

Sulfhydrylbystrite, $\text{Na}_5\text{K}_2\text{Ca}(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{S}_5)(\text{SH})$, a new mineral with the LOS framework, and re-interpretation of bystrite: cancrinite-group minerals with novel extra-framework anions

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ABSTRACT

Sulfhydrylbystrite, $\text{Na}_5\text{K}_2\text{Ca}(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{S}_5)(\text{SH})$, cell parameters $a = 12.9567(6)$ Å, $c = 10.7711(5)$ Å, space group $P31c$, is a new mineral belonging to the cancrinite group. It was found at Malaya Bystraya lazurite deposit, Lake Baikal area, Eastern Siberian Region, Russia, associated with lazurite, calcite, diopside, phlogopite and pyrite. The mineral develops at the margins of masses of lazurite, replacing it in some areas with the formation of nonequilibrium lazurite-diopside-sulfhydrylbystrite association. It is translucent, yellow to orange, with vitreous lustre, yellow streak and Mohs hardness of 4.5–5. The empirical formula, based on 12 (Si + Al), is $\text{Na}_{5.17}\text{K}_{1.87}\text{Ca}_{0.99}[\text{Al}_{6.01}\text{Si}_{5.99}\text{O}_{24}](\text{S}_5)_{0.86}^2-(\text{SH})_{0.86}^-\text{Cl}_{0.07}$, $Z = 2$. The crystal structure of sulfhydrylbystrite may be described as an ABAC stacking of six-membered rings of SiO_4 and AlO_4 tetrahedra and extra-framework cations and anions located within structural cages. There are two type of cages, cancrinite and losod, stacked into chains at $(0, 0, z)$ and $(\frac{2}{3}, \frac{1}{3}, z)$, respectively. The cancrinite cage hosts Ca^{2+} and $(\text{SH})^-$ ions, whereas the $(\text{S}_5)^{2-}$ polyanion is in the losod cage associated with Na^+ and K^+ cations. In addition, $(\text{SH})^-$ and $(\text{S}_5)^{2-}$ anions are detected in the structure of a mineral for the first time.

For comparison, a structural and compositional study of a bystrite sample from the same deposit was carried out. Bystrite is confirmed to contain pentasulfide anions in the losod cages, similar to those of sulfhydrylbystrite, in contrast to previous studies. However, bystrite has chloride in cancrinite cages, whereas sulfhydrylbystrite has hydrosulfide in that position. The unit-cell parameters are distinctly different: bystrite has $a = 12.8527(6)$ Å, $c = 10.6907(5)$ Å in the same $P31c$ space group.

KEYWORDS: new mineral, sulfhydrylbystrite, bystrite, cancrinite group, crystal structure, electron microprobe analysis.

Introduction

BYSTRITE was found on the Malaya Bystraya lazurite deposit in the Lake Baikal region, Eastern Siberian, Russia, and described by Pobedinskaya *et al.* (1991), who determined the crystal structure

of the mineral. However, their results showed some inconsistencies. In particular, the contents of K, Cl and H_2O derived from site occupancies disagreed with those obtained from electron microprobe analysis. The chemical formula, reported in Pobedinskaya *et al.* (1991), calculated on the basis of $(\text{Si} + \text{Al}) = 12$, is $(\text{Na}_{5.17}\text{K}_{1.80}\text{Ca}_{1.01})_{\Sigma=7.98}(\text{Si}_{6.17}\text{Al}_{5.83})_{\Sigma=12}\text{O}_{24}(\text{CO}_3)_{0.08}(\text{S}_3)_{1.39}(\text{SO}_4)_{0.07}\text{Cl}_{0.08} \cdot 1\text{H}_2\text{O}$, whereas the structural formula according to single crystal X-ray diffraction (SCXRD) data,

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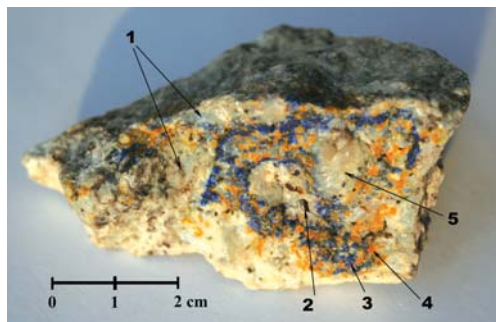


FIG. 1. Sulfhydrylbystrite-containing rock: 1 – diopside, 2 – pyrite, 3 – lazurite, 4 – sulfhydrylbystrite, 5 – calcite.

obtained by Pobedinskaya *et al.* (1991), would be: $(\text{Ca}_{0.94}\text{Na}_{6.40})_{\Sigma=7.34}(\text{Si},\text{Al})_{12}\text{O}_{24}(\text{S}_{3.1.18}^{2-}\text{Cl}_{0.48}(\text{H}_2\text{O})_{0.48})$. The structural formula contains six times less chlorine, while the amount of sulfur is greater than in the chemical formula.

In the present work, a detailed comparative structural and chemical study on two mineral phases with similar structural model and composition, but having different additional anions, was carried out. One phase is actually bystrite, which contains sulfur and chlorine, while another one, the new mineral phase, sulfhydrylbystrite, has a deficiency of chlorine and larger amount of sulfur.

The minerals of cancrinite group, represented by trigonal and hexagonal feldspathoids, have a

framework, formed by layers containing six-membered rings of Al- and Si-centred tetrahedra. The layers are stacked along [001] following an ‘ABC-based’ scheme as detailed in Bonaccorsi and Merlino (2005). The cancrinite group currently contains 27 minerals, which can be divided into two subgroups: (1) those with the two-layer AB sequence; and (2) those with more complex stacking sequences. The different stacking sequences produce different types of cage in the framework. Twelve minerals have the AB sequence, characterized by continuous channels and cancrinite-type cages only. The longer stacking sequences of the other 15 minerals may contain sodalite-, losod-, liottite- or giuseppettite-type cages in different combinations, and can have up to 36 layers for c translation with the c parameter ranging from 10 to 95 Å.

In this paper, a new cancrinite-group mineral, sulfhydrylbystrite of composition $\text{Na}_5\text{K}_2\text{Ca}(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{S}_5)(\text{SH})$, having an ABAC layer sequence, is described. The same layer sequence was described previously in bystrite, $(\text{Na},\text{K})_7\text{Ca}[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{S}_3)_{1.5}\cdot\text{H}_2\text{O}$ (Pobedinskaya *et al.*, 1991), its K-deficient $(\text{CO}_3)\text{-Na}$ analogue, carbo-bystrite, $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{CO}_3)\cdot 4\text{H}_2\text{O}$ (Khomyakov *et al.*, 2010) and synthetic $\text{Na}_8(\text{Al}_6\text{Ge}_6\text{O}_{24})(\text{CO}_3)\cdot 3\text{H}_2\text{O}$ (Sokolov *et al.*, 1978). Thus, the natural mineral sulfhydrylbystrite can be included in the bystrite structural subgroup of the minerals with the same layer sequence but different contents of cages, proposed by Bonaccorsi *et al.* (2012).

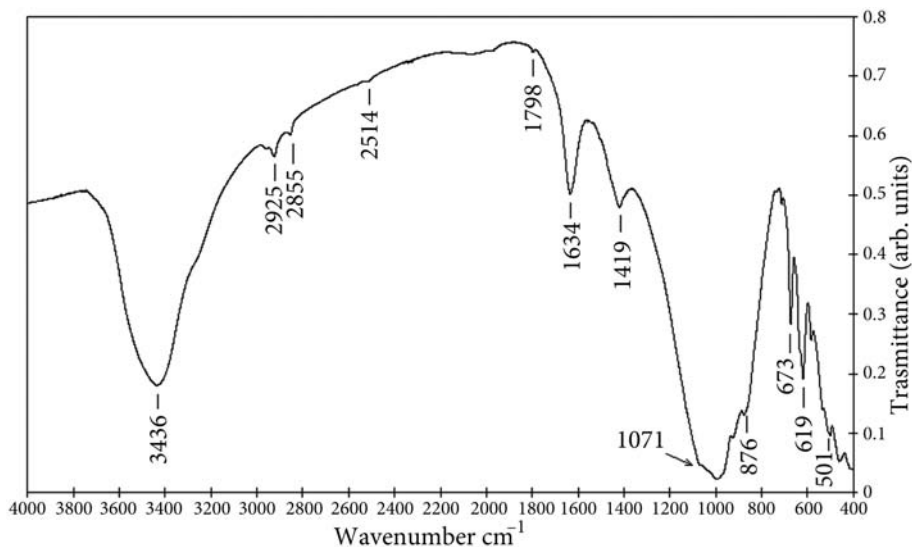


FIG. 2. FTIR spectrum of sulfhydrylbystrite.

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TABLE 1. Chemical composition determined using EPMA (mean of 16 analyses for sulfhydrylbystrite and 12 analyses for bystrite) and number of atoms on the basis of 12 (Si + Al).

Constituent	Sulfhydrylbystrite		Bystrite		Sulfhydrylbystrite		Bystrite
	Wt.%	Range	Wt.%	Range	Atoms per formula unit		
SiO ₂	32.0(5)	32.94–31.28	32.9(8)	33.50–31.03	Si	5.99	6.04
Al ₂ O ₃	27.2(8)	28.42–25.65	27.2(4)	27.75–26.79	Al	6.01	5.96
CaO	4.9(1)	5.01–4.57	5.1(1)	5.21–4.89	Ca	0.99	1.01
Na ₂ O	14.3(7)	15.40–12.89	19.5(3)	20.48–19.51	Na	5.17	7.03
K ₂ O	7.8(7)	9.03–6.86	0.18(6)	0.35–0.11	K	1.87	0.04
S	14.7(9)	15.30–13.94	13.8(9)	14.26–12.81	S	5.17	4.82
Cl	0.2(2)	0.46–0.08	2.79(9)	2.79–2.47	Cl	0.07	0.88
Sum	101.15		101.47				
O = S	–1.82		–1.38				
O = Cl	–0.05		–0.63				
Total	99.28		99.46				

The name sulfhydrylbystrite comes from the chemical relationship with bystrite and carbo-bystrite. The new mineral species and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA no.2015-010, Sapozhnikov *et al.*, 2015). The holotype specimen of sulfhydrylbystrite is deposited at the Mineralogical Museum of Saint-Petersburg State University (catalogue no. 1/19636).

