IRIS AperTO

UNIVERSITÀ DEGLI STUDI DI TORINO

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

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

This is the author's manuscript

Original Citation:

Availability:

This version is available http://hdl.handle.net/2318/124924 since

Published version:

DOI:10.2138/am.2012.4109

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

12 October 2024

This is the author's final version of the contribution published as:

Nestola F; Cámara F; Chukanov NV; Atencio D; Coutinho JMV; Contreira Filho RR; Färber G. Witzkeite: a new rare nitrate-sulphate mineral from a guano deposit at Punta de Lobos, Chile. AMERICAN MINERALOGIST. 97 (10) pp: 1783-1787.
DOI: 10.2138/■am.2012.4109

When citing, please refer to the published version.

Link to this full text:
http://hdl.handle.net/2318/124924

This full text was downloaded from iris - AperTO: https://iris.unito.it/

iris - AperTO

University of Turin's Institutional Research Information System and Open Access Institutional Repository

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

Fabrizio Nestola[1]*, Fernando Cámara[2], Nikita V. Chukanov[3], Daniel Atencio[4], José M.V. Coutinho[4], Reynaldo R. Contreira Filho[5] and Gunnar Färber[6]

[1]Dipartimento di Geoscienze, Università di Padova, Via Gradenigo 6, I-35131, Padova, Italy
[2]Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, I-10125, Torino, Italy
[3]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia
[4]Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080, São Paulo, SP, Brazil
[5]Rua Murici 62, 13.098-315 Campinas, SP, Brazil
[6]Bornsche Strasse 9, 39326 Samswegen, Germany
*E-mail: fabrizio.nestola@unipd.it

Abstract

Witzkeite, ideally $Na_4K_4Ca(NO_3)_2(SO_4)_4 \cdot 2H_2O$, 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 μm 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) g cm^{-3}, calculated density is 2.403 g cm^{-3}. Witzkeite is biaxial (-) with refractive indexes α = 1.470(5), β = 1.495(5), γ = 1.510(5), measured 2V = 50-70°. The empirical composition is (electron microprobe, mean of 5 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 100.63; CO_2 was not detected. The chemical formula, calculated based on 24 O, is: $Na_{3.40}K_{3.95}Ca_{1.11}Fe_{0.05}(NO_3)_{1.93}(SO_4)_{4.10}(H_{4.10}O_{1.81})$. Witzkeite is monoclinic, space group *C*2/*c*, with unit-cell parameters: a = 24.902(2) Å, b = 5.3323(4) Å, c =17.246(1) Å, β = 94.281(7)°, V = 2283.6(3) $Å^3$ (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 cm^{-1}. The spectrum shows the typical bands of SO_4^{2-} ions (1192, 1154, 1116, 1101, 1084, 993, 634, 617 cm^{-1}) and of NO_3^- ions (1385, 1354, 830, 716, 2775 cm^{-1}). Moreover, a complex pattern of bands relatively to the H_2O is visible (bands at 3565, 3419, 3260, 2405, 2110, 1638, 499 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, $Na_3(SO_4)(NO_3)\cdot H_2O$, space group $P2_1/m$ (Sabelli 1967), ungemachite, $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)_2\cdot 6H_2O$, space group $R\bar{3}$ (Groat and Hawthorne 1986) and humberstonite, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2\cdot 6H_2O$, 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 × 1 m^2 in size located in a guano mining area (400 × 200 m across) on the southeast slope of Punta de Lobos, Tarapacá region (Chile), approximately 90 km south of Iquique (21°12′S 70°05′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 μm 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) g cm^{-3}, which is in excellent agreement with the calculated density, 2.403 g cm^{-3}, using the empirical formula.

Witzkeite is biaxial (-) with refractive indices α = 1.470(5), β = 1.495(5), γ = 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 (s*uperior*).

