0.0153(2)
<b>S(2)</b>	0.41680(3)	-0.27020(15)	0.22437(5)	0.0157(2)
<b>Na(1)</b>	0.41977(5)	0.24195(22)	0.07588(7)	0.0214(3)
<b>Na(2)</b>	0.50009(6)	-0.26669(23)	0.08618(7)	0.0241(3)
<b>N(1)</b>	0.75732(13)	0.2462(6)	0.12315(21)	0.0323(8)
<b>O1</b>	0.43161(10)	0.4724(4)	0.20028(13)	0.0258(6)
<b>O2</b>	0.35931(9)	-0.2587(4)	0.23440(14)	0.0226(6)
<b>O3</b>	0.43758(10)	-0.0133(4)	-0.02829(13)	0.0239(6)
<b>O4</b>	0.43613(10)	0.5377(4)	-0.01849(13)	0.0227(6)
<b>O5</b>	0.55222(10)	-0.2044(4)	0.20292(13)	0.0238(6)
<b>O6</b>	0.38488(9)	0.2567(4)	0.37627(14)	0.0250(6)
<b>O7</b>	0.51776(9)	0.2672(4)	0.11856(13)	0.0210(5)
<b>O8</b>	0.43192(10)	-0.0888(4)	0.16526(13)	0.0259(6)
<b>O9</b>	0.25780(11)	0.0436(5)	0.34995(17)	0.0413(8)
<b>O10</b>	0.25789(11)	0.4491(5)	0.34928(17)	0.0417(8)
<b>O11</b>	0.78891(14)	0.2472(5)	0.07049(19)	0.0504(9)
<b>H1</b>	0.3102(17)	0.377(7)	0.059(2)	0.037(14)
<b>H2</b>	0.308(2)	0.134(8)	0.060(3)	0.07(2)
<b>Ow</b>	0.32731(13)	0.2459(7)	0.05085(18)	0.0383(7)

**Table 4**

Ca-O1 ×2	2.441(2)	K(1)-O2	2.784(2)	K(2)-O1	3.030(3)
Ca-O5 ×2	2.562(2)	K(1)-O3	2.882(2)	K(2)-O2	2.797(2)
Ca-O7 ×2	2.394(2)	K(1)-O4	2.995(2)	K(2)-O2	2.814(2)
Ca-O8 ×2	2.568(2)	K(1)-O5	3.104(3)	K(2)-O6	2.808(2)
<b>&lt;Ca-O&gt;</b>	<b>2.491</b>	K(1)-O6	2.876(2)	K(2)-O9	2.884(3)
		K(1)-O6	2.811(2)	K(2)-O9	2.911(3)
Fe-O1 ×2	1.993(11)	K(1)-O9	2.794(3)	K(2)-O10	2.861(3)
Fe-O7 ×2	2.368(5)	K(1)-O10	2.819(3)	K(2)-O10	2.914(3)
<b>&lt;Fe-O&gt;</b>	<b>2.181</b>	K(1)-O <sub>w</sub>	2.795(3)	K(2)-O <sub>w</sub>	3.138(3)
		<b>&lt;K(1)-O&gt;</b>	<b>2.873</b>	<b>&lt;K(2)-O&gt;</b>	<b>2.906</b>
Na(2)-O3	2.422(3)				
Na(2)-O3	2.772(2)	Na(1)-O1	2.311(3)	S(1)-O3	1.470(2)
Na(2)-O4	2.500(3)	Na(1)-O3	2.323(2)	S(1)-O4	1.471(2)
Na(2)-O4	2.540(3)	Na(1)-O4	2.324(2)	S(1)-O6	1.452(2)
Na(2)-O5	2.336(2)	Na(1)-O7	2.347(2)	S(1)-O7	1.492(2)
Na(2)-O7	2.578(2)	Na(1)-O8	2.471(2)	<b>&lt;S(1)-O&gt;</b>	<b>1.471</b>
Na(2)-O7	2.928(2)	Na(1)-O <sub>w</sub>	2.499(3)	<b>TAV*</b>	2.416
Na(2)-O8	2.447(3)	<b>&lt;Na(1)-O&gt;</b>	<b>2.379</b>		
<b>&lt;Na(2)-O&gt;</b>	<b>2.565</b>			S(2)-O1	1.488(2)
		O <sub>w</sub> -H(1)	0.84(4)	S(2)-O2	1.456(2)
N(1)-O9	1.245(4)	O <sub>w</sub> -H(2)	0.79(5)	S(2)-O5	1.465(2)
N(1)-O10	1.252(4)	O <sub>w</sub> -O11	2.855	S(2)-O8	1.474(2)
N(1)-O11	1.245(5)	H(1)-O <sub>w</sub> -H(2)	105.05°	<b>&lt;S(2)-O&gt;</b>	<b>1.471</b>
<b>&lt;N(1)-O&gt;</b>	<b>1.247</b>	O11...O <sub>w</sub> -H	152.6°	<b>TAV</b>	<b>2.066</b>