Occurrence and associated minerals

Sulfhydrylbystrite was identified in the Malaya Bystraya lazurite deposit, Lake Baikal area, Eastern Siberian Region, Russia, the same locality where bystrite was first found. The Malaya Bystraya deposit, discovered in 1851, is located in the area between the Malaya Bystraya river and the Lazurnyi creek, ~6 km above of their confluence, ~25 km from Sludyanka and 18 km from the Kultuk settlement. The geological structure of the deposit was described in detail by Ivanov and Sapozhnikov (1985). The deposit is contained in dolomites, with brecciated boudins of diopside-bearing microclinized granitoids. Sulfhydrylbystrite-containing rocks occur in a dolomite marble body reaching 90 m in thickness, crumpled in a NE-trending synclinal fold and separated by faults from the adjacent alkali granite and syenite bodies. Within the deposit, there are two lazurite-bearing zones, which consist of a series of lenses and vein-shaped bodies of calciphyres with boudins of granites and cavities of

lazurite. Sulfhydrylbystrite occurs in lazurite-bearing rocks of metasomatic origin, which are disseminated irregularly through their host rocks. The feldspathoids of Malaya Bystraya formed in the presence of H₂S-rich fluids, which also caused the syngenetic and later precipitation of pyrite and its subsequent replacement by pyrrotite (Aleksandrov and Senin, 2006).

Sulfhydrylbystrite associates with lazurite, diopside, calcite, phlogopite and pyrite (Fig. 1). The mineral develops at the contact with lazurite, replacing it in some areas with the formation of a disequilibrium lazurite-diopside-sulfhydrylbystrite association, containing up to 15–20% of sulfhydrylbystrite. It occurs as small platy crystals up to 5 mm in elongation, intimately intergrown with lazurite, diopside and calcite. Rarely, sulfhydrylbystrite forms irregularly shaped individual grains ~3 mm in size or aggregates of such grains. These isometric grains have rounded or irregular edges, and sometimes contain relicts of earlier minerals, especially diopside and lazurite.

There is a strong resemblance between bystrite and sulfhydrylbystrite occurrences. The bystrite sample studied was found in a partially recrystallized lazurite-bearing calciphyre, where its crystals coexist with lazurite without any occurrences of a reaction relationship.

Physical and optical properties

Sulfhydrylbystrite is translucent, yellow, yellow-brown, orange-yellow or orange, with a yellow streak and vitreous lustre. It is brittle with good

TABLE 2. Powder X-ray diffraction data for sulphhydrylbystrite and bystrite.

Sulphhydrylbystrite			Bystrite			<i>hkl</i>
<i>I</i> _{meas}	<i>d</i> _{meas}	<i>d</i> _{calc.}	<i>I</i> _{meas}	<i>d</i> _{meas}	<i>d</i> _{calc.}	
13	7.757	7.770	8	7.731	7.710	101
15	6.480	6.478	9	6.436	6.426	110
48	4.857	4.855	32	4.821	4.819	102
10	4.248	4.241	8	4.210	4.207	210
9	4.136	4.141	5	4.114	4.110	112
38	3.948	3.946	38	3.915	3.915	211
94	3.739	3.740	100	3.712	3.710	300
25	3.417	3.420	16	3.394	3.394	103
100	3.331	3.332	50	3.307	3.306	212
25	2.805	2.805	18	2.782	2.783	400
32	2.715	2.715	22	2.692	2.693	401
56	2.692	2.693	30	2.673	2.673	004
7	2.618	2.618	5	2.600	2.599	104
28	2.487	2.488	23	2.468	2.468	402
8	2.349	2.352	5	2.332	2.333	313
15	2.211	2.211	7	2.193	2.193	403
8	2.183	2.185	5	2.169	2.169	304
27	2.156	2.160	15	2.142	2.142	330
13	2.070	2.071	6	2.054	2.055	224
11	1.941	1.943	6	1.927	1.928	404
7	1.888	1.888	9	1.869	1.855	512
19	1.811	1.812	9	1.798	1.798	414
10	1.796	1.797	8	1.782	1.782	520
8	1.772	1.773				106
6	1.710	1.709	5	1.696	1.697	405
6	1.682	1.685				334
10	1.653	1.653				216
12	1.615	1.614	6	1.606	1.601	514
6	1.584	1.586				531
10	1.536	1.536				532
						604
						702
10	1.523	1.522	6	1.523	1.524	434
9	1.510	1.512	5	1.501	1.500	604
11	1.486	1.486				710
7	1.460	1.464				533
13	1.388	1.388	8	1.377	1.377	444
8	1.357	1.357				802
9	1.344	1.346				008

The strongest lines are given in bold

cleavage on {100} and poor parting on {001}, and it has a conchoidal fracture. Calculated density from the empirical formula is $D_{\text{calc}} = 2.368 \text{ g/cm}^3$ and the measured density is $D_{\text{meas}} = 2.391(1) \text{ g/cm}^3$. The density was measured in a thermogradient tube (45 cm long). At a lower end of the tube a temperature of 20°C was maintained, at the upper end a temperature of +45°C. The liquid in

which specimens were immersed in the tube was a solution of bromoform and methyl alcohol. The obtained value is probably slightly overestimated due to intergrowth of sulphhydrylbystrite with denser minerals (diopside, calcite). Vickers hardness was measured by means of a UI PMT-3 microhardness tester, with an applied load of 100 g. Results showed an average Vickers hardness of 598 (with

range 554–657). The mineral has a Mohs hardness of 4.5–5.

Sulphdrylbystrite displays strong pleochroism from deep yellow or orange to pale yellow. It is uniaxial (+) with $\omega = 1.661(2)$ and $\varepsilon = 1.584(2)$.

Infrared spectroscopy

The Fourier-transform infrared spectrum (FTIR) of sulphdrylbystrite powder in a KBr pellet was recorded by means of Vertex 70 FT-IR Bruker infrared spectrometer and Varian 3 100ATR/FT-IR (RAM II) spectrophotometer. The spectrum was acquired from 4000 to 400 cm^{-1} and is displayed in Fig. 2.

In the 800–400 cm^{-1} region of the spectra there is a group of well-defined bands at 462, 501, 534, 583, 619, 673, 712 cm^{-1} , assigned to bending vibrations of the tetrahedral framework (Chukanov *et al.*, 2010; Pekov *et al.*, 2011). A very intense absorption observed in the 1100–900 cm^{-1} region can be assigned to the stretching vibrations of the tetrahedral framework (peaks at 926, 1000, 1071 cm^{-1}) (Chukanov *et al.*, 2010; Pekov *et al.*, 2011). A weak absorption assigned to a stretching mode of the SH-group is found around 2514 cm^{-1} (Coates, 2000).

In addition, the presence of a broad band at 3436 cm^{-1} is due to stretching vibrations of water molecules, absorbed by the sample, having characteristic bending vibration modes at 1634 cm^{-1} . Ballirano *et al.* (1996) noted the strong tendency of all cancrinite-like minerals to absorb water. Bands at 1798 and 1419 cm^{-1} are assigned to stretching vibrations of a CO_3 group (Della Ventura *et al.*, 2007, 2009; Coates, 2000), while a peak observed at 876 cm^{-1} is due to the bending vibration of CO_3 (Coates, 2000). The presence of bands related to carbonate groups is most probably caused by calcite impurities (see Ballirano *et al.*, 1996). Finally, a triplet at 2959, 2925, 2855 cm^{-1} was interpreted as grease peaks (see Cámara *et al.*, 2010, 2012), i.e. symmetric and asymmetric C–H-stretching vibration of a methyl group (CH_3), caused by impurities absorbed during sample preparation.

Chemical composition

A single crystal of sulphdrylbystrite was broken into two equal fragments. One of them was used for the SCXRD study and another one was analysed using a JEOL JXA-8200 electron microprobe

equipped with a high-resolution scanning electron microscope, an energy-dispersive spectrometer with Si(Li) detector and five wavelength-dispersive spectrometers (WDS). The mineral was found to be unstable under the electron beam, which caused sulfur volatilization, and the apparent composition was dependent upon operating conditions. However, it was found that the mineral was stable under the beam for WDS with accelerating voltage = 15 kV, probe current = 5 nA, beam diameter = 20 μm . Counting time on peak was 20 s and counting time on background = 10 s. The following standards were used: pyrope (Si, PETH, $K\alpha$), albite (Al, Na, TAPH, $K\alpha$), diopside (Ca, PETH, $K\alpha$), orthoclase (K, PETJ,

TABLE 3. Selected data about the single crystal, the data-collection parameters and the structure refinement of sulphdrylbystrite and bystrite.

	Sulphdrylbystrite	Bystrite
Crystal dimensions (mm)	0.140 × 0.100 × 0.067	0.350 × 0.320 × 0.250
Space group	<i>P31c</i>	<i>P31c</i>
<i>a</i> (Å)	12.9567(6)	12.8527(6)
<i>c</i> (Å)	10.7711(5)	10.6907(5)
<i>V</i> (Å ³)	1566.0(1)	1529.4(1)
<i>Z</i>	2	2
Data collection		
Theta range	2.621 to 28.316°	2.642 to 36.341°
Refl. measured	81,548	54,538
Independent refl.	2616	2489
<i>R</i> _{int}	5.5	3.8
<i>h</i> _{min} , <i>h</i> _{max}	−17, 17	−21, 21
<i>k</i> _{min} , <i>k</i> _{max}	−17, 17	−21, 21
<i>l</i> _{min} , <i>l</i> _{max}	−14, 14	−17, 17
Completeness to Theta _{max}	99.8%	99.9%
Refinement		
Refl. used in the refinement (<i>I</i> > 3σ _(<i>I</i>))	2295	2358
No. of refined parameters	247	219
<i>R</i> (%) ^a	2.6	3.0
<i>R</i> _w (%) ^b	3.1	3.5
Goof	1.07	1.10
ρ _{min} /ρ _{max} (e [−] /Å ³)	−0.27/0.45	−0.45/0.60

$$^a R = \frac{\sum[|F_o| - |F_c|]}{\sum|F_o|}$$

$$^b R_w = \frac{[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}}{N - P}$$

optimized weights.
^cGoof = $[\sum[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where *N* and *P* are the number of reflections and parameters, respectively.

TABLE 4a. Crystallographic coordinates, occupancies and equivalent isotropic displacement parameters (\AA^2) of sulfhydrylbystrite.