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 μm beam diameter, 70 seconds live count time). H_2O, CO_2 and N_2O_5 were determined by gas chromatography (CHN analysis of gaseous products obtained by heating of the mineral at 1400°C). No CO_2 was detected (detection limit ≅ 0.05 wt.%).

Analytical data are given in Table 1. The empirical formula (based on 24 anions) is $Na_{3.40}K_{3.95}Ca_{1.11}Fe_{0.05}(NO_3)_{1.93}(SO_4)_{4.10}(H_{4.10}O_{1.81})$. The idealized formula is

$Na_4K_4Ca(NO_3)_2(SO_4)_4 \cdot 2H_2O$, which requires Na_2O = 14.89; K_2O = 22.62; CaO = 6.73; N_2O_5 = 12.97; SO_3 = 38.46; H_2O = 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) Å, b = 5.3323(4) Å, c =17.246(1) Å, β = 94.281(7)(°), V = 2283.6(3) Å^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 *C*2/*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 incidence (being thus a plausible candidate for H_2O 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 O8 atom and 2.21 Å of the O1 atom. This maximum is close to the Ca site (1.83 Å) but farther form 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 SO_4 groups is protonated being $[HSO_4]$ 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 adscribed 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 Cu*K*α 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, β = 94.22(1)°, V = 2275.7(5) Å^3.

IR spectroscopy

Witzkeite was mixed with anhydrous KBr, pelletized, and analysed using ALPHA FT-IR spectrometer (Bruker Optics) with the resolution of 4 cm^{-1}. 16 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 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_4 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_4 groups. The cation site is occupied by Na (*Na* site), and coordinates with 5 oxygen atoms and one H_2O group (<Na1 – O> = 2.379 Å; Table 4). The SO_4 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 $Na_4Ca(SO_4)_4 \cdot 2H_2O$, with an overall charge of -2.

The $Na_4Ca(SO_4)_4 \cdot 2H_2O$ slab alternates along [100] with s potassium nitrate slabs $[K_4(NO_3)_2]^{2+}$: this slab is built by a planar (NO_3) group with the *N* site in 3-fold coordination (<N-O> = 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 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 H_2O group. One oxygen coordinating the *N* site is forming hydrogen bond from the Ow site (O11…Ow = 2.855 Å). 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 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, <Fe-O> = 2.181 Å; Table 4); observed occupancies 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 cm^{-1}; s – strong band, w – weak band, sh – shoulder) are 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 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 relatively high intensity of the symmetric S-O stretching vibrations at 993 cm^{-1} show relatively strong distortion of both SO_4 tetrahedra and NO_3^- groups. Taking into account weak IR bands in the range 2100-2500 cm^{-1}, one cannot exclude the presence of trace amounts of HSO_4^{2-} ions in witzkeite. In fact, a maximum was observed at 1 Å 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 SO_4 and NO_3 groups . However, in

darapskite there is only one independent SO_4 group and one NO_3 group versus 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 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, $K_6(Na,K)_4Na_6Mg_{10}(SO_4)_{12}(IO_3)_{12}\cdot 12(H_2O)$, and carlosruizite $K_6(Na,K)_4Na_6Mg_{10}(SeO_4)_{12}(IO_3)_{12}\cdot 12(H_2O)$ (Konnert 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 (Ericksen et al. 1989), which shows a similar but anhydrous stoichiometry, $Na_9(IO_3)(SO_4)_4$ (considering one planar IO_3 group of instead of two NO_3 groups). However, there are no available structural data for hectorfloresite to allow us to verify its degree of crystallographic similarity with witzkeite.

Acknowledgements

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.

References

Burns, P.C. and Hawthorne, F.C. (1994) The crystal structure of humberstonite, a mixed sulfate-nitrate mineral. Canadian Mineralogist, 32, 381-385.

Farrugia, L.J. (1999) WinGX suite for small-molecule single-crystal crystallography. Journal of Applied Crystallography, 32, 837-838.

