The Canadian Mineralogist
Vol. 51, pp. 559-568 (2013)
DOI: 10.3749/canmin.51.4.559

VENDIDAITE, $Al_2(SO_4)(OH)_3Cl{\cdot}6H_2O$, A NEW MINERAL FROM LA VENDIDA COPPER MINE, ANTOFAGASTA REGION, CHILE

NIKITA V. CHUKANOV§

Institute of Problems of Chemical Physics, 142432 Chernogolovka, Moscow Oblast, Russia

SERGEY V. KRIVOVICHEV AND ANASTASIYA P. CHERNYATIEVA

Faculty of Geology, St Petersburg State University, Universitetskaya Nab. 7/9, St Petersburg, 199034 Russia

GERHARD MÖHN

Dr J. Wittemannstrasse 5, 65527 Niedernhausen, Germany

IGOR V. PEKOV

Faculty of Geology, Moscow State University, Leninskie Gory, 119991 Moscow, Russia

DMITRIY I. BELAKOVSKIY

Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskiy Prospekt 18-2, Moscow, 119071 Russia

KONSTANTIN V. VAN

Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

JOACHIM A. LORENZ

Graslitzer Strasse 5, D-63791 Karlstein, Germany

ABSTRACT

The new mineral vendidaite was discovered in the abandoned La Vendida mine, near Sierra Gorda, Antofagasta Region, Atacama desert, Chile. Associated minerals are aubertite, magnesioaubertite, belloite, eriochalcite, alunite, kaolinite, and halloysite. Vendidaite forms colorless platy crystals up to 0.01 × 0.3 × 0.3 mm in size; these occur in clusters up to 0.5 mm across. Vendidaite is brittle, with estimated Mohs' hardness of 2–2½ and perfect cleavage on (010). D_{meas} = 1.97(1) g/cm^3, D_{calc} = 1.974 g/cm^3. The new mineral is optically biaxial (+), α = 1.522(2), β = 1.524(2), γ = 1.527(2), $2V$ (meas.) = 75(15)°, $2V$ (calc.) = 79°. Infra-red spectrum is given. The chemical composition (electron microprobe, H_2O by gas chromatography) is (in wt.%): Al_2O_3 28.51, Fe_2O_3 1.39, SO_3 22.38, Cl 9.87, H_2O 38.8, O = Cl –2.23, total 98.72. The empirical formula is: $Al_{1.96}Fe^{3+}_{0.06}(SO_4)_{0.98}Cl_{0.98}(OH)_{3.12}{\cdot}5.98H_2O$. The crystal structure was solved using single-crystal X-ray diffraction data ($R1$ = 0.044). Vendidaite is monoclinic, space group $C2/c$, a 11.9246(16), b 16.134(2), c 7.4573(9) Å, β 125.815(2)°, V 1163.4(3) Å^3, and Z = 4. The structure is based upon $[Al_2(OH)_3(H_2O)_6]^{3+}$ chains of edge- and corner-sharing $[Al(OH,H_2O)]$ octahedra running parallel to the a axis. The chains are linked by hydrogen bonds to (SO_4) tetrahedra and Cl^- anions to form pseudolayers parallel to the (010) plane. The strongest lines of the powder X-ray diffraction pattern [d, Å (I, %) (hkl)] are: 6.78 (59) (11$\bar{1}$), 4.849 (94) (021), 4.366 (80) (13$\bar{1}$), 4.030 (75) (040, 111), 3.855 (100) (31$\bar{1}$), 3.285 (59) (131), 2.435 (52) (26$\bar{1}$). Type material is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4335/1.

Keywords: vendidaite, La Vendida mine, Chile, new mineral, aluminum chloride hydroxide sulfate, crystal structure.

§ *Corresponding author:* chukanov@icp.ac.ru

Introduction

The abandoned open pit of the La Vendida copper mine (Mina La Vendida, until 1990 known as Rio Tinto mine) is situated about 3 km WNW of the Sierra Gorda village, Antofagasta Region, Atacama desert, Chile. The copper sulfide mineralization is associated with dacitic-andesitic volcanic breccias. The supergene mineralization is represented mainly by sulfates, chlorides, and clay minerals. La Vendida mine is the type locality for the copper hydroxychloride minerals belloite Cu(OH)Cl (Schlüter *et al*. 2000) and anatacamite $Cu_2(OH)_3Cl$ (Malcherek & Schlüter 2010).

The present paper describes a new mineral species from the La Vendida mine, vendidaite. The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2012-089). Vendidaite is a representative of a new structure type. Among 12 natural hydrous aluminum sulfates without additional cations, vendidaite is the only mineral containing Cl as a species-defining component.

The type material is deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4335/1.

General appearance and physical properties

Specimens with vendidaite were collected in the La Vendida open pit by one of the authors (GM) in January 2011. The holotype material originates from a 2 × 1 × 1 m^3 block at the edge of the quarry. Subsequently vendidaite was found on the dumps of the La Vendida mine. Associated minerals are intermediate members of the aubertite-magnesioaubertite solid-solution series, belloite, eriochalcite, alunite, kaolinite, and halloysite. Belloite (formed as a product of alteration of eriochalcite) and vendidaite are the latest minerals in this association.

Sulfate minerals (mainly alunite and jarosite) are abundant in the quarry. Associations of copper sulfates and chlorides (like that bearing vendidaite) are located in small areas from 1 to 5 m across where secondary minerals occur in thin fissures. The host rocks (dacitic-andesitic volcanic breccias) are strongly altered.