Site	Atom	x/a	y/b	z/c	Occupancy	$U(\text{iso})$
T1	Si1	0.07974(5)	0.41675(5)	0.7592(1)	1.000(1)	0.0086
T2	Si2	0.25102(6)	0.25077(6)	0.0092(1)	1.000(1)	0.0080
T3	Al1	0.25669(6)	0.00014(6)	0.0093(1)	1.000(1)	0.0087
T4	Al2	0.67599(5)	0.08567(6)	0.2591(1)	1.000(1)	0.0085
	O1	0.3405(2)	0.0095(2)	0.3825(2)	1.000(1)	0.0231
	O2	0.2298(2)	0.1172(2)	-0.0071(2)	1.000(1)	0.0215
	O3	0.6800(2)	0.0100(2)	0.1311(2)	1.000(1)	0.0188
	O4	0.6811(2)	0.0090(2)	0.3912(2)	1.000(1)	0.0173
	O5	0.2319(2)	0.1183(2)	0.5264(2)	1.000(1)	0.0210
	O6	0.0770(1)	0.5382(2)	0.7588(4)	1.000(1)	0.0263
	O7	0.2167(2)	0.4511(1)	0.7592(3)	1.000(1)	0.0183
	O8	-0.0103(2)	0.3319(2)	0.1400(2)	1.000(1)	0.0199
M1	Ca1	0	0	0.0101(2)	0.919(1)	0.0179
M2	Na2	2/3	1/3	0.2588(4)	1.110(1)	0.0243
M3	K30	0.4687(5)	0.5252(5)	0.0279(5)	0.132(1)	0.0272
	Na31	0.4959(4)	0.4981(4)	0.0077(4)	0.559(1)	0.0385
	Na32	0.5224(5)	0.4709(5)	-0.0053(6)	0.325(1)	0.0385
M4	K40	0.2069(1)	0.4125(1)	0.2580(2)	0.531(1)	0.0312
	Na41	0.173(1)	0.351(1)	0.256(2)	0.105(1)	0.0252
	Na42	0.1376(3)	0.2797(2)	0.2595(5)	0.342(1)	0.0252
X1	S1	0.2780(6)	0.6858(6)	0.0251(6)	0.127(1)	0.0313
	S11	0.2713(5)	0.5947(5)	0.0262(6)	0.128(1)	0.0313
X2	S2	0.2482(5)	0.5979(7)	0.1073(7)	0.165(1)	0.0519
	S22	0.2483(6)	0.6500(7)	0.1021(8)	0.151(1)	0.0519
X3	S3	0.2678(5)	0.5351(2)	0.2593(5)	0.288(1)	0.0614
X4	S4	0.24669(5)	0.6512(7)	0.4131(7)	0.147(1)	0.0428
	S44	0.2484(5)	0.5970(6)	0.4111(6)	0.161(1)	0.0428
X5	S5	0.2896(5)	0.5884(3)	0.4938(4)	0.241(1)	0.0524
	S55	0.357(1)	0.6292(8)	0.4767(8)	0.100(1)	0.0524
X6	S6	0	0	0.2578(2)	1.018(1)	0.0704

$K\alpha$), ZnS (S, PETH, $K\alpha$), Cl-apatite (Cl, PETH, $K\alpha$). A conversion from X-ray counts to oxide weight percentages was obtained with the ZAF data reduction system. Analytical errors are 1–2% relative for Al and Si, 2–3% relative for Na, Ca, K, S and 4% relative for Cl. The chemical formula was normalized on the basis of $(\text{Si} + \text{Al}) = 12$. Chemical data are reported in Table 1. As the analytical total is <100%, we presume a minor loss of sulfur during the microprobe analysis. This is also suggested by the results of the SCXRD investigation (see below).

According to the SCXRD data, sulfur presents in the mineral in form of the S_5^{2-} polysulfide ion and sulfhydryl group $(\text{SH})^-$ in quite equal proportions (see below). The empirical formula of sulfhydrylbystrite is: $\text{Na}_{5.17}\text{K}_{1.87}\text{Ca}_{0.99}[\text{Al}_{6.01}\text{Si}_{5.99}\text{O}_{24}](\text{S}_5)_{0.86}(\text{SH}_{0.86}\text{Cl}_{0.07})$. A slight burnout of sulfur during electron probe microanalysis (EPMA) leads

to the minor deficit of negative charge in the proposed chemical formula of sulfhydrylbystrite (+51.01 vs. -50.65).

Using the same procedures, the chemical study of a bystrite crystal was carried out. Chemical data, represented in the Table 1, show that bystrite is substantially free of potassium (~0.2 wt.% K_2O), in contrast, sulfhydrylbystrite contains quite a lot of potassium (~8 wt.% K_2O). The main difference between the chemistry of the minerals is that bystrite contains sulfide sulfur and chlorine as additional anions, whereas sulfhydrylbystrite has only sulfide sulfur, but in larger amounts. The empirical formula of bystrite is: $\text{Na}_{7.03}\text{K}_{0.04}\text{Ca}_{1.01}[\text{Si}_{6.04}\text{Al}_{5.96}\text{O}_{24}](\text{S}_5)_{0.94}(\text{Cl}_{0.88}\text{SH}_{0.12})$. The crystal structure determination of bystrite (see below) confirms that the polysulfide species in the losod cage is largely S_5^{2-} , as for sulfhydrylbystrite. This is in contrast to the study of Pobedinskaya *et al.*

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TABLE 4b. Crystallographic coordinates, occupancies and equivalent isotropic displacement parameters (\AA^2) of bystrite.

Site	Atom	x/a	y/b	z/c	Occupancy	U(iso)
T1	Si1	0.07810(4)	0.41590(3)	0.75830(6)	1.000(1)	0.0064
T2	Si2	0.25170(4)	0.25208(4)	0.00751(6)	1.000(1)	0.0059
T3	Al1	0.25715(4)	0.00059(4)	0.00742(7)	1.000(1)	0.0063
T4	Al2	0.67485(4)	0.08369(4)	0.25877(7)	1.000(1)	0.0066
	O1	0.3572(1)	0.0140(1)	0.3909(1)	1.000(1)	0.0147
	O2	0.2442(1)	0.1249(1)	-0.0210(2)	1.000(1)	0.0165
	O3	0.6896(1)	0.0003(1)	0.1408(1)	1.000(1)	0.0170
	O4	0.6672(1)	0.0133(1)	0.4000(1)	1.000(1)	0.0144
	O5	0.2215(1)	0.1134(1)	0.5053(1)	1.000(1)	0.0141
	O6	0.0765(1)	0.5386(1)	0.7342(1)	1.000(1)	0.0164
	O7	0.2162(1)	0.4492(1)	0.7552(2)	1.000(1)	0.0189
	O8	-0.0013(1)	0.3228(1)	0.1498(1)	1.000(1)	0.0170
M1	Ca1	0	0	0.01207(8)	0.924(1)	0.0133
M2	Na2	2/3	1/3	0.2387(2)	1.108(1)	0.0199
M3	Na31	0.4793(2)	0.5135(2)	0.0261(2)	0.601(1)	0.0457
	Na32	0.5092(3)	0.4846(3)	0.0092(3)	0.416(1)	0.0457
M4	Na41	0.1890(2)	0.3791(2)	0.2710(2)	0.626(1)	0.0430
	Na42	0.1372(3)	0.2767(4)	0.2540(4)	0.390(1)	0.0430
X1	S1	0.2927(3)	0.5865(2)	0.0152(2)	0.310(1)	0.0462
X2	S2	0.2584(4)	0.6061(5)	0.1160(5)	0.152(1)	0.0327
	S22	0.2570(4)	0.6456(5)	0.1197(4)	0.171(1)	0.0327
X3	S3	0.2752(4)	0.5438(2)	0.2515(3)	0.306(1)	0.0499
X4	S4	0.2623(5)	0.6515(6)	0.3866(5)	0.170(1)	0.0438
	S44	0.2618(5)	0.6069(6)	0.3899(5)	0.169(1)	0.0438
X5	S5	0.2891(3)	0.5790(2)	0.4814(2)	0.329(1)	0.0481
X6	Cl1	0	0	0.2404(1)	1.018(1)	0.0646

(1991), who interpreted the polyanion to be S_n^{2-} with predominantly $n=3$ and positional disorder over two z positions in the cage. Thus, the distinction between the species is whether Cl^- or SH^- is the dominant occupant of the cancrinite cage. The much lower content in bystrite of K substituting for Na is not species-determining.

The minerals are unstable even in dilute acids, where they quickly discolour and decompose under H_2S evolution.

X-ray diffraction study

Powder X-ray diffraction study

The powder X-ray diffraction data for the minerals (Table 2) were collected using a diffractometer D8 ADVANCE Bruker equipped with a Göbel mirror and VÄNTEC-1 PSD detector with radial Soller slits on the diffraction beam. Data were recorded in step scan mode in the 2θ range from 5 to 70° , using $CuK\alpha$ radiation. Experimental conditions were

following: 40 kV, 40 mA, time per step = 1 s and step size = $0.02^\circ 2\theta$.

The unit-cell parameters of sulfhydrylbystrite, refined using *TOPAS 4* (Bruker, 2008), are $a = 12.958(1) \text{ \AA}$, $c = 10.765(1) \text{ \AA}$, $V = 1565.38(1) \text{ \AA}^3$. As sulfhydrylbystrite is intergrown closely with associated minerals (calcite, phlogopite and diopside), the powder diffraction data were obtained on material carrying minor impurity phases. Therefore additional and superposed lines can be observed on the diffraction patterns of the mineral.

The unit-cell parameters of bystrite are $a = 12.852(1) \text{ \AA}$, $c = 10.692(1) \text{ \AA}$, $V = 1529.39(1) \text{ \AA}^3$.

Structural determination and refinement

A fragment of yellowish-orange sulfhydrylbystrite crystal was mounted on a Bruker AXS D8 VENTURE dual source diffractometer with a Photon 100 detector under monochromatized $MoK\alpha$ radiation. Three sets of 20 frames were

TABLE 5a. Anisotropic displacement parameters (\AA^2) of sulfhydrylbystrite.