Ericksen, G.E., Evans, H.T., Mrose, M.E., McGee, J.J., Marinenko, J.W. and Konnert, J.A. (1989) Mineralogical studies of the nitrate deposits of Chile: VI. Hectorfloresite, $Na_9(IO_3)(SO_4)_4$, a new saline mineral. American Mineralogist, 74, 1207-1214.

Groat, L.A. and Hawthorne, F.C. (1986) Structure of ungemachite, $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)2{\cdot}6H_2O$, a mixed sulfate-nitrate mineral. American Mineralogist, 71, 826-829.

Konnert, J.A., Evans, H.T., Mcgee, J.J. and Ericksen, G.E. (1994) Mineralogical studies of the nitrate deposits of Chile: VII. Two new saline minerals with the composition $K_6(Na,K)_4Na_6Mg_{10}(XO_4)_{12}(IO_3)_{12}{\cdot}12H_2O$: fuenzalidaite (X = S) and carlosruizite (X = Se). American Mineralogist, 79, 1003-1008.

Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. Science 172, 567-570.

Sabelli, C. (1967) La struttura della darapskite. Atti della Academia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti, 42, 874-887

Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112-122.

Stoe and Cie (1999) Crystal Optimization for Numerical Absorption Correction. Stoe and Cie GmbH, Darmstadt, Germany.

Stoe and Cie (2001) Data Reduction Program. Stoe and Cie GmbH, Darmstadt, Germany.

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_{eq} (Å^2) values (with exception of oxygens, Fe, O2 and O10 sites for which U_{iso} is reported) for witzkeite.

Table 4. Selected bond lengths (Å) and angles (^{o}) 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 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_2O	12.83	12.64-12.96	Albite
K_2O	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_2O_5	12.7		
H_2O	4.5		
Total	100.64		

Table 2

Cell determination	
Crystal system	Monoclinic
Unit cell parameters a, b, c, β	24.902(2) Å 5.3323(4) Å 17.246(1) Å 94.281(7) (°)
Unit cell volume	2283.6(3) $Å^3$
Space group	*C2/c*
Z	4
Crystal size (mm)	0.080x0.060x0.030
Software	Crysalis (Oxford Diffraction)
Data collection	
Diffractometer	STOE STADI IV (CCD detector, Oxford diffraction)
Temperature (K)	298(2)
Radiation, wavelength (Å)	$Mo_{K\alpha}$, 0.71073
θ range for data collection (º)	2.98 – 27.87
h, k, l ranges	-31 +31, -6 +6, -22 +22
Omega scan width (º), exposure time (s)	1, 60
Total reflections collected	22565
Unique reflections (R_{int} %)	2484 (6.78)
Unique reflections $F > 4\sigma(F)$	1847
Absorption correction method	XRED, XSHAPE (Stoe and Cie 2000; 2001)
Structure refinement	
Structure solution and Refinement software	SHELXS-SHELXL-97 (Sheldrick 1997, Farrugia, 1999)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2484/0/190
R_1 [$F > 4\sigma(F)$]	0.043
R_1 all	0.072
wR^2	0.101
Goodness-of-fit on F^2	1.09
Highest peak, deepest hole (e $Å^{-3}$)	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)

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

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

$\text{GooF} = \{\sum [w (F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

Table 3

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)
K(1)	0.15202(3)	0.25031(14)	0.10623(4)	0.0247(3)
K(2)	0.32417(3)	0.24292(14)	0.23240(5)	0.0275(3)
S(1)	0.56605(3)	-0.75113(15)	0.07266(4)	0.0153(2)
S(2)	0.41680(3)	-0.27020(15)	0.22437(5)	0.0157(2)
Na(1)	0.41977(5)	0.24195(22)	0.07588(7)	0.0214(3)
Na(2)	0.50009(6)	-0.26669(23)	0.08618(7)	0.0241(3)
N(1)	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)