Vendidaite forms colorless transparent (with vitreous luster) platy crystals up to 0.01 × 0.3 × 0.3 mm in size, flattened on (010), and forming clusters up to 0.5 mm across (Fig. 1a,b), as well as white, fine-grained aggregates. The major form of the vendidaite crystals is {010}; the subordinate forms are {100}, {001}, and {101}. Vendidaite is brittle, with Mohs' hardness of 2–2½ (estimated using cleavage planes of gypsum and calcite) and perfect cleavage on (010). The density measured by flotation in heavy liquids is equal to 1.97(1) g/cm^3, which agrees well with the value of 1.974 g/cm^3 calculated from the empirical formula.

Vendidaite is optically biaxial (+), α = 1.522(2), β = 1.524(2), γ = 1.527(2), $2V_{calc}$ = 79º. Due to the lack of material, the refractive indexes and other optical properties were measured from one mount in immersion liquids with no possibility to rotate the grains. Thus $2V_{meas}$ could only be very roughly estimated as

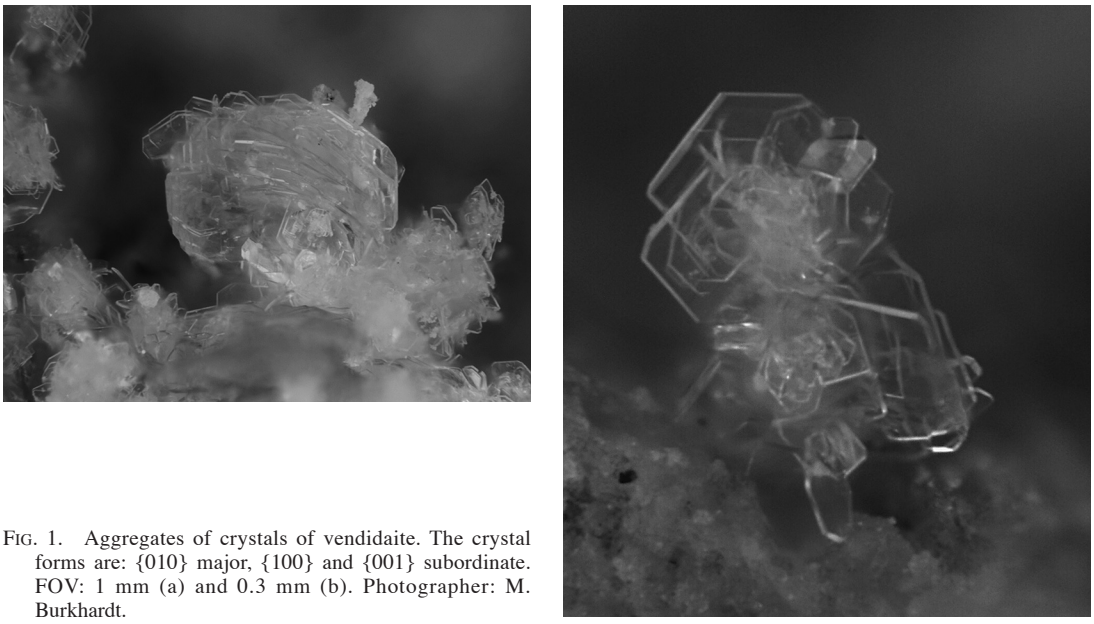


FIG. 1. Aggregates of crystals of vendidaite. The crystal forms are: {010} major, {100} and {001} subordinate. FOV: 1 mm (a) and 0.3 mm (b). Photographer: M. Burkhardt.

large (between 60° and 90°) by the conoscopic interference pattern on the section perpendicular to the 2*V* bisector. Grains with orientation more suitable for the 2*V* measurement were not found because of the perfect cleavage. No dispersion of optical axes was observed. The orientation is $Z = b$; X and Y lie in the *ac* plane.

In order to obtain an infrared (IR) absorption spectrum, vendidaite powder was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{-1} and using 16 scans. IR spectrum of an analogous pellet of pure KBr was used as a reference. Absorption bands in the IR spectrum of vendidaite (Fig. 2) and their assignments are (cm^{-1}; s – strong band, w – weak band, sh – shoulder): 3640sh, 3585, 3490sh, 3421, 3293s, 3190sh, 3164s, 2989 (O–H stretching vibrations of OH^- anions and H_2O molecules), 2521w, 2445w, 2299w (combination modes and/or O–H stretching vibrations of acid OH groups), 1685sh, 1646 (bending vibrations of H_2O molecules), 1168, 1107s, 1040 (asymmetric stretching vibrations of SO_4^{2-} anions), 993w (symmetric S–O stretching vibrations of SO_4^{2-} anions), 882w, 843, 760sh, 700 (Al···O–H bending vibrations), 639, 620, 609 (O–S–O bending vibrations of SO_4^{2-} anions), 547, 497 (Al–O stretching vibrations, possibly combined with librational vibrations of H_2O molecules), 460, 379 (mixed lattice vibrations). A relatively low intensity of the symmetric S–O stretching vibrations of the SO_4^{2-} anions [at 993 cm^{-1}, non-degenerate $\nu_1(A_1)$ mode] and a weak splitting of the asymmetric stretching vibrations of SO_4^{2-} anions [in the range 1040–1170 cm^{-1}, degenerate $\nu_3(F_2)$ mode] reflect a relatively weak distortion of the SO_4 tetrahedra.

Bands of B-, C-, and N-bearing groups are absent in the IR spectrum of vendidaite. Weak IR bands at 2299, 2445, and 2521 cm^{-1} indicate the presence of trace amounts of HSO_4^- ions that could have formed as a result of reversible proton transfer from a water molecule in accordance with the following dynamic equilibrium: $H_2O + SO_4^{2-} \leftrightarrow OH^- + HSO_4^-$. This phenomenon is very typical for nominally neutral sulfates, phosphates and arsenates (see, *e.g*., Chukanov *et al*. 2010, 2012; Nestola *et al*. 2012).