Site	Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
T1	Si1	0.0110(2)	0.0079(2)	0.0074(3)	-0.0004(2)	-0.0001(2)	0.0052(2)
T2	Si2	0.0083(2)	0.0084(20)	0.0079(2)	0.0001(2)	0.0011(2)	0.0045(2)
T3	Al1	0.0089(2)	0.0081(3)	0.0090(3)	0.0009(2)	-0.0010(2)	0.0040(2)
T4	Al2	0.0077(3)	0.0112(3)	0.0070(3)	-0.0001(2)	0.0000(2)	0.0050(2)
	O1	0.0267(5)	0.0206(5)	0.0204(5)	0.0005(4)	0.0065(5)	0.0106(4)
	O2	0.0207(5)	0.0138(5)	0.0321(5)	-0.0055(4)	-0.0065(4)	0.0102(4)
	O3	0.0218(5)	0.0209(5)	0.0110(5)	-0.0058(4)	0.0008(4)	0.0085(4)
	O4	0.0221(5)	0.0219(5)	0.0045(5)	0.0038(4)	-0.0057(4)	0.0085(4)
	O5	0.0202(5)	0.0115(4)	0.0341(5)	0.0040(4)	0.0032(5)	0.0100(4)
	O6	0.0344(5)	0.0153(5)	0.0367(5)	0.0010(4)	0.0004(5)	0.0179(4)
	O7	0.0150(5)	0.0194(4)	0.0248(4)	0.0010(5)	0.0011(4)	0.0118(4)
	O8	0.0210(5)	0.0273(5)	0.0097(5)	-0.0076(4)	0.0043(4)	0.0108(4)
M1	Ca1	0.0145(2)	0.0145(2)	0.0247(3)	0	0	0.00723(8)
M2	Na2	0.0150(3)	0.0150(3)	0.0427(5)	0	0	0.0075(1)
M3	K30	0.0241(8)	0.0257(8)	0.0144(8)	0.0026(8)	-0.0054(8)	-0.0005(8)
	Na31	0.0313(6)	0.0280(6)	0.0273(5)	0.0056(5)	-0.0056(5)	-0.0068(5)
	Na32	0.0313(6)	0.0280(6)	0.0273(5)	0.0056(5)	-0.0056(5)	-0.0068(5)
M4	K40	0.0247(5)	0.0474(4)	0.0294(3)	-0.0018(6)	-0.0008(4)	0.0239(5)
	Na41	0.0214(5)	0.0404(6)	0.0173(5)	-0.0029(6)	-0.0015(5)	0.0180(5)
	Na42	0.0214(5)	0.0404(6)	0.0173(5)	-0.0029(6)	-0.0015(5)	0.0180(5)
X1	S1	0.0214(6)	0.0328(6)	0.0324(6)	-0.0066(6)	-0.0155(6)	0.0081(5)
	S11	0.0214(6)	0.0328(6)	0.0324(6)	-0.0066(6)	-0.0155(6)	0.0081(5)
X2	S2	0.0340(6)	0.0524(6)	0.0560(6)	0.0091(6)	0.0072(6)	0.0117(6)
	S22	0.0340(6)	0.0524(6)	0.0560(6)	0.0091(6)	0.0072(6)	0.0117(6)
X3	S3	0.0929(8)	0.0358(7)	0.0325(7)	-0.0018(8)	-0.0018(7)	0.0149(8)
X4	S4	0.0318(6)	0.0557(6)	0.0349(6)	0.0008(6)	-0.0047(6)	0.0173(6)
	S44	0.0318(6)	0.0557(6)	0.0349(6)	0.0008(6)	-0.0047(6)	0.0173(6)
X5	S5	0.0730(6)	0.0190(6)	0.0322(6)	-0.0068(5)	0.0042(6)	-0.0018(6)
	S55	0.0730(6)	0.0190(6)	0.0322(6)	-0.0068(5)	0.0042(6)	-0.0018(6)
X6	S6	0.0965(5)	0.0965(5)	0.0181(4)	0	0	0.0483(2)

used for initial cell determination, whereas complete data collections were accomplished by several φ and ω scans with 0.5° rotation, 9 s exposure time per frame and a crystal-to-detector distance of 40 mm. The data collection strategies were optimized by the *APEX2* program suite (Bruker, 2003) and the reflection intensities were extracted and corrected for Lorentz-polarization by the *SAINTE* package (Bruker, 2007). A semi-empirical absorption correction was applied by means of the *SADABS* software (Sheldrick, 2003). The *XPREP* software assisted in the determination of the space group and in the calculation of the intensity statistics. Finally, least-squares refinements were performed using the program *CRYSTALS* (Betteridge *et al.*, 2003). Information concerning the data collection and refinement are listed in Table 3.

The refined parameters were: scale factors, atomic positions, occupancies and atomic

displacement factors. Starting atomic coordinates of framework anions (O) and cations (T) were taken from Pobedimskaya *et al.* (1991), while the extra-framework atoms were found successively in difference-Fourier maps. The extra-framework cation sites are labelled as 'M'; those situated in the centre of the bases of the cages (M1, M2) and within the cages (M3, M4); and as 'X' the extra-framework anion sites within the cages. Ionized X-ray scattering curves were employed for non-tetrahedral cations and anions, whereas ionized vs. neutral species were used for Si, Al and O (Hawthorne *et al.*, 1995). At tetrahedral sites the use of restraints (Watkin, 1994) allowed the occupancy to assume values greater or less than 1.

In anisotropic refinement the *R* values converged to $R \approx 6\%$. Calculated difference-Fourier maps showed significant residual electron density: the highest peaks ($\sim 2-4 e^-/\text{\AA}^3$) were found at $\sim 0.8-1.5 \text{\AA}$ from M3 and M4 sites, indicating atom

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TABLE 5*b*. Anisotropic displacement parameters (\AA^2) of bystrite.

Site	Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
T1	Si1	0.0076(1)	0.0057(1)	0.0072(2)	0.000(1)	0.0006(1)	0.0043(1)
T2	Si2	0.0055(1)	0.0056(1)	0.0067(2)	0.0003(1)	-0.0009(1)	0.0028(1)
T3	Al1	0.0060(2)	0.0057(2)	0.0072(2)	-0.0008(1)	-0.0007(1)	0.0030(1)
T4	Al2	0.0051(2)	0.0077(2)	0.0068(2)	0.0003(1)	-0.0002(1)	0.0031(1)
	O1	0.0174(4)	0.0212(4)	0.0084(4)	0.0049(3)	0.0053(3)	0.0117(3)
	O2	0.0203(4)	0.0089(3)	0.0246(4)	-0.026(3)	-0.0047(4)	0.0105(3)
	O3	0.0230(4)	0.0226(4)	0.0101(4)	-0.0019(3)	0.0055(3)	0.0149(3)
	O4	0.0125(4)	0.0212(4)	0.0085(4)	0.0039(3)	-0.0015(3)	0.0077(3)
	O5	0.0158(4)	0.0082(3)	0.0201(4)	-0.0004(3)	-0.0006(3)	0.0074(3)
	O6	0.0235(4)	0.0099(3)	0.0215(4)	0.0004(3)	0.0003(4)	0.0124(3)
	O7	0.0107(4)	0.0232(4)	0.0278(4)	0.0035(4)	0.0020(3)	0.0120(3)
	O8	0.0189(4)	0.0235(4)	0.0111(4)	-0.0039(4)	0.0020(3)	0.0125(3)
M1	Ca1	0.0123(1)	0.0123(1)	0.0151(3)	0	0	0.00617(7)
M2	Na2	0.0139(2)	0.0139(2)	0.0317(6)	0	0	0.0070(1)
M3	Na31	0.0302(5)	0.0348(5)	0.0338(5)	0.0171(5)	-0.0155(5)	-0.0124(4)
	Na32	0.0302(5)	0.0348(5)	0.0338(5)	0.0171(5)	-0.0155(5)	-0.0124(4)
M4	Na41	0.0350(4)	0.0780(5)	0.0326(5)	0.0069(5)	0.0038(4)	0.0408(4)
	Na42	0.0350(4)	0.0780(5)	0.0326(5)	0.0069(5)	0.0038(4)	0.0408(4)
X1	S1	0.0591(8)	0.0265(6)	0.0386(7)	-0.0115(6)	-0.0034(7)	0.0106(6)
X2	S2	0.0252(5)	0.0388(6)	0.0355(6)	0.0005(6)	0.0042(5)	0.0171(6)
	S22	0.0252(5)	0.0388(6)	0.0355(6)	0.0005(6)	0.0042(5)	0.0171(6)
X3	S3	0.0744(8)	0.0207(6)	0.0332(7)	-0.0006(6)	0.0001(7)	0.0078(7)
X4	S4	0.0314(5)	0.0508(6)	0.0477(6)	-0.0022(6)	-0.0035(5)	0.0195(6)
	S44	0.0314(5)	0.0508(6)	0.0477(6)	-0.0022(6)	-0.0035(5)	0.0195(6)
X5	S5	0.0708(8)	0.0287(6)	0.0282(6)	0.0045(6)	-0.0008(7)	0.0125(6)
X6	Cl1	0.0909(5)	0.0909(5)	0.0119(4)	0	0	0.0455(2)

splitting. The lower intensity peaks ($\sim 1-2 e^-/\text{\AA}^3$) were found $\sim 0.2-0.6 \text{\AA}$ from S1, S2, S4 and S5 positions, pointing to a splitting of the relevant sites. When these atoms were introduced into the refinement the values of the disagreement factor dropped to $R = 2.6\%$ ($R_w = 3.1\%$).

Likewise, the study of the bystrite crystal structure was performed. As in the case of sulfhydrylbystrite, a fragment of a suitable bystrite crystal was used for the SCXRD study and another piece was taken for EPMA. In anisotropic refinement the R values converged to $R \approx 7\%$. The difference-Fourier maps showed two highest peaks of $\sim 4 e^-/\text{\AA}^3$ and $3.5 e^-/\text{\AA}^3$ at ~ 0.8 and 1.1\AA from M3 and M4 sites, respectively, indicating cation splitting. The lower intensity peaks of $\sim 2 e^-/\text{\AA}^3$ were found close to S2 and S4 positions, respectively, pointing to a splitting of the relevant sites. The insertion of these atoms in the model allowed a further decrease of the disagreement factor to $R = 3.0\%$ ($R_w = 3.5\%$).