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)
<Ca–O>	**2.491**	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)
<Fe-O>	**2.181**	K(1)-Ow	2.795(3)	K(2)-O_W	3.138(3)
		<K(1)–O>	**2.873**	**<K(2)–O>**	**2.906**
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)	**<S(1)–O>**	**1.471**
Na(2)-O7	2.928(2)	Na(1)-O_W	2.499(3)	**TAV***	2.416
Na(2)-O8	2.447(3)	**<Na(1)–O>**	**2.379**		
<Na(2)–O>	**2.565**			S(2)-O1	1.488(2)
		O_W– H(1)	0.84(4)	S(2)-O2	1.456(2)
N(1)-O9	1.245(4)	O_W– H(2)	0.79(5)	S(2)-O5	1.465(2)
N(1)-O10	1.252(4)	O_W-O11	2.855	S(2)-O8	1.474(2)
N(1)-O11	1.245(5)	H(1)-O_W-H(2)	105.05°	**<S(2)–O>**	**1.471**
<N(1)-O>	**1.247**	O11…Ow-H	152.6°	**TAV**	**2.066**

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

Table 5

I_{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

*Indexed with a = 24.88(1) Å, b = 5.323(2) Å, c = 17.23(1) Å, β = 94.22(1)°. All lines were used for unit cell refinement.