The IR spectrum of vendidaite is unique and can be used as a reliable diagnostic tool.

Chemical data

Five electron-microprobe analyses were carried out using a VEGA TS 5130MM SEM equipped with an EDX analyzer [INCA Si(Li) detector], at an operating voltage of 20 kV and a beam current of 0.6 nA. The program INCA Energy 200 was used for the analytical data calculation. Attempts to use the WDS mode with higher beam currents were unsuccessful because of the instability of the mineral containing significant amounts of volatile components. H_2O was determined by gas chromatography of products of ignition at 1200 °C with a Vario MICRO cube analyzer (Elementar GmBH, Germany). CO_2, N_2O_5, and B_2O_3 were not analyzed because of the absence of absorption bands corresponding to vibrations of C–O, N–O, and B–O

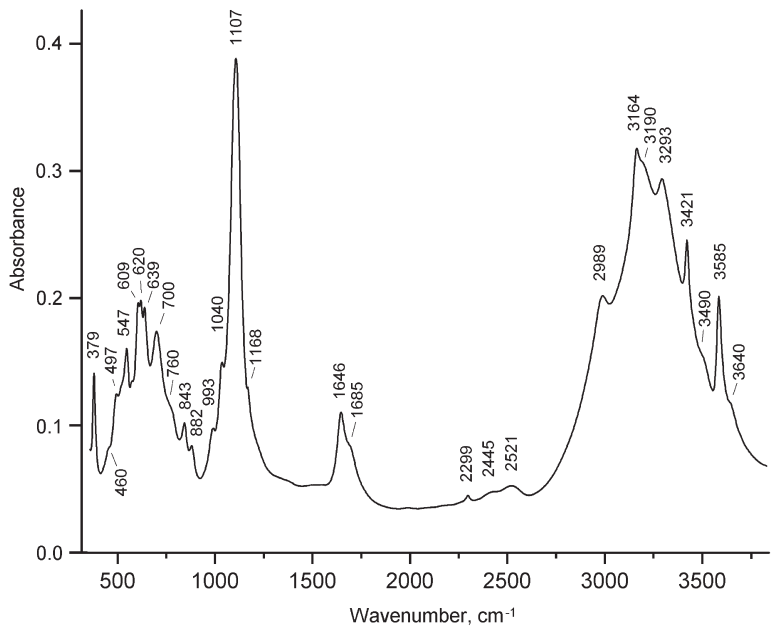


Fig. 2. The IR spectrum of vendidaite.

bonds in the IR spectrum. The analytical data are given in Table 1. Contents of F, Na, Mg, Si, P, K, Ca, Mn, Cu, Zn, As, Br, Sr, Pb are below detection limits.

The empirical formula (based on 14 atoms O + Cl *pfu* and OH/H_2O ratio calculated for charge balance) is $Al_{1.96}Fe^{3+}_{0.06}(SO_4)_{0.98}Cl_{0.98}(OH)_{3.12}\cdot 5.98H_2O$. The simplified formula is $Al_2(SO_4)(OH)_3Cl\cdot 6H_2O$, which requires Al_2O_3 29.59, SO_3 23.23, Cl 10.29, H_2O 39.21, O = Cl –2.32, total 100.00 wt.%.

The Gladstone-Dale compatibility index is: $1 - (K_p/K_c) = 0.035$ ("excellent").

Vendidaite is insoluble in water and dissolves slowly in warm 20% hydrochloric acid. The aqueous extract from vendidaite-bearing aggregates has a pH value of about 4, which indicates that this mineral is stable in a weak-acid environment.

X-ray diffraction data and crystal structure

Powder X-ray diffraction data (Table 2) were measured with a Stoe IPDS II image plate diffractometer using the Gandolfi method (Mo$K\alpha$ radiation; the distance between sample and detector was 200 mm). The obtained diffraction pattern was indexed in the monoclinic (space group *C*2/*c*) unit cell, in agreement with the single-crystal diffraction data. Unit-cell parameters refined from the powder data are: *a* 11.91(4), *b* 16.13(2), *c* 7.46(3) Å, β 125.8(2)°, *V* 1164(7) Å^3.

A crystal of vendidaite was mounted on a Bruker Kappa APEX DUO diffractometer with a crystal-to-detector distance of 4 cm. A hemisphere of three-dimensional data was collected using Mo$K\alpha$ X-radiation and frame widths of 0.5° in ω, with 60 s used to acquire each frame. The unit-cell dimensions were refined on the basis of 9817 reflections (Table 3). The systematic absences of reflections are consistent with the space-group *C*2/*c*. The data were reduced using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied, and the data were corrected for Lorentz, polarization, and background effects.

The Bruker SHELXTL system of programs was used for the refinement of the crystal structure on the basis of F^2. The structure was solved by direct methods. Refinement of all atom-position parameters, allowing for the anisotropic displacement of all atoms except H, and the inclusion of a refinable weighting-scheme of the structure factors, resulted in a final agreement index (*R*1) of 0.044, calculated for the 2034 unique observed reflections ($|Fo| > 4\sigma F$), and a goodness-of-fit (*S*) of 1.024. The final atom parameters are listed in Table 4, and selected interatomic distances and the geometrical parameters of the hydrogen bonding scheme are given in Table 5. Observed and calculated structure-factors can be acquired from the Depository of Unpublished Data on the MAC website [document Vendidaite CM51_559].