The structure refinement located a chain of five partially occupied S atom sites in each losod cage,

similar to that found in sulfhydrylbystrite but distinct from the pattern of S sites found in the refinement of Pobedinskaya *et al.* (1991), who represented the sulfur electron density by four partially occupied sites. Their sites S1-S4 correspond to X3, X1, X5 and X4, of the current study, respectively, but it appears that X2 electron density is merged into their highest-occupancy site X3. Our new refinement suggests that the polysulfide anion in bystrite is substantially the same as that of sulfhydrylbystrite in chain length and conformation.

The small amount of Ca^{2+} probably occupies the M2 site, as suggested by excess of Na^+ occupancy (~ 1.1) and microprobe analysis data of both minerals (Tables 4*a,b* and 1). In the same way, Na most likely partially occupies the M1 site.

Final atomic coordinates and displacement parameters are given in Table 4*a,b* and 5*a,b*, selected interatomic bond distances and angles are listed in Table 6*a,b*. Assigned site population on the basis of observed site scattering, site geometry, bond lengths and valence-sum calculation are reported in Table 7*a,b*.

TABLE 6a. Selected bond distances (Å) and angles (°) of the framework tetrahedra for sulfhydrylbystrite and bystrite.

	Sulfhydrylbystrite	Bystrite		Sulfhydrylbystrite	Bystrite
Si1–O1	1.634(2)	1.624(1)	Si2–O2	1.620(2)	1.618(2)
Si1–O6	1.591(3)	1.608(2)	Si2–O3	1.631(2)	1.610(1)
Si1–O7	1.600(2)	1.604(2)	Si2–O4	1.584(2)	1.614(1)
Si1–O8	1.588(2)	1.619(1)	Si2–O5	1.622(3)	1.617(2)
<Si1–O>	1.603(5)	1.614(3)	<Si2–O>	1.614(5)	1.615(3)
Al1–O1	1.711(3)	1.731(2)	Al2–O3	1.708(2)	1.731(2)
Al1–O2	1.727(3)	1.729(2)	Al2–O4	1.755(2)	1.738(2)
Al1–O5	1.727(2)	1.731(1)	Al2–O6	1.732(2)	1.727(2)
Al1–O8	1.756(2)	1.734(2)	Al2–O7	1.722(1)	1.720(1)
<Al1–O>	1.730(5)	1.731(4)	<Al2–O>	1.729(4)	1.729(4)
O1–Si1–O6	108.6(2)	110.08(7)	O2–Si2–O3	113.5(1)	114.56(8)
O1–Si1–O7	112.0(1)	112.27(9)	O2–Si2–O4	109.4(1)	108.21(8)
O1–Si1–O8	108.3(1)	107.10(7)	O2–Si2–O5	104.51(7)	104.40(9)
O6–Si1–O7	107.13(7)	106.84(9)	O3–Si2–O4	107.52(8)	107.73(8)
O6–Si1–O8	108.3(2)	107.94(8)	O3–Si2–O5	108.5(1)	109.04(9)
O7–Si1–O8	112.4(1)	112.56(9)	O4–Si2–O5	113.5(1)	113.03(8)
<O–Si1–O>	109.5(3)	109.5 (2)	<O–Si2–O>	109.3(2)	109.5(2)
O1–Al1–O2	110.6(2)	109.30(8)	O3–Al2–O4	108.00(9)	107.72(7)
O1–Al1–O5	114.4(1)	113.72(8)	O3–Al2–O6	106.7(1)	106.24(9)
O1–Al1–O8	106.77(8)	107.53(7)	O3–Al2–O7	113.8(1)	113.44(7)
O2–Al1–O5	101.14(7)	101.65(7)	O4–Al2–O6	107.1(1)	108.21(8)
O2–Al1–O8	114.4(1)	115.30(8)	O4–Al2–O7	113.3(1)	113.74(8)
O5–Al1–O8	109.8(1)	109.75(8)	O6–Al2–O7	107.54(7)	107.12(8)
<O–Al1–O>	109.5(3)	109.5(2)	<O–Al2–O>	109.4(2)	109.4(1)

Description of the structure

The crystal structure of sulfhydrylbystrite is illustrated in Fig. 3a and b. The framework of sulfhydrylbystrite is schematically shown in Fig. 4. It is formed by layers containing six-membered rings of Al- and Si-centred tetrahedra. On the basis of observed <T–O> distances for Si and Al-centred tetrahedra (Table 6a) it is possible to state that Si and Al regularly alternate on the T sites. In the bystrite studied, Al and Si are also distributed orderly over the tetrahedral framework positions. In contrast, Pobedinskaya *et al.*, (1991) reported disorder of Si and Al in crystal structure of bystrite. The Si–Al framework contains two types of cages: cancrinite and losod cages arranged along [001], which will be described separately.

The structural cavities host extra-framework alkaline (Na, K) and earth-alkaline (Ca) cations, and sulfhydryl, chlorine and polysulfide anionic groups.

Cancrinite cage

The cancrinite cage, [4⁶6⁵] following the International Union of Pure and Applied Chemistry (IUPAC) nomenclature (McCusker *et al.*, 2001), is hendecahedral and composed of six four-membered and five six-membered rings (Fig. 5). In the refined structures, a chain of cancrinite cages occurs at (00z).

Sulfhydrylbystrite has two cancrinite cages per unit cell, each of which contains M1 and X6 positions located on the 3-fold axis. The M1 site is occupied dominantly by Ca atoms (84% Ca and 16% Na, Table 7a). According to the results of chemical analysis and refined occupancy, it can be inferred that the X6 site is occupied by S atoms, with 7% substitution of Cl (Table 7a). The S6 atom belongs to a sulfhydryl group (SH)[–] as indicated by bond-valence calculations (S6 site receives ~1.1 vu instead of ~1.9 vu, hypothesized for this site in the case of S^{2–} presence, Table 7a). We did not find H

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TABLE 6b. Selected bond distances (Å) and angles (°) for extra-framework polyhedra and anion clusters of sulfhydrilbystrite and bystrite.

Sulfhydrilbystrite		Bystrite		Sulfhydrilbystrite		Bystrite	
Polyhedra							
M1				M2			
Ca1–O2 (×3)	2.585(2)	Ca1–O2 (×3)	2.720(1)	Na2–O6	2.877(2)	Na2–O6	2.860(2)
Ca1–O5 (×3)	2.608(2)	Ca1–O5 (×3)	2.473(1)	Na2–O6 (×2)	2.876(1)	Na2–O6 (×2)	2.859(1)
Ca1–S6	2.668(3)	Ca1–Cl1	2.647(2)	Na2–O7	2.421(2)	Na2–O7	2.428(2)
Ca1–S6	2.717(3)	Ca1–Cl1	2.699(2)	Na2–O7 (×2)	2.422(2)	Na2–O7 (×2)	2.429(1)
<Ca1–O>	2.597(5)	<Ca1–O>	2.570(2)	Na2–S1 (×3)	2.997(8)	Na2–S1 (×3)	3.088(3)
<Ca1–S>	2.693(4)	<Ca1–Cl1>	2.673(3)	Na2–S11 (×3)	3.010(8)		
				Na2–S5 (×3)	2.987(6)	Na2–S5 (×3)	2.919(3)
				Na2–S55 (×3)	3.12(1)		
				<Na2–O>	2.649(4)	<Na2–O>	2.644(3)
				<Na2–S>	3.03(3)	<Na2–S>	3.004(7)
M3				M4			
K30–Na31	0.65(1)			K40–Na41	0.70(1)		
K30–Na32	1.26(1)			K40–Na42	1.490(3)		
Na31–Na32	0.62(1)	Na31–Na32	0.679(6)	Na41–Na42	0.79(1)	Na41–Na42	1.154(5)
K30–O1	2.726(5)			K40–O1	2.796(3)		
K30–O3	2.599(5)			K40–O3	2.785(3)		
K30–O4	2.740(5)			K40–O4	2.808(3)		
K30–O6	2.904(7)			K40–O8	2.773(3)		
K30–O6	2.908(7)			K40–S1	3.227(7)		
K30–O8	2.578(5)			K40–S11	3.246(7)		
<K30–O>	2.74(1)			K40–S2	3.276(7)		
				K40–S22	3.306(9)		
Na31–O1	2.554(4)	Na31–O1	2.455(2)	K40–S4	3.322(9)		
Na31–O3	2.599(4)	Na31–O3	2.714(2)	K40–S44	3.300(6)		
Na31–O4	2.576(4)	Na31–O4	2.437(2)	K40–S5	3.218(4)		
Na31–O6	2.810(6)	Na31–O6	2.544(3)	K40–S55	3.428(9)		
Na31–O6	2.847(6)	Na31–O6	3.156(3)	K40–S55	3.56(1)		
Na31–O8	2.584(4)	Na31–O8	2.706(2)	<K40–O>	2.791(6)		
Na31–S1	3.16(1)	Na31–S1	2.983(5)	<K40–S>	3.32(2)		
Na31–S11	3.08(1)	Na31–S1	2.993(5)				
Na31–S2	2.99(1)	Na31–S2	2.696(8)	Na41–O1	2.63(2)	Na41–O1	2.731(3)
Na31–S22	2.96(1)	Na31–S22	2.680(7)	Na41–O2	2.89(2)	Na41–O2	2.684(3)
Na31–S4	2.99(1)			Na41–O3	2.62(2)	Na41–O3	2.553(3)
Na31–S44	3.02(1)			Na41–O4	2.70(2)	Na41–O4	2.745(3)
Na31–S5	3.368(9)			Na41–O5	2.81(2)	Na41–O5	3.338(3)
Na31–S5	3.462(9)			Na41–O8	2.59(2)	Na41–O8	2.506(3)
Na31–S55	3.10(2)			Na41–S2	3.86(1)	Na41–S2	3.573(5)
<Na31–O>	2.66(1)	<Na31–O>	2.669(4)	Na41–S22	3.87(2)	Na41–S22	3.481(7)
<Na31–S>	3.13(3)	<Na31–S>	2.84(1)	Na41–S4	3.91(1)	Na41–S4	3.373(8)
				Na41–S44	3.91(2)	Na41–S44	3.430(6)
						Na41–S5	3.164(3)
Na32–O1	2.578(6)	Na32–O1	2.376(3)	<Na41–O>	2.71(5)	<Na41–O>	2.760(7)
Na32–O3	2.706(6)	Na32–O3	2.794(3)	<Na41–S>	3.89(3)	<Na41–S>	3.40(1)
Na32–O4	2.596(6)	Na32–O4	2.374(3)				
Na32–O6	2.859(8)	Na32–O6	2.474(4)	Na42–O1	2.664(5)	Na42–O1	2.882(5)
Na32–O6	2.922(8)	Na32–O6	3.148(4)	Na42–O2	2.576(6)	Na42–O2	2.433(5)
Na32–O8	2.703(6)	Na32–O8	2.784(3)	Na42–O3	2.664(5)	Na42–O3	2.373(5)
Na32–S5	2.78(1)	Na32–S4	2.961(9)	Na42–O4	2.665(5)	Na42–O4	2.869(4)
Na32–S5	2.87(1)	Na32–S44	2.953(9)	Na42–O5	2.568(6)	Na42–O5	2.729(5)

(continued)

TABLE 6*b*. (contd.)