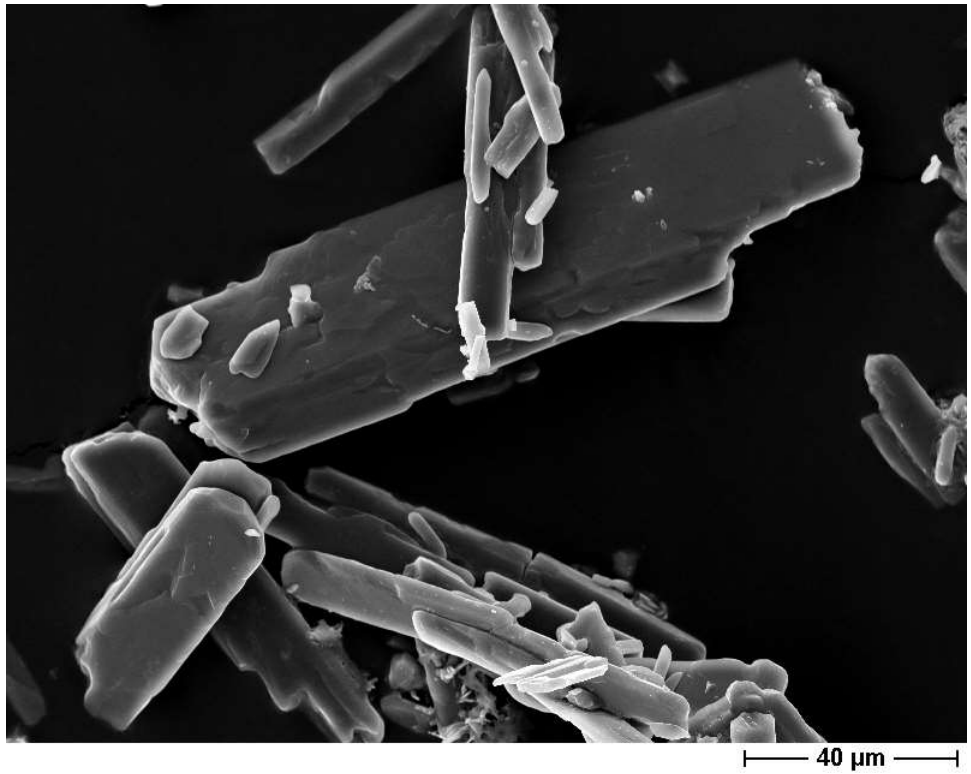

Figure 1

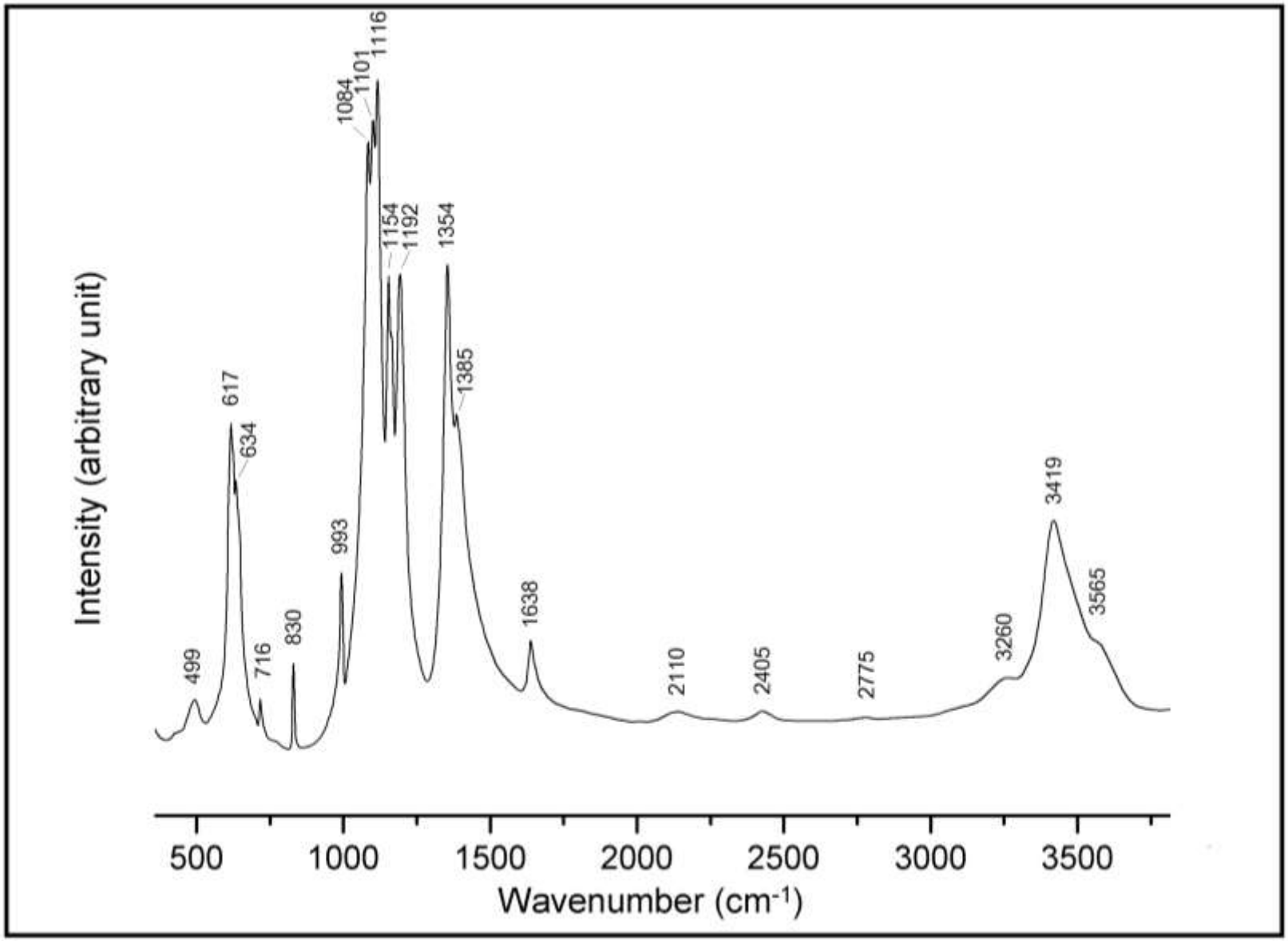
Intensity (arbitrary unit)
Wavenumber (cm-1)
500
1000
1500
2000
2500
3000
3500
499
617
634
716
830
993
1084
1101
1116
1154
1192
1354
1385
1638
2110
2405
2775
3260
3419
3565