The structure of vendidaite contains one symmetrically independent Al site octahedrally coordinated by three OH groups and three H_2O molecules (Fig. 3a). Two adjacent $[Al(OH)_3(H_2O)_3]$ octahedra share the $O_h1\cdots O_h1$ edge to form a $[Al_2(OH)_4(H_2O)_6]$ dimer with the O_h1–Al–O_h1 bond angle equal to 76.96(6)°, *i.e.*, considerably more acute than the ideal angle of 90°. The dimers are further linked by sharing the O_h4 atoms to form $[Al_2(OH)_3(H_2O)_6]^{3+}$ chains running parallel to the *a* axis.

The crystal structure contains $(SO_4)^{2-}$ groups and Cl^- anions held in the structure by hydrogen bonds alone (Fig. 3b, c). The average <S–O> bond length in the sulfate group is 1.478 Å, which is in a good agreement with the grand average distance of 1.473 Å given for sulfate minerals by Hawthorne *et al.* (2000). The sulfate group is located on the twofold symmetry axis and consists of two O5 and two O7 atoms. The O5 atom accepts three H bonds from the OH(1), H_2O(3), and H_2O(6) groups, whereas the O7 atom accepts two bonds from two symmetrically equivalent H_2O(2) molecules (Fig. 3b). The Cl atom is also on the two-fold axis and accepts six H bonds from two H_2O(2), two H_2O(3), and two H_2O(6) groups (Fig. 3c). In total, each H_2O molecule is linked to the Al atom and donates two H bonds to O and/or Cl atoms. Each OH group is linked to two Al^{3+} cations and donates one H bond to either an O or Cl atom.

TABLE 1. CHEMICAL COMPOSITION OF VENDIDAITE BASED ON FIVE ELECTRON-MICROPROBE ANALYSES

Constituent	Mean content, wt.%	Range	Standard deviation	Probe Standard
Al_2O_3	28.51	27.71–29.24	0.4	albite
Fe_2O_3	1.39	1.21–1.68	0.15	Fe
SO_3	22.38	21.86–22.73	0.3	$BaSO_4$
Cl	9.87	9.67–10.17	0.15	NaCl
H_2O	38.8(2)*			
O = Cl	–2.23			
Total	98.72			

Note: *Determined by gas chromatography

TABLE 2. POWDER X-RAY DIFFRACTION DATA FOR VENDIDAITE

I_{obs}	d_{obs}, Å	I_{calc}*	d_{calc}, Å**	*h k l*
13	8.12	10	8.067	020
59	6.78	53	6.762	$11\bar{1}$
94	4.849	74	4.839	021
80	4.366	68	4.360	$13\bar{1}$
75	4.030	39, 29	4.034, 4.020	040, 111
100	3.855	100	3.852	$31\bar{1}$
43	3.745	41	3.724	$20\bar{2}$
3	3.480	2	3.453	$11\bar{2}$
59	3.285	63	3.286	131
12	3.187	12	3.192	$33\bar{1}$
34	2.973	12	2.961	$15\bar{1}$
22	2.871	17	2.882	$40\bar{2}$
32	2.831	28	2.831	022
45	2.764	45	2.765	330
5	2.544	5	2.547	$15\bar{1}$
52	2.435	44	2.437	$26\bar{1}$
23	2.333	11, 10	2.330, 2.316	$22\bar{3}$, 420
32	2.254	28	2.254	$33\,\bar{3}$
4	2.182	2, 4	2.180, 2.176	$26\bar{2}$, $53\,\bar{2}$
14	2.072	17	2.074	440
13	2.007	1, 8, 4	2.010, 2.009, 2.006	222, 062, 261
17	1.965	11, 8	1.968, 1.966	$35\bar{3}$, $46\bar{2}$
12	1.908	4, 4	1.911, 1.904	$37\bar{2}$, $28\bar{1}$
8	1.854	6, 8	1.862, 1.848	$40\bar{4}$, 15-3
7	1.800	1, 9, 2	1.803, 1.803, 1.798	043, $62\bar{1}$, 460
8	1.764	5, 4, 1	1.767, 1.766, 1.763	$20\bar{4}$, 113, 190
11	1.746	10, 4	1.746, 1.742	$33\bar{4}$, 312
15	1.680	2, 14, 5	1.682, 1.681, 1.676	$71\bar{3}$, $64\bar{1}$, 281
7	1.653	2, 7, 1	1.657, 1.656, 1.652	$48\bar{1}$, $57\bar{2}$, $48\bar{2}$
6	1.602	2, 6	1.602, 1.599	$35\bar{4}$, $19\bar{2}$
2	1.562	4, 1	1.563, 1.559	$66\bar{3}$, 0.10.1
4	1.495	2, 2, 1	1.498, 1.498, 1.492	$73\bar{1}$, 75-3, $75\bar{2}$
6	1.444	8	1.443	66-4
7	1.422	8, 2	1.422, 1.422	2.10.1, 391
2	1.311	1, 2	1.315, 1.310	590, 571
2	1.285	2	1.284	$66\bar{5}$
4	1.253	5, 4	1.253, 1.250	392, 204
2	1.186	1, 1	1.186, 1.186	$64\bar{6}$, 373
1	1.103	2, 2	1.103, 1.103	065, 860

*For the calculated X-ray powder pattern only reflections with $I_{calc} \geq 1$ are given.
**Calculated for unit cell parameters obtained from single-crystal data.

Together with the $[Al_2(OH)_3(H_2O)_6]^{3+}$ chains, the Cl^- anions and $(SO_4)^{2-}$ groups form pseudo-layers parallel to (010) (Fig. 4). The pseudo-layers are characterized by the high density of hydrogen bonds: eight out of ten H bonds formed by each SO_4 tetrahedron and four out of six bonds formed by each Cl atom belong to the layer. The presence of pseudo-layers in the structure of vendidaite may explain the platy morphology of its crystals and their perfect cleavage.

