

**CHLORBARTONITE, $K_6Fe_{24}S_{26}(Cl,S)$, A NEW MINERAL SPECIES
FROM A HYDROTHERMAL VEIN IN THE Khibina MASSIF, KOLA PENINSULA,
RUSSIA: DESCRIPTION AND CRYSTAL STRUCTURE**

VICTOR N. YAKOVENCHUK AND YAKOV A. PAKHOMOVSKY

Geological Institute, Kola Science Centre of the Russian Academy of Sciences, Apatity 184200, Russia

YURY P. MEN'SHIKOV

Laplandia Minerals Ltd., Apatity 184200, Russia

GREGORY YU. IVANYUK

Geological Institute, Kola Science Centre of the Russian Academy of Sciences, Apatity 184200, Russia

SERGEY V. KRIVOVICHEV[§] AND PETER C. BURNS

*Department of Civil Engineering and Geological Sciences, University of Notre Dame,
156 Fitzpatrick Hall, Notre Dame, Indiana 46556-5602, U.S.A.*

ABSTRACT

Chlorbartonite, ideally $K_6Fe_{24}S_{26}(Cl,S)$, is a new potassium iron sulfide chloride found as an accessory mineral in a microcline – pectolite – sodalite – aegirine vein within feldspathic urtite at Mount Koashva, Khibina massif, Kola Peninsula, Russia. The mineral occurs as roundish grains up to 2 cm across included in sodalite and natrolite crystals; it is associated with djerfisherite and rasvumite. Chlorbartonite is weakly magnetic, brittle, and has a conchoidal fracture. Cleavage and parting were not observed. Macroscopically, the mineral is opaque, brown-black, with a black streak and submetallic luster. In reflected light, it appears optically isotropic, yellowish brown, and without internal reflections; interpolated values of reflectance (R , %) at the standard wavelengths (nm) are: 10.8 (470), 13.5 (546), 15.1 (589), and 17.2 (650). The hardness VHN_{40} is 203–212, average 207 kg/mm^2 ; the Mohs hardness is 4. The density is 3.70 g/cm^3 (measured) and 3.65 g/cm^3 (calculated). The electron-microprobe analysis of six grains gave, as an average composition: S 33.84, Cl 0.99, K 9.62, Fe 54.09, Co 0.04, Cu 0.57, total 99.15 wt.%. The empirical formula calculated on the basis of a total of 57 atoms is $K_{6.08}(Fe_{23.93}Cu_{0.22}Co_{0.01})_{\Sigma 24.16}S_{26.00}(Cl_{0.69}S_{0.07})_{\Sigma 0.76}$, which yields an ideal formula of $K_6Fe_{24}S_{26}(Cl,S)$. The mineral is tetragonal, $I4/mmm$, a 10.3810(8), c 20.614(2) Å, V 2221.5(3) Å³, Z = 2. The strongest eight lines in the X-ray powder-diffraction pattern [d in Å (I)(hkl)] are: 9.25(33)(101), 5.97(65)(112), 3.121(45)(312), 2.986(100)(224), 2.380(38)(332), 2.374(57)(316), 1.834(51)(440), and 1.830(82)(408). The crystal structure has been refined to an $R1$ of 0.020 (447 unique observed reflections with $F_o \geq 4\sigma F_o$). The structure consists of a framework of the Fe_8S_{14} clusters of eight edge-sharing FeS_4 tetrahedra. The framework has large cavities occupied by ClK_6 octahedra. As the name indicates, chlorbartonite is the Cl-dominant analogue of bartonite.

Keywords: chlorbartonite, new mineral species, bartonite, Khibina alkaline massif, Kola Peninsula, Russia.

SOMMAIRE

La chlorbartonite, une nouvelle espèce de sulfure chloruré de potassium et de fer dont la formule idéale est $K_6Fe_{24}S_{26}(Cl,S)$, est un minéral accessoire dans une veine à microcline – pectolite – sodalite – aegirine dans une urtite feldspathique au mont Koashva, complexe alcalin de Khibina, péninsule de Kola, en Russie. La chlorbartonite se présente en grains xénomorphes atteignant deux cm dans des cristaux de sodalite et de natrolite; elle est associée à djerfisherite et rasvumite. Elle est faiblement magnétique, cassante, et possède une fracture conchoïdale. Nous ne décelons aucun clivage ou plan de séparation. Du point de vue macroscopique, le minéral est opaque, brun à noir, avec une rayure noire et un éclat sub-métallique. En lumière réfléchie, la

[§] *Permanent address:* Department of Crystallography, St. Petersburg State University, St. Petersburg 199034, Russia. *E-mail address:* skrivovi@mail.ru. *Current mailing address:* Mineralogisch-Petrographisches Institut, Christian-Albrechts-Universität Kiel, Olshausenstrasse 40, D-24118 Kiel, Germany.