Figure 2
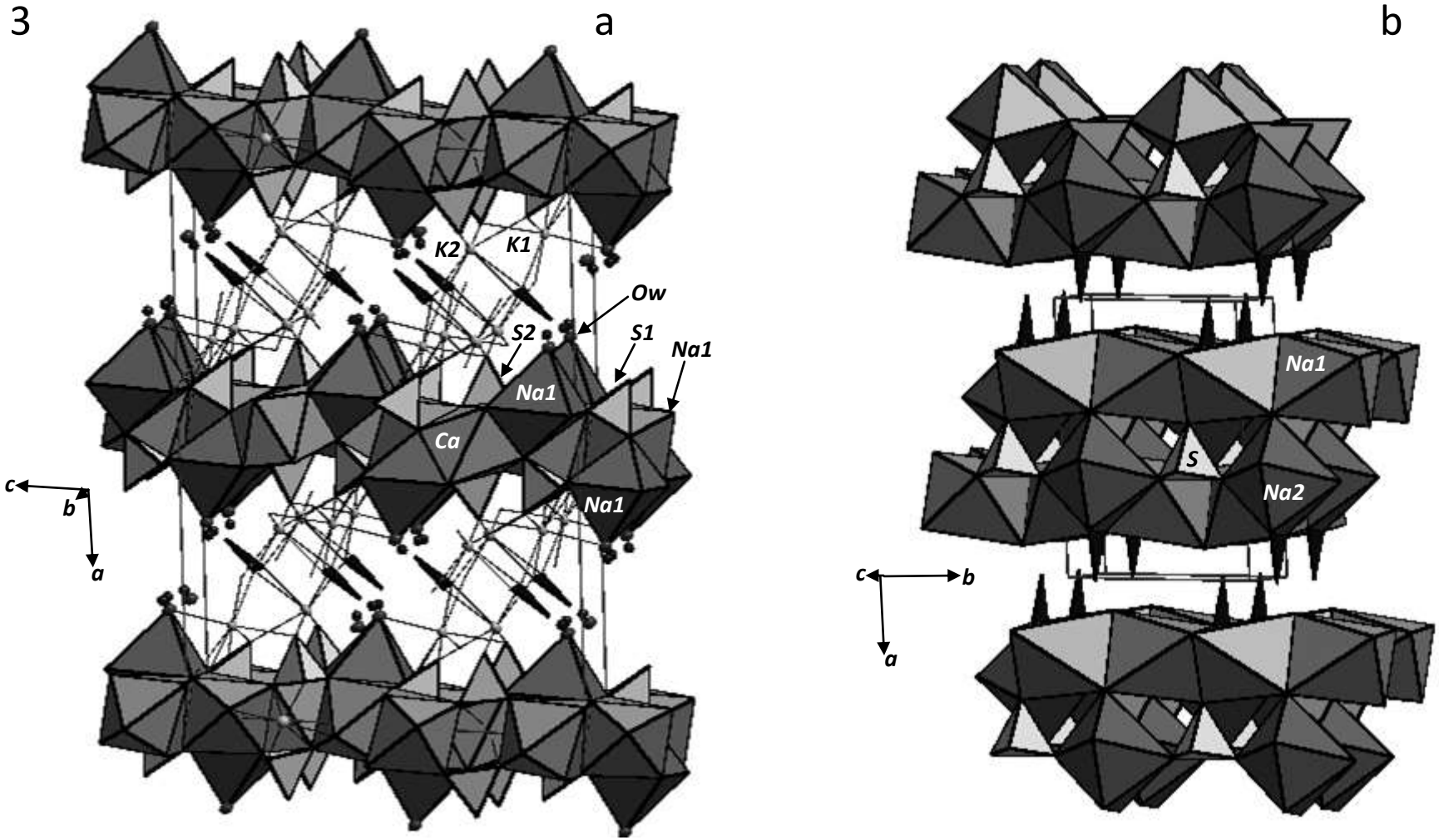
Figure 3