Discussion

No minerals related to vendidaite in terms of its crystal structure or powder X-ray diffraction pattern, IR spectrum, and optical data are known. Vendidaite is the first natural chloride sulfate with Al as the only species-defining metal cation, although synthetic polyaluminium chloride hydroxide sulfate materials (PACS) are well-known for their use as a coagulant, and sometimes as a precipitant for treatment of water intended for human consumption (European Standard EN 883, 2005). Unfortunately, information about the details of synthesis and crystal structures of aluminium chloride sulfates is patented.

Hypothetically, the source of aluminum for vendidaite formation and associated clay minerals was feldspar alteration. Indeed, grains of feldspar in the host rocks are strongly altered, which could be partly the result of

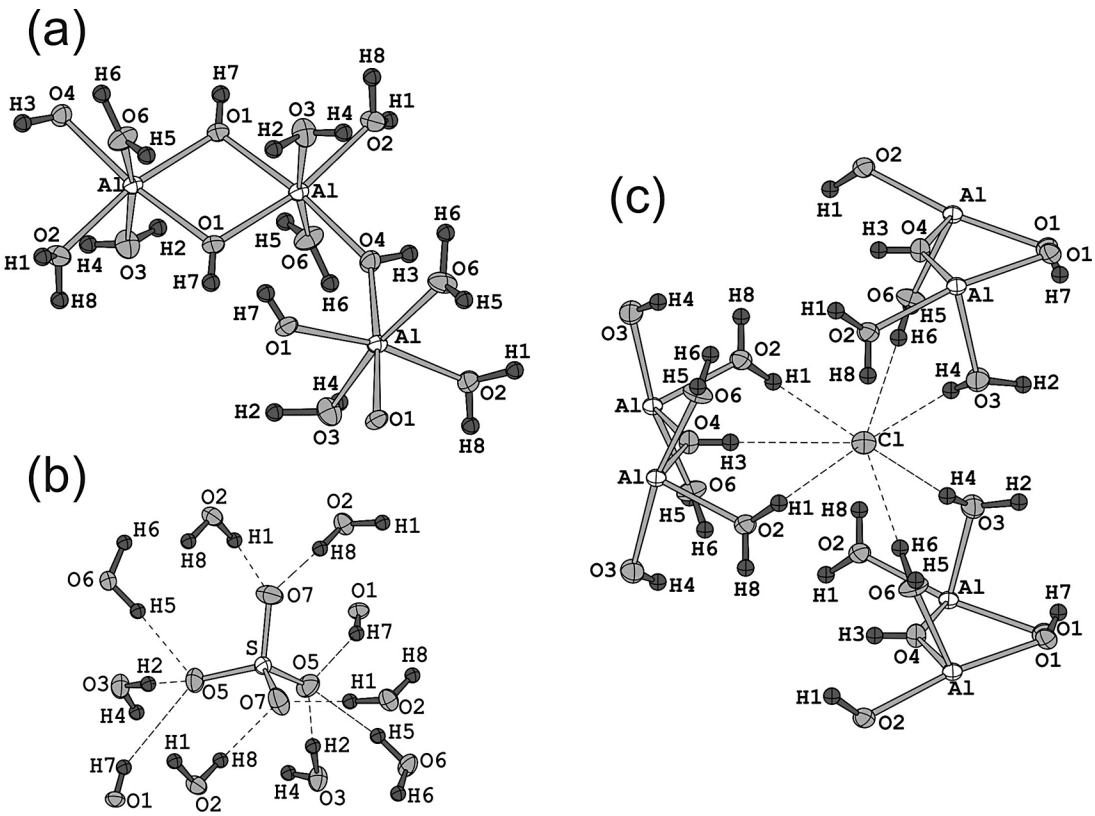


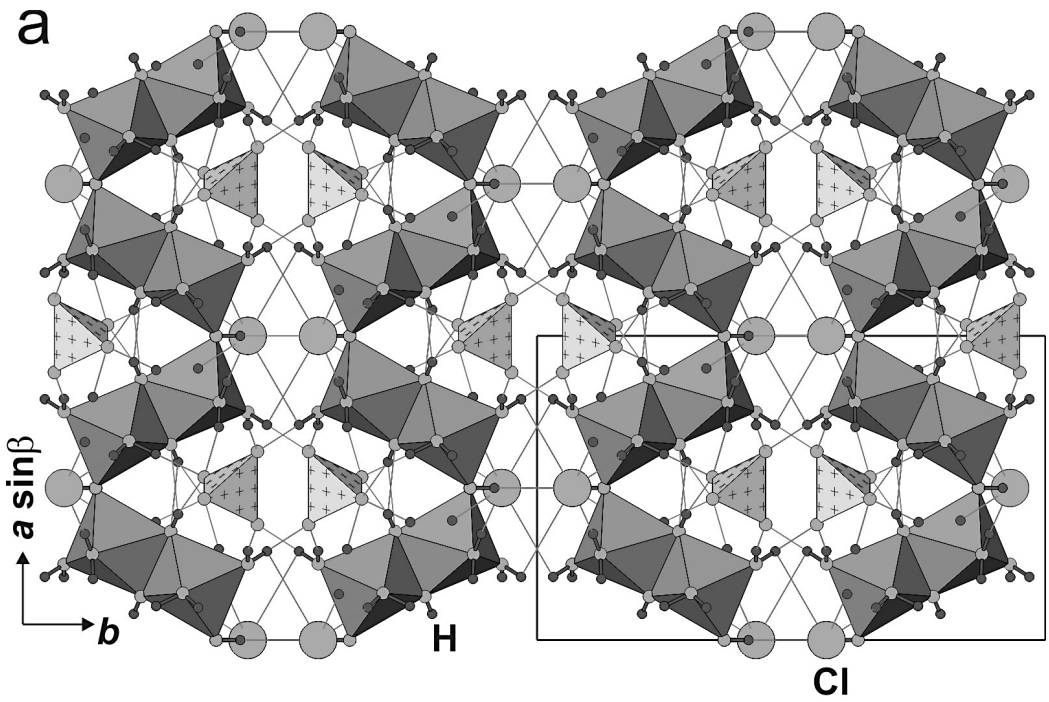
FIG. 3. Constituents of the crystal structure of vendidaite: linkage mode of the $[Al(OH)_3(H_2O)_3]$ octahedra (a), and coordination environment of the SO_4 groups (b) and Cl^- anions (c). Ellipsoids are drawn at 50% probability level; H···**A** bonds are shown as dashed lines (**A** = acceptor; cf. Table 5).