chlorbartonite est optiquement isotrope, brun jaunâtre, sans réflexions internes. Nous présentons ici des valeurs de la réflectance (R , %) aux longueurs d'onde standards, telles qu'obtenues par interpolation (nm): 10.8 (470), 13.5 (546), 15.1 (589), et 17.2 (650). La dureté VHN₄₀ est 203–212, en moyenne 207 kg/mm²; la dureté de Mohs est 4. La densité est 3.70 g/cm³ (mesurée) et 3.65 g/cm³ (calculée). Une analyse à la microsonde électronique de six grains a donné, en moyenne: S 33.84, Cl 0.99, K 9.62, Fe 54.09, Co 0.04, Cu 0.57, pour un total de 99.15% (poids). La formule empirique, calculée sur une base de 57 atomes, est K_{6.08}(Fe_{23.93}Cu_{0.22}Co_{0.01})Σ_{24.16}S_{26.00}(Cl_{0.69}So_{0.07})Σ_{0.76}, ce qui mène à la formule idéale K₆Fe₂₄S₂₆(Cl,S). Le minéral est tétragonal, $I4/mmm$, a 10.3810(8), c 20.614(2) Å, V 2221.5(3) Å³, Z = 2. Les huit raies les plus intenses du spectre de diffraction X [d en Å (hkl)] sont: 9.25(33)(101), 5.97(65)(112), 3.121(45)(312), 2.986(100)(224), 2.380(38)(332), 2.374(57)(316), 1.834(51)(440), et 1.830(82)(408). La structure cristalline a été affinée jusqu'à un résidu $R1$ de 0.020 (447 réflexions uniques observées avec $F_o \geq 4\sigma F_o$). La structure contient une trame de groupes Fe₈S₁₄ contenant huit tétraèdres Fe₄ à arêtes partagées. Cette trame possède des cavités volumineuses qu'occupent des octaèdres ClK₆. Comme le nom l'indique, la chlorbartonite est l'analogue de la bartonite à dominance de chlor.

(Traduit par la Rédaction)

Mots-clés: chlorbartonite, nouvelle espèce minérale, bartonite, complexe alcalin de Khibina, péninsule de Kola, Russie.

INTRODUCTION

Bartonite, ideally K₆Fe₂₄S₂₆(S,Cl), a rare potassium iron sulfide, was first described by Czamanske *et al.* (1981) from Coyote Peak, Humboldt County, California. Among the minerals associated with bartonite, Czamanske *et al.* (1981) found pyrrhotite, djerfisherite, erdite, rasvumite and small grains of a Cl-dominant analogue of bartonite, K₆Fe₂₄S₂₆(Cl,S). The small amounts of the latter mineral available at that time prevented its complete investigation. In 1998, a Cl-rich analogue of bartonite was found in an alkaline hydrothermal vein within feldspathic urtite at Mount Koashva, Khibina massif, Kola Peninsula, Russia. The volume of material allowed the detailed description of this phase, which was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association as a new mineral, chlorbartonite (proposal 2000–048). Cotype samples of the mineral are deposited in the Gorny Museum of St. Petersburg Mining Institute (Technical University), Russia, at the Mineralogical Museum of St. Petersburg State University, Russia, the Geological and Mineralogical Museum of the Geological Institute of the Kola Science Centre, Apatity, Russia, and in the Natural History Museum (London, UK). The aim of this paper is to report the occurrence and properties of this new mineral species.

OCCURRENCE

Chlorbartonite occurs in a microcline – pectolite – sodalite – aegirine hydrothermal vein in the heterogeneous feldspathic urtite at Mount Koashva, within the Koashva apatite–nepheline deposit of the Khibina massif. The ore zone of the Koashva deposit is made of a series of closely related lens-shaped bodies, widespread over more than 3 km. It strikes northwest, 330°–340°, and the dip is 30°–40°. The width of the ore zone as a whole decreases with depth, from 200–300 m down to several meters. The host rocks are massive urtite. Every

orebody is practically uniform and has a length up to 200 m. Lens-shaped bodies of apatite–titanite rock, up to 20 m wide, are dominant (Kamenev *et al.* 1982). The vein containing chlorbartonite is located in the upper part of the deposit, near the contact between apatite–nepheline rocks and urtite.

The chlorbartonite-bearing microcline – pectolite – sodalite – aegirine assemblage is exposed in a large vein (6.5 × 2.5 m) with a bilaterally symmetrical structure (Fig. 1; Yakovenchuk *et al.* 1999) located within the host apatite–nepheline rocks (Fig. 1, zone 1). The marginal zone (Fig. 1, zone 2) is up to 1 m wide and consists of a “giant-grained” aggregate of microcline, nepheline and sodalite, and aggregates of dark red villiamite (up to 25 cm across). Villiamite contains inclusions of lomonosovite, pectolite, aegirine, arfvedsonite, thermonatrite, and chkalovite. Small, irregularly shaped and subhedral, tabular crystals of lisitsynite (up to 0.5 mm) also are present. The intermediate zone (zone 3 in Fig. 1), up to 1 m wide, is composed of snow-white, radiating crystals of pectolite with interstitial villiamite.

The border between the 2nd and 3rd zones is marked by extremely large lenses of dark red villiamite up to 3 × 0.3 m (zone 5 in Fig. 1). These lenses also contain white, sheaf-shaped aggregates of acicular pectolite (up to 5 cm across) and dark grey spherulites of lomonosovite (up to 7 cm across), as well as other minerals: light pink or light green equant crystals of sodalite, prismatic crystals of annite (up to 6 mm across and 4 cm long), wedge-shaped pseudomorphs (up to 5 cm long) of nefedovite together with sidorenkite and lorenzenite after an unknown mineral, nacaphite, vitusite-(Ce) crystals (up to 1 cm in diameter), colorless euhedral crystals of chkalovite (up to 7 cm in diameter), light green tabular microcline, prismatic yellowish green fluorcaphite (up to 3 cm long), cubo-octahedral galena, pseudocubic cobaltite, equant aggregates of dark brown sphalerite, dark green fibrous nodules of aegirine, segregations of golden brown astrophyllite and ice-like translucent