Sulfhydrylbystrite		Bystrite		Sulfhydrylbystrite		Bystrite	
		Na32–S5	3.076(6)	Na42–O8	2.661(5)	Na42–O8	2.383(5)
		Na32–S5	3.088(6)	Na42–S3	2.866(3)	Na42–S3	2.974(5)
<Na32–O>	2.73(2)	<Na32–O>	2.658(8)	Na42–S6	3.139(2)	Na42–Cl1	3.083(5)
<Na32–S>	2.83(2)	<Na32–S>	3.02(2)	<Na42–O>	2.63(1)	<Na42–O>	2.61(1)
				<Na42–S>	3.003(4)		
S–cluster							
S1–S11	0.573(7)			S1–S2	2.08(1)	S1–S2	2.056(6)
S2–S22	0.68(1)	S2–S22	0.52(1)	S2–S3	1.90(1)	S2–S3	2.060(7)
S4–S44	0.71(1)	S4–S44	0.57(1)	S3–S4	1.907(9)	S3–S4	2.064(8)
S5–S55	0.78(1)			S4–S5	2.088(9)	S4–S5	2.054(7)
S5–S55	0.87(2)						
S11–S22	2.055(8)			S1–S22	1.98(1)	S1–S22	2.082(5)
S22–S3	1.95(1)	S22–S3	2.014(7)	S11–S2	1.97(1)		
S3–S44	1.893(9)	S3–S44	2.088(6)	S4–S55	1.73(2)		
S44–S55	1.79(1)			S44–S5	2.058(7)	S44–S5	2.047(6)
S1–S2–S3	113.8(4)	S1–S2–S3	102.8(3)	S11–S2–S3	106.2(4)		
S2–S3–S4	137.5(3)	S2–S3–S4	108.6(3)	S2–S3–S44	119.2(4)	S2–S3–S44	89.8(3)
S3–S4–S5	110.5(4)	S3–S4–S5	101.1(2)	S3–S44–S5	109.9(4)	S3–S44–S5	101.7(3)
S11–S22–S3	114.2(4)			S1–S22–S3	106.9(5)	S1–S22–S3	102.4(2)
S22–S3–S44	137.1(2)	S22–S3–S44	109.4(2)	S22–S3–S4	120.694	S22–S3–S4	88.8(3)
S3–S44–S55	119.9(5)			S3–S4–S55	122.3(5)		
Torsion angles							
		<i>trans</i> -isomer				<i>cis</i> -isomer	
S1S2S3/ S2S3S4	52.6(8)	S1S2S3/ S2S3S4	77.0(3)	S1S2S3/ S2S3S44	99.7(5)	S1S2S3/ S2S3S44	121.0(3)
S2S3S4/ S3S4S5	55.3(8)	S2S3S4/ S3S4S5	75.9(3)	S2S3S44/ S3S44S5	106.9(5)	S2S3S44/ S3S44S5	120.0(3)
S11S22S3/ S22S3S44	47.7(8)			S11S2S3/ S2S3S44	114.7(5)		
S22S3S44/ S3S44S55	38.7(9)			S2S3S44/ S3S44S55	85.3(7)		
S1S22S3/ S22S3S44	63.1(8)	S1S22S3/ S22S3S44	78.6(3)	S1S22S3/ S22S3S4	111.6(5)	S1S22S3/ S22S3S4	121.9(3)
S11S2S3/ S2S3S4	67.6(9)			S22S3S4/ S3S4S5	103.1(5)	S22S3S4/ S3S4S5	122.5(3)
S2S3S4/ S3S4S55	32.0(1)			S11S22S3/ S22S3S4	96.2(6)		
S22S3S44/ S3S44S5	103.1(5)	S22S3S44/ S3S44S5	73.2(3)	S22S3S4/ S3S4S55	79.8(8)		

positions in the difference-Fourier map because of the low occupancy expected (1/3). The S6 atom is bonded strongly to the Ca1 cation on the one side and to a second Ca1 cation of neighbouring cancrinite cage on another side, with bond distances of 2.668(3) Å and 2.717(3) Å, respectively (Table 6*b*).

The M1 site in the bystrite structure studied is occupied by 83% Ca and 17% Na (Table 7*b*),

whereas the X6 position hosts 88% Cl and 12% (SH)[−], with <M1–X6> = 2.673(3) Å (Table 6*b*).

Losod cage

The losod cage, [4⁶6¹¹] according to IUPAC rules (McCusker *et al.*, 2001), is a 17-hedron limited by

SULFHYDRYLBYSTRITE, A NEW CANCRINITE-GROUP MINERAL

TABLE 7a. Cation and anion distribution, site-scattering values (epfu – electrons per formula unit), site assignment (apfu – atoms per formula unit), coordination number (CN), bond-valence sum (BVS (vu)), valence sum (VS (vu)), average bond-lengths (ABL (Å)) and ideal bond lengths (IBL (Å)) for extra-framework cation and anion positions of the studied sulfhydrylbystrite crystal structure.

Site		epfu _{obs}	apfu	epfu _{calc}	CN	BVS*	VS	ABL	IBL**
Extra-framework cation positions									
M1	Ca1	18.40	Ca _{0.84} Na _{0.16}	18.56	8	2.14	1.84	2.62	2.63
M2	Na2	12.21	Na _{0.85} Ca _{0.15}	12.35	8	0.99	1.15	2.74	2.67
M3	K30	12.15	K _{0.13}	2.47	6	0.92	1.01	2.74	2.76
	Na31		Na _{0.56}	6.16	8	~0.8–0.9 ^a		2.77	2.68
	Na32		Na _{0.32}	3.52	7	0.75		2.74	2.57
M4	K40	15.02	K _{0.53}	10.07	6	~1.12 ^a	0.98	3.01	3.04
	Na41		Na _{0.11}	1.21	6–8 ^a	~0.5–0.6 ^a		2.86	2.55
	Na42		Na _{0.34}	3.74	8	0.94		2.73	2.68
Extra-framework anion positions									
X1	S1,S11	72.32	S _{0.76}	12.16	11	0.42	1.78	–	–
X2	S2,S22		S _{0.95}	15.2		0.37			
X3	S3		S _{0.87}	13.92		0.21			
X4	S4,S44		S _{0.92}	14.72		0.30			
X5	S5,S55		S _{1.02}	16.32		0.45			
X6	S6	16.28	S _{0.93} Cl _{0.07}	16.07	3 ^b	1.14	1.93 ^b	–	–

*Bond-valence parameters (average) from Brown and Altermatt (1985).

**Ideal bond lengths are calculated on the basis of the ionic radii of Shannon (1976).

^aDepends on S-cluster configuration; ^bSupposes that the S anion of the S6 site is represented in form of S²⁻

TABLE 7b. Cation and anion distribution, site-scattering values (epfu – electrons per formula unit), site assignment (apfu – atoms per formula unit), coordination number (CN), bond-valence sum (BVS (vu)), valence sum (VS (vu)), average bond-lengths (ABL (Å)) and ideal bond lengths (IBL (Å)) for extra-framework cation and anion positions of the studied bystrite crystal structure.

Site		epfu _{obs}	apfu	epfu _{calc}	CN	BVS*	VS	ABL	IBL**
Extra-framework cation positions									
M1	Ca1	18.47	Ca _{0.83} Na _{0.17}	18.47	8	2.04	1.83	2.62	2.62
M2	Na2	12.18	Na _{0.87} Ca _{0.13}	12.17	8	0.82	1.13	2.73	2.67
M3	Na31	11.18	Na _{0.56} Ca _{0.02}	6.56	8	~0.7–0.8 ^a	1.02	2.71	2.68
	Na32		Na _{0.42}	4.62	7	0.80		2.75	2.56
M4	Na41	11.18	Na _{0.59} Ca _{0.02}	6.89	6–8 ^a	~0.6–0.7 ^a	1.02	2.96	2.55
	Na42		Na _{0.39}	4.29	8	0.93		2.72	2.68
Extra-framework anion positions									
X1	S1	77.28	S _{0.93}	14.88	11	0.41	1.92	–	–
X2	S2,S22		S _{0.97}	15.52		0.33			
X3	S3		S _{0.92}	14.72		0.16			
X4	S4,S44		S _{1.02}	16.32		0.35			
X5	S5		S _{0.99}	15.84		0.50			
X6	Cl1	17.31	Cl _{0.88} S _{0.12}	16.88	3 ^b	0.92	1.12 ^b	–	–

*Bond-valence parameters (average) from Brown and Altermatt (1985).