its exposure to sulfuric acid formed during the oxidation of primary sulfides. The source of the chlorine is unclear. Most probably, formation of secondary Cl-bearing minerals in oxidation zones of ore deposits in the Atacama Desert of northern Chile is an ongoing process that has occurred intermittently since the onset of hyperaridity and is related to saline ground waters (see Reich *et al*. 2008).

Strongly altered magmatic rocks containing aggregates of secondary sulfates (kröhnkite, tamarugite, jarosite, aubertite, botryogen, *etc*.), as well as clay minerals, are exposed in different parts of the quarry, but the vendidaite-bearing mineral association has only been found in a small area. One can suppose that the formation of vendidaite is possible in narrow ranges of pH and/or activities of species-forming cations and anions. Another possible cause of the uniqueness of vendidaite is the strongly pronounced tendency of the system $Al_2(SO_4)_3$–$AlCl_3$–H_2O to form glasses with stoichiometry $Al(SO_4)Cl{\cdot}nH_2O$ (Kirilenko 2010). Hypothetically, the formation of crystalline aluminium chloride sulfates (known mainly as basic salts) is promoted by a high activity of OH groups, *i.e*., by relatively high pH values of mineral-forming solutions.

The eight hydrogen bonds determined from structural data for vendidaite correspond well to the eight bands of the O–H stretching vibrations observed in the IR spectrum in the range 2900–3700 cm^{-1}. The following empirical correlation between O–H stretching frequencies ν in IR spectra of minerals (in cm^{-1}) and O···O distances d(O···O) determined from structural data (in Å) were established by Libowitzky (1999): $\nu = 3592 - 304{\cdot}10^9{\cdot}\exp[-d(O{\cdots}O)/0.1321]$. As was noted earlier by Chukanov *et al*. (2011), at high frequencies

FIG. 4. Crystal structure of vendidaite projected along *c* (a) and *b* (b) axes. Legend: $[Al(OH)_3(H_2O)_3]$ octahedra are dark grey, SO_4 tetrahedra are cross-hatched; H···**A** bonds are shown as light grey lines.