\*TAV: tetrahedral angel variance (Robinson et al. 1971)

**Table 5**

$I_{\text{rel}}$	$d_{\text{meas.}}(\text{\AA})$	$d_{\text{calc.}}(\text{\AA})$	$h$	$k$	$l$
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

\*Indexed with  $a = 24.88(1) \text{ \AA}$ ,  $b = 5.323(2) \text{ \AA}$ ,  $c = 17.23(1) \text{ \AA}$ ,  $\beta = 94.22(1)^\circ$ . All lines were used for unit cell refinement.



Figure 1

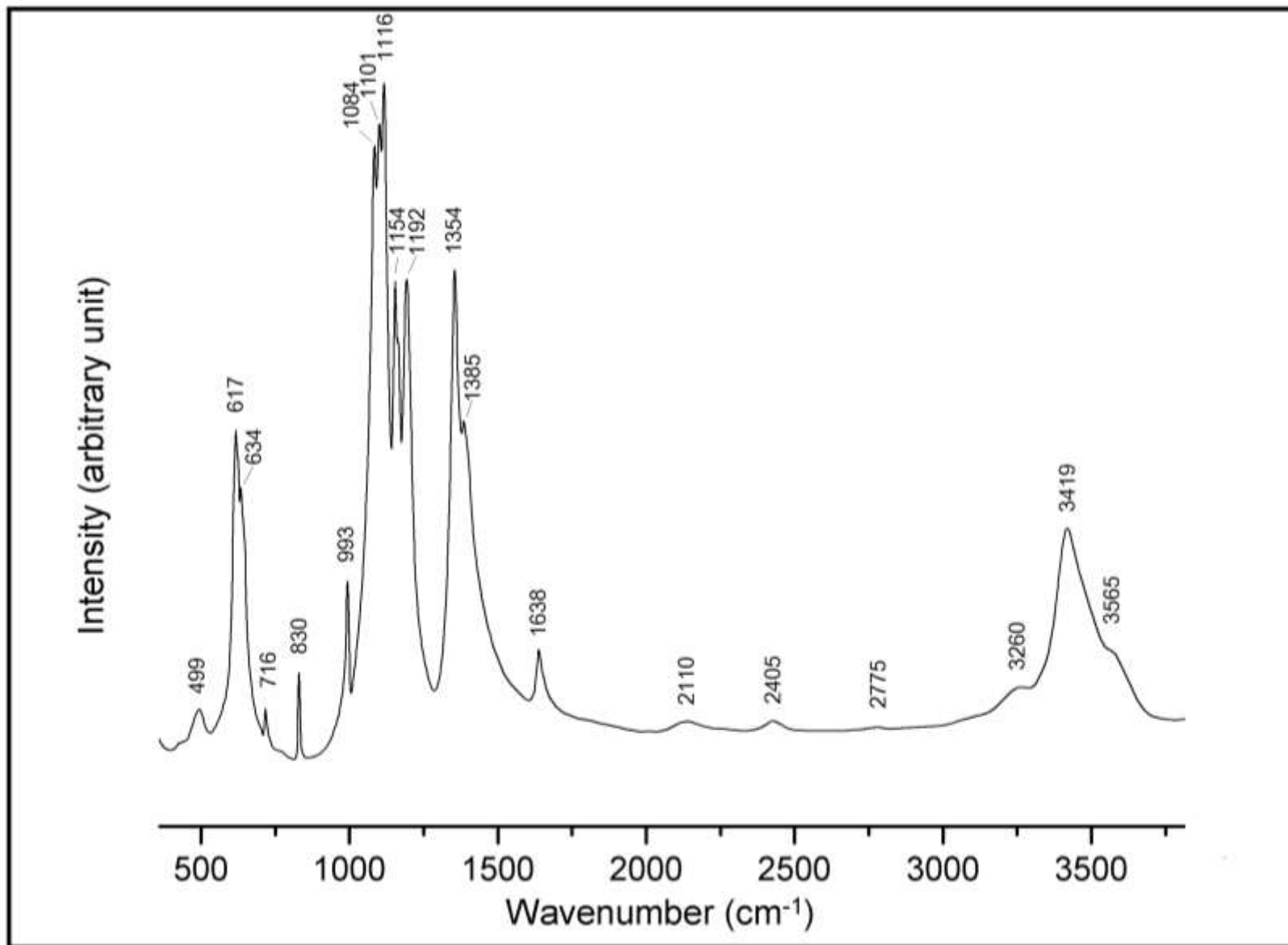


Figure 2

Figure 3