**Ideal bond lengths are calculated on the basis of the ionic radii of Shannon (1976).

^aDepends on S-cluster configuration; ^bSupposes that the S anion of the S6 site is represented in form of S²⁻

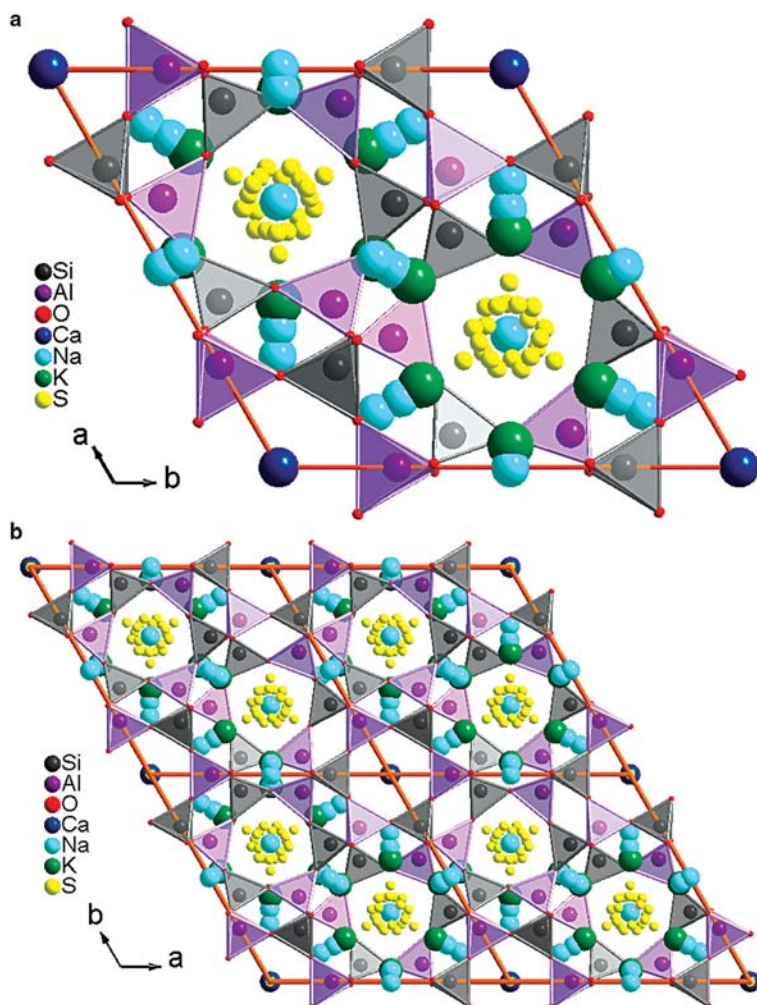


FIG. 3. Crystal structure of sulfhydrylbystrite viewed down the c axis. (a) – single unit cell; (b) – quadruple unit cell.

six four-membered and eleven six-membered rings (Fig. 6). This cage was first described from the structure of the synthetic ‘losod’ (‘low sodium’) zeolite, $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 18\text{H}_2\text{O}$ (Sieber and Meier, 1974). This type compound is the source for the LOS symbol used by the International Zeolite Association (<http://www.iza-structure.org>) to denote the corresponding tetrahedral framework, which is shared by bystrite, carbobystrite and sulfhydrylbystrite. The losod cage also occurs in many of the more complex structures in the sodalite-cancrinite supergroup (Bonaccorsi *et al.*, 2012).

The chains of losod-type cages in sulfhydrylbystrite is located at $(2/3, 1/3, z)$. The mineral has two cages of this type per unit cell.

The M2 site is positioned on the 3-fold axis in the centre of the cage base and occupied by 0.85 Na and 0.15 Ca (Table 7a). Five X positions (X1–X5, Table 4a), occupied by S and situated one after another along the axis under M2, are shifted apart the 3-fold axis, four of them are split. The short distances (S1–S1 = 1.50(1) Å, S11–S11 = 1.52(1) Å, S2–S2 = 1.76(1) Å, S22–S22 = 1.75(1) Å, S4–S4 = 1.80(1) Å, S44–S44 = 1.76(1) Å, S5–S5 = 1.52(1) Å, S55–S55 = 1.19(1) Å) and site occupancies (Table 4a) ensure the statistical distribution of corresponding sulfur atoms with a probability of 1/3. Sulfur atoms of X1, X2, X3, X4, X5 sites are bonded in sequence, forming a cluster $(\text{S}_5)^{2-}$.

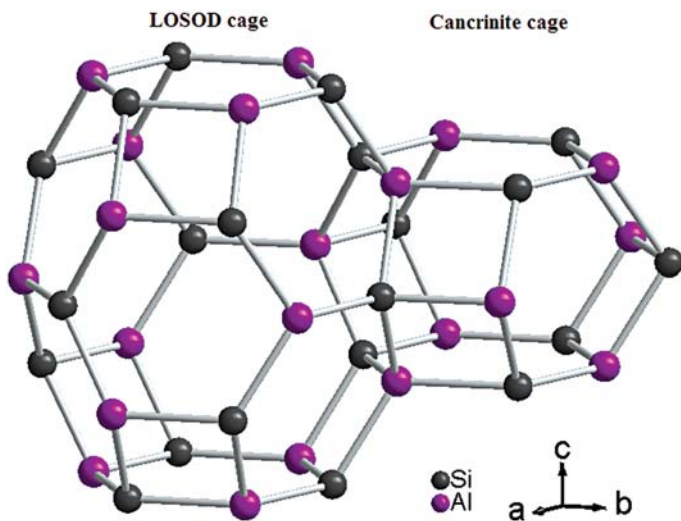


FIG. 4. Sketch of the cages in the sulfhydrylbystrite structure.

The $(S_5)^{2-}$ cluster forms a chain that is extended along [001]. However, the X1–X5 sites are split around the 3-fold axis, and sulfur atoms may occupy any of the symmetry-related subsites, so several conformational possibilities arise, depending on the position of the occupied X1 and X5 sites relative to the plane defined by X2–X3–X4. These include a *cis* isomer and right- and left-handed enantiomeric *trans* isomers (Fig. 7*a,b,c*), all of which may occur in multiple orientations around the 3-fold axis. Wong (2003) notes that unbranched S_n^{2-} clusters tend to resemble fragments of helical chains, which suggests that the *trans* configurations are preferred.

Early studies of the $(S_5)^{2-}$ ion in simple inorganic compounds characterized it as a zigzag chain: Tl_2S_5 (Leclerc and Kabrè, 1975), K_2S_5 (Kelly and Woodwar, 1976), Rb_2S_5 (Böttcher, 1979), α - Na_2S_5 (Böttcher and Keller, 1984), $(NH_4)_2S_5$ (Schnering *et al.*, 1985) and $CsS_5 \cdot H_2O$ (Böttcher and Trampe, 1985).

The $(S_5)^{2-}$ ion has S–S bond lengths of 1.73–2.09 Å (terminal) and 1.89–1.95 Å (central) (Table 6*b*), which are somewhat shorter than those reported for pentachalcogenides structures (2.02–2.16). The S–S–S angles of the polysulfide anion in sulfhydrylbystrite vary from 106.2 to 122.3° (terminal) and from 119.2 to 137.5°

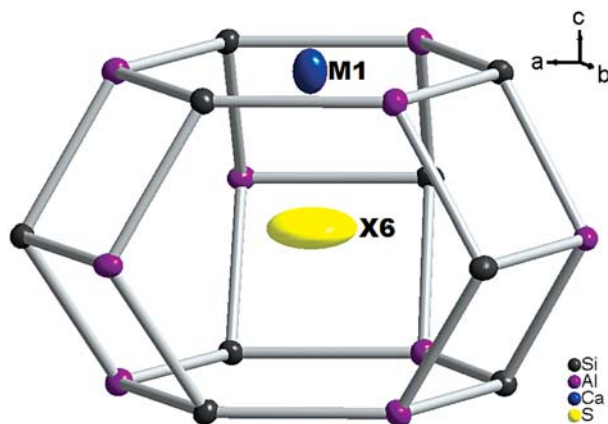


FIG. 5. Sketch of the cancrinite cage of sulfhydrylbystrite.

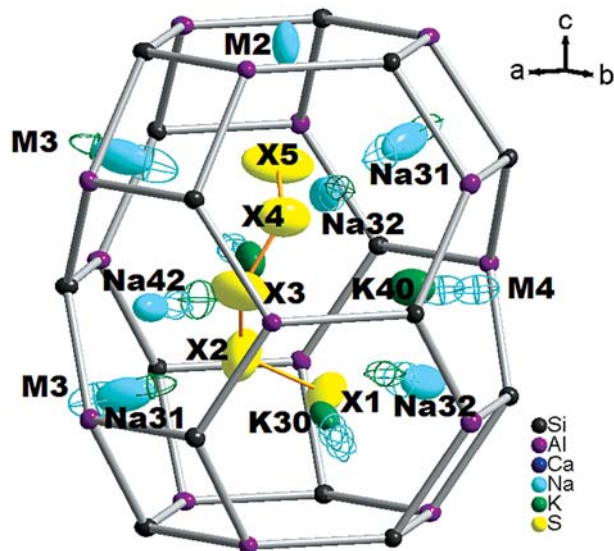


FIG. 6. Sketch of the LOSOD cage of sulfhydrylbystrite. One of the possible configurations of polysulfide ion (S_5)²⁻ is shown in the plot. Empty cation positions are indicated by open ellipses.

(central) (Table 6*b*), while S–S–S angles in M_2X_5 compounds range from 106.4 to 111.2°. Thus, the S_5 chain fragment in the mineral shows greater variation in bond angles, probably due to the different sizes of surrounding cations (Na and K). Each of the sulfur atoms in the chain may be bonded to any cation situated in the losod cage. The terminal sulfur atoms have two, their next neighbours one or two (depends on chain isomerism) and the central S atom one cation in the distance range 2.78–3.91 Å. On average, X1, X2, X3, X4 and X5 sites receive ~0.4, ~0.4, ~0.2, ~0.3 and ~0.5 valence units (vu), respectively (Table 7*a*). This contrasts with the situation in simple polysulfides, where the negative charge on the polyanion is concentrated almost completely on the terminal S atoms (Wong, 2003; Steudel, 2003). The site occupancies of Table 7*a* suggest that not all five S atoms are present in all cases, suggesting that some smaller polymers (S_n)²⁻ with $n = 1-4$ may be present.

K^+ and Na^+ cations are located around the sulfur polyanion. M3 cations around the terminal and M4 cations around the central S atoms are distributed into three split sites: K30, Na31, Na32 and K40, Na41, Na42, respectively. Owing to the very short distances between the three positions (0.6–1.5 Å, Table 6*b*), only one can be occupied in any given group of them. The splitting arises from the different conformations of S_5^{2-}

anion and their arrangement around the 3-fold axis of the structure.

Atoms of M3 are situated close to the planes of the lateral six-membered rings and simultaneously belong to two neighbouring losod cages. The K30 site has low occupancy (~0.13 apfu), and is coordinated by only the framework oxygen atoms with $\langle K30-O \rangle = 2.74(1)$ Å. The Na31 site is occupied more fully (~0.56 apfu), makes two bonds to terminal sulfur atoms: X1 and X2 or X4 and X5 with average 3.05 Å or 3.16 Å, respectively. The Na32 site is coordinated by six oxygens and can also make two bonds to S_5 atoms; it has short Na32–S4, Na32–S44 and Na32–S55 distances of 2.38(1) Å, 2.42(1) Å and 2.49(1) Å, respectively. However, as Na32 has a relatively low occupancy (~0.32 apfu), and the S4, S44 and S55 positions are partially occupied (~0.15, ~0.16 and ~0.10 apfu, respectively), we assume that these contacts never occur.