a
a sinβ
b
H
Cl

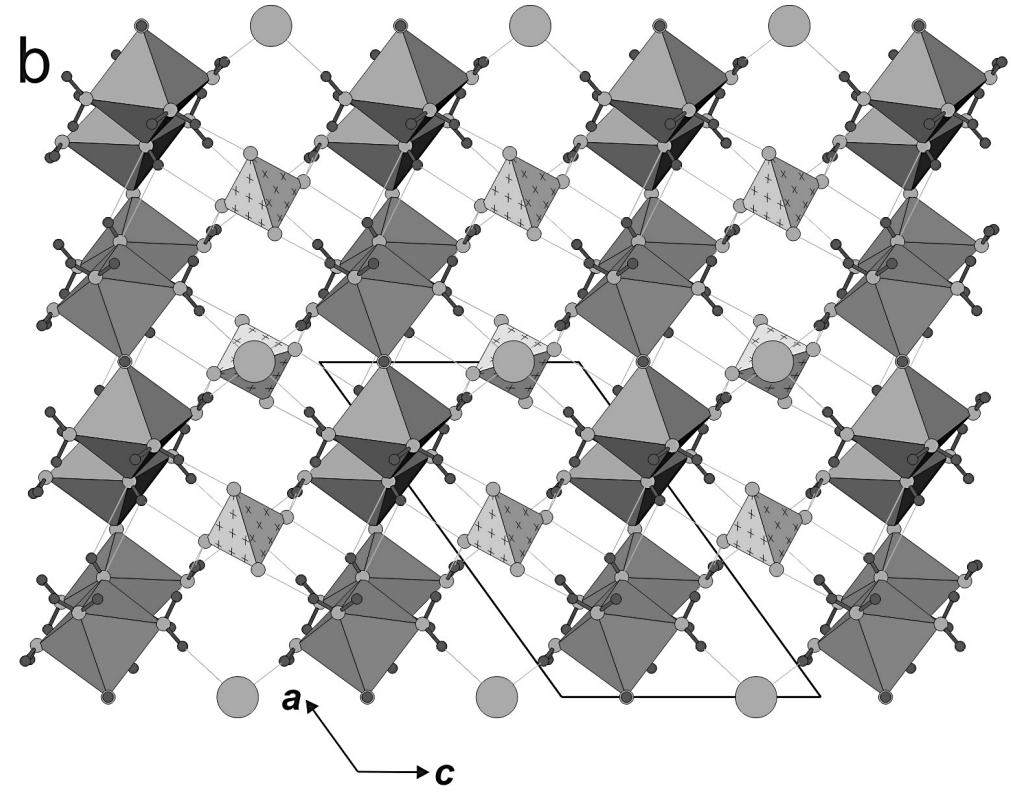

b
a
c

TABLE 3. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR VENDIDAITE

Crystal data	
Temperature	296 K
Radiation, wavelength	MoK_α, 0.71073 Å
Crystal system	monoclinic
Space group	*C*2/*c*
Unit-cell dimensions *a*, *b*, *c* (Å), β (°)	11.9246(16), 16.134(2), 7.4573(9), 125.815(2)
Unit-cell volume (Å^3)	1163.4(3)
Z	8
Calculated density (g/cm^3)	1.967
Absorption coefficient (mm^{-1})	0.722
Crystal size (mm^3)	0.12×0.10×0.11
Data collection	
θ range	2.46 – 36.50°
h, *k*, *l* ranges	–17→ 19, –26→ 26, –10→ 12
Total reflections collected	9817
Unique reflections (R_{int})	2831 (0.052)
Unique reflections $F > 4\sigma(F)$	2034
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients *a*, *b*	0.0579, 0
Data/restraints/parameters	2831/0/111
R_1 [$F > 4\sigma(F)$], wR_2 [$F > 4\sigma(F)$]	0.044, 0.097
R_1, wR_2 [all data]	0.072, 0.111
Goodness-of-fit on F^2	1.024
Largest diff. peak and hole, *e* Å^{-3}	0.875, –0.574

(above 3500 cm^{-1}), substantial deviations from this correlation are possible because the O–H stretching frequencies depend not only on the O···O distances, but also on the nature of cations coordinating O–H groups and H_2O molecules, as well as on the O–H···O bond angle. The influence of these factors becomes most pronounced for weak hydrogen bonds. The above correlation predicts that the maximum possible value of the O–H stretching frequency for minerals is 3592 cm^{-1}. However, in IR spectra of many minerals bands of O–H stretching vibrations with higher ν values are present. For example, in the IR spectra of the magnesium serpentine-group minerals brucite and kaolinite, strong absorption bands with frequencies even higher than 3660 cm^{-1} can be observed.

The frequencies of the O–H stretching vibrations for hydrogen bonds with O as an acceptor, measured from the IR spectrum and calculated from the Libowitzky equation and corresponding d(O···O) distances (Å) are [ν_{meas}/ν_{calc}/d(O···O)]: 3421/3476/2.986, 3293/3234/2.716, 3190/3215/2.709, 3164/3195/2.699, 2989/2919/2.632. Consequently, the IR bands at 3490, 3585, and 3640 cm^{-1} can be assigned to weaker hydrogen bonds with Cl as an acceptor, with the distances O···Cl equal to 3.055, 3.128, and 3.241 Å, respectively.

In accordance with the Libowitzky equation, the strongest hydrogen bond corresponds to the shortest O···O distance of 2.632 Å between O_w2 and O7 and to the lowest frequency of O–H stretching vibrations of 2989 cm^{-1}. Note that the O7 atom has the largest displacement parameters, which provides a possible explanation for the occurrence of weak IR bands (at 2299, 2445, and 2521 cm^{-1}) that can be assigned to small amounts of protonated HSO_4^- groups.

Acknowledgements

This work was financially supported by the Russian Foundation for Basic Research (grants nos. 11-05-00397-a, 11-05-00407-a). SVK and APC were supported in this work by the Russian Federal Grant-in-Aid Program 'Cadres' (state contract 16.740.11.0490). X-ray diffraction studies were performed at the SPbSU X-ray diffraction Resource Centre. The authors are grateful to P.C. Piilonen, J. Schlüter, H. Friis, and L.A. Groat for valuable comments.

References

Brese, N. & O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica* **B47,** 192–197.

Chukanov, N.V., Mukhanova, A.A., Möckel, S., Belakovskiy, D.I., & Levitskaya, L.A. (2010) Nickeltalmessite, $Ca_2Ni(AsO_4)_2{\cdot}2H_2O$, a new mineral species of the fairfieldite group, Bou Azzer, Morocco. *Geology of Ore Deposits* **52,** 606–611.

Chukanov, N.V., Pekov, I.V., Jonsson, E., Zubkova, N.V., Filinchuk, Y.E., Belakovsliy, D.I., & Pushcharovsky D.Yu. (2011) Långbanshyttanite, a new arsenate mineral from Långban, Sweden. *European Journal of Mineralogy* **23,** 675–681.

Chukanov, N.V., Scholz, R., Aksenov, S.M., Rastsvetaeva, R.K., Pekov, I.V., Belakovskiy, D.I., Krambrock, K., Paniago, R.M., Righi, A., Martins, R.F., Belotti, F.M., & Bermanec, V. (2012) Metavivianite, $Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2{\cdot}6H_2O$: new data and formula revision. *Mineralogical Magazine* **76,** 725–741.

European Standard EN 883 (2005) *Chemicals used for treatment of water intended for human consumption – Polyaluminium chloride hydroxyde and polyaluminium chloride hydroxyde sulfate*. Brussels: European Committee of Standartization. 18 p.

Hawthorne, F.C., Krivovichev, S.V., & Burns, P.C. (2000) Crystal chemistry of sulfate minerals. *Reviews in Mineralogy and Geochemistry* **40,** 1–112.

Kirilenko, I.A. (2010) Glass formation in the $Al_2(SO_4)_3$–$AlCl_3$–H_2O system. *Russian Journal of Inorganic Chemistry* **55(7),** 1133–1135.

TABLE 4. COORDINATES, DISPLACEMENT PARAMETERS (Å^2), AND BOND-VALENCE SUMS (BVS, V.U.) OF ATOMS IN THE STRUCTURE OF VENDIDAITE

Atom	BVS*	*x*	*y*	*z*	U_{iso}
S	5.94	0	0.10237(3)	¼	0.01429(11)
Al	3.08	0.31915(4)	–0.17116(3)	0.60126(7)	0.01191(11)
Cl	-	½	0.06935(3)	¾	0.02098(13)
O_h1	1.14	0.35676(12)	–0.27909(7)	0.5655(2)	0.0148(2)
O_w2	0.50	0.24890(13)	–0.06937(7)	0.6279(2)	0.0175(2)
O_w3	0.45	0.34579(14)	–0.19724(8)	0.8792(2)	0.0208(2)
O_h4	1.12	½	–0.13153(10)	¾	0.0156(3)
O5	1.47	0.03589(13)	0.15476(8)	0.4400(2)	0.0234(3)
O_w6	0.47	0.28253(14)	–0.12493(8)	0.3328(2)	0.0202(2)
O7	1.50	0.11995(14)	0.05040(8)	0.3153(2)	0.0258(3)
H1	-	0.208(3)	–0.0315(19)	0.517(5)	0.055(9)
H2	-	0.388(3)	–0.2496(16)	0.948(5)	0.044(8)
H3	-	½	–0.084(2)	¾	0.028(9)
H4	-	0.393(3)	–0.1671(19)	0.970(5)	0.054(9)
H5	-	0.201(3)	–0.1262(16)	0.206(4)	0.045(8)
H6	-	0.349(3)	–0.110(2)	0.321(5)	0.071(11)
H7	-	0.414(3)	–0.2935(19)	0.573(5)	0.058(10)
H8	-	0.207(3)	–0.069(2)	0.684(5)	0.065(10)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	0.0134(2)	0.0174(2)	0.0127(2)	0	0.00799(19)	0
Al	0.0101(2)	0.01417(19)	0.0116(2)	–0.00004(15)	0.00643(17)	–0.00024(14)
Cl	0.0224(3)	0.0212(2)	0.0231(3)	0	0.0154(2)	0
O_h1	0.0108(5)	0.0166(5)	0.0176(5)	–0.0012(4)	0.0086(4)	0.0004(4)
O_w2	0.0201(6)	0.0173(5)	0.0201(5)	0.0028(4)	0.0145(5)	0.0039(4)
O_w3	0.0266(7)	0.0194(5)	0.0154(5)	0.0004(4)	0.0117(5)	–0.0007(5)
O_h4	0.0122(7)	0.0138(6)	0.0185(7)	0	0.0077(6)	0
O5	0.0224(6)	0.0274(6)	0.0178(5)	–0.0082(5)	0.0104(5)	–0.0039(5)
O_w6	0.0159(5)	0.0314(6)	0.0132(5)	0.0031(4)	0.0084(4)	–0.0028(5)
O7	0.0262(7)	0.0313(6)	0.0291(7)	0.0138(5)	0.0213(6)	0.0133(5)

* calculated using bond-valence parameters taken from Brese & O'Keeffe (1991); contribution from H bonds are not included.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND GEOMETRY OF HYDROGEN BONDING IN THE STRUCTURE OF VENDIDAITE

S–O7	1.4737(13) ×2	Al–O_h1	1.8559(12)		
S–O5	1.4820(13) ×2	Al–O_h4	1.8682(7)		
<S–O>	1.478	Al–O_h1	1.8810(12)		
		Al–O_w2	1.9061(13)		
Cl–O_w3	3.0552(14) ×2	Al–O_w6	1.9315(13)		
Cl–O_w6	3.1282(14) ×2	Al–O_w3	1.9502(14)		
		<Al–O>	1.899		
D–H	d(**D**–H)	d(H···**A**)	<**D**H**A**	d(**D**···**A**)	**A**
O_h1–H7	0.690	2.343	155.72	2.986	O5
O_w2–H1	0.909	1.804	173.06	2.709	O7
O_w2–H8	0.816	1.823	171.07	2.632	O7
O_w3–H2	0.963	1.737	176.59	2.699	O5
O_w3–H4	0.752	2.315	168.38	3.055	Cl
O_h4–H3	0.767	2.474	180.00	3.241	Cl
O_w6–H5	0.876	1.856	166.85	2.716	O5
O_w6–H6	0.881	2.251	173.63	3.128	Cl

D = donor; **A** = acceptor

LIBOWITZKY, E. (1999) Correlation of O–H stretching frequencies and O–H···O hydrogen bond lengths in minerals. *Monatshefte für Chemie* **130,** 1047–1059.

MALCHEREK, T. & SCHLÜTER, J. (2010) Anatacamite from La Vendida mine, Sierra Gorda, Atacama desert, Chile: a triclinic polymorph of $Cu_2(OH)_3Cl$. *Neues Jahrbuch für Mineralogie, Monatshefte*, **187(3),** 307–312.

NESTOLA, F., CÁMARA, F., CHUKANOV, N.V., ATENCIO, D., COUTINHO, J.M.V., CONTREIRA FILHO, R.R., & FÄRBER, G. (2012) Witzkeite: a new rare nitrate-sulphate mineral from a guano deposit at Punta de Lobos, Chile. *American Mineralogist* **97,** 1783–1787.

REICH, M., PALACIOS, C., PARADA, M.A., FEHN, U., CAMERON, E.M., LEYBOURNE, M.I., & ZÚÑIGA, A. (2008) Atacamite formation by deep saline waters in copper deposits from the Atacama Desert, Chile: evidence from fluid inclusions, groundwater geochemistry, TEM, and ^{36}Cl data. *Mineralium Deposita* **43,** 67–73.

SCHLÜTER, J., KLASKA, K.H., & GEBHARD, G. (2000) Belloite, Cu(OH)Cl, a new mineral from Sierra Gorda, Antofagasta, Chile. *Neues Jahrbuch für Mineralogie, Monatshefte* **2,** 67–73.

Received April 28, revised manuscript accepted september 19, 2013.