The most highly occupied M4 site is K40 (~0.53 apfu). The K40 site is shifted appreciably towards the centre of the losod cage, with $\langle K40-O \rangle = 2.791(6)$ Å. It makes two long, but plausibly bonded, distances to S atoms at 3.2–3.6 Å (Table 6*b*). However, it is also at the physically impossible distance of 1.376 Å from one of the S3 positions. Hence, the potential S2, S22, S4 and S44 neighbours at 2.72–2.76 Å that are coupled to this S3 atom cannot be present, either. The Na41

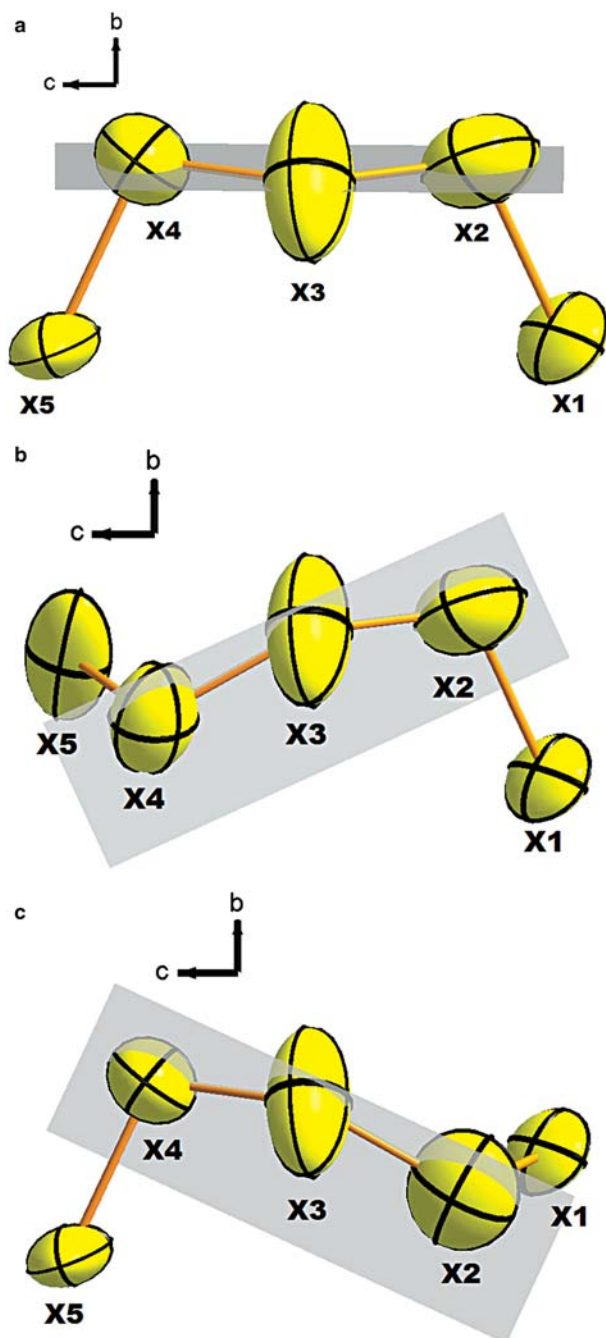


FIG. 7. Polysulfide ion $(S_5)^{2-}$ of sulfhydrylbystrite. (a) *cis* configuration, (b) *trans* configuration (left), (c) *trans* configuration (right).

atom is bonded to one or two S atoms depending on the configuration of the nearby polyanion. Long

distances from Na41 to O and S (2.86 Å) and a low valence sum for Na at Na41 (0.5–0.6 vu) indicate

TABLE 8. Comparison of sulfhydrylbystrite, bystrite and carbobystrite.

	Sulfhydrylbystrite This work	Bystrite This work	Carbobystrite Khomyakov <i>et al.</i> (2010)
Formula	Na ₅ K ₂ Ca(Al ₆ Si ₆ O ₂₄)(S ₅)(SH)	Na ₇ Ca(Al ₆ Si ₆ O ₂₄)(S ₅)Cl	Na ₈ (Al ₆ Si ₆ O ₂₄)CO ₃ ·4H ₂ O
[cancrinite cage content]	[Ca(SH)]	[CaCl]	[NaH ₂ O]
[losod cage content]	[Na ₅ K ₂ (S ₅)]	[Na ₇ (S ₅)]	[Na ₇ (H ₂ O,CO ₃)]
<i>a</i>	12.957(1)	12.853(1)	12.668(1)
<i>b</i>	10.771(1)	10.691(1)	10.340(1)
<i>V</i>	1566.0(1)	1529.4	1437.0(2)
<i>Z</i>	2	2	2
Crystal system	Trigonal	Trigonal	Trigonal
Space group	<i>P</i> 31 <i>c</i>	<i>P</i> 31 <i>c</i>	<i>P</i> 31 <i>c</i>
D _{meas} (g/cm ³)	2.39	2.41	2.37
Colour	yellow to orange	yellow	colourless
Optical characteristics	uniaxial (+) ω = 1.661 ε = 1.584	uniaxial (+) ω = 1.662 ε = 1.585	uniaxial (-) ω = 1.500 ε = 1.488

very weak bonding to Na in this position, consistent with its very low occupancy (0.11 apfu). The Na42 site is coordinated by six framework oxygen atoms and located between two sulfur positions (X3 and X6), with distances Na42–S3 = 2.866(3) Å and Na42–S6 = 3.139(2) Å, and is not significantly underbonded (0.96 vu; Table 7*a*).

Similarly, in the crystal structure of bystrite, sulfur atoms in the losod cage are located over five levels along the *c* axis, forming the S₅ polyanion with S–S bond lengths of 2.05–2.08 Å (terminal) and 2.01–2.09 Å (central), and S–S–S angles of 101.1 to 102.8° (terminal) and from 88.8 to 109.4° (central) (Table 6*b*). The distances and angles of the S₅ chain in bystrite are more regular with respect to those of sulfhydrylbystrite. Na⁺ cations are located in splitting M3 (Na31–Na32 = 0.70 Å) and M4 (Na41–Na42 = 1.15 Å) positions. The split positions have a close relative occupancy of ~0.6:0.4 for both Na31:Na32 and Na41:Na42 ratios (Table 4*b*, 7*b*).

Tables 4*a,b* and 6*a,b* show that the structure of bystrite is close to the sulfhydrylbystrite structure. However, the anion that occupies the cancrinite cage is 87% Cl⁻ and 13% SH⁻ in bystrite, but 93% SH⁻ and 7% Cl⁻ in sulfhydrylbystrite. The two species are distinguished by the different predominant occupant of this site, in accord with the criteria of the Commission on New Minerals, Classification and Nomenclature of the International Mineralogical Association. Other differences between these species include: (1) The M4 position in the losod cage of sulfhydrylbystrite

is occupied by 53% K, 45% Na, while this position is filled completely by Na in bystrite, which contains almost no K (only ~0.04 apfu). (2) The columns of cancrinite cages in bystrite contain chains of –Ca–Cl–Ca–Cl ions, which are already known in the related structures of afghanite and tounkite. However, sulfhydrylbystrite contains chains –Ca–SH–Ca–SH–, currently unique in minerals. The amount of chlorine and sulfur in bystrite and sulfhydrylbystrite, detected by X-ray analysis confirms the results of the EPMA of the minerals. Another difference between bystrite and sulfhydrylbystrite is a diverse filling of the M4 cationic structural site in the losod cage. The M4 position in sulfhydrylbystrite is occupied by 53% K atoms, with 45% substitution of Na. The bystrite studied contains practically no K (only ~0.04 apfu), and the M4 position in the mineral is completely filled by Na.

Taking into account the criteria that at least one structural site in the potential new mineral should be predominantly occupied by a different chemical component than that which occurs in the equivalent site in an existing mineral species (Nickel and Grice, 1998), it is argued that bystrite and sulfhydrylbystrite are different mineral species.

Conclusion

The results obtained allow us to understand the cause of the discordance between the chemical and the structural formulas of bystrite in Pobedimskaya

et al. (1991). The comparison shows that the chemical formula of bystrite, reported by Pobedimskaya *et al.* (1991), corresponds to the composition of sulfhydrylbystrite, as it contains a sufficiently large amount of potassium and has no chlorine. Conversely, a complete coincidence of the cell parameters of bystrite specimens published by Pobedimskaya *et al.* (1991) and studied by us, shows that these are the same mineral. The unit-cell parameters of the bystrite and sulfhydrylbystrite, described and compared here, are different. Thus, Pobedimskaya *et al.* (1991) in their description of bystrite shows the characteristics of two minerals: chemical composition data correspond to sulfhydrylbystrite, while cell parameters and structure of the mineral were defined for a bystrite crystal.

Sulfhydrylbystrite is a member of the cancrinite group, chemically related to bystrite and carbobystrite and topologically isotopic with them. The main properties of these minerals are compared in Table 8. Sulfhydrylbystrite is very similar to bystrite in physical properties, but differs significantly from carbobystrite. Three types of cation-anion chain occur in the cancrinite cages of the minerals of the bystrite subgroup: $-Ca-Cl-Ca-Cl-$ in bystrite, $-Na-H_2O-Na-H_2O-$ in carbobystrite and $-Ca-SH-Ca-SH-$ in the sulfhydrylbystrite structure.

Sulfhydrylbystrite is the first cancrinite-group mineral with $(SH)^-$ groups in cancrinite cages, and indeed the first mineral to contain this anion. In addition, the pentasulfide anion S_5^{2-} is confirmed for the first time in minerals, occurring in both sulfhydrylbystrite and bystrite. In the case of bystrite, this is a new interpretation of the polysulfide content, arising from our new structure determination.

The accuracy of the determination of the refractive indexes, density and chemical composition of the mineral is confirmed by an 'excellent' compatibility index (Mandarino, 1981): $(1-K_p/K_C) = 0.031$ for measured density and $(1-K_p/K_C) = 0.022$ for the density estimated from the empirical formula.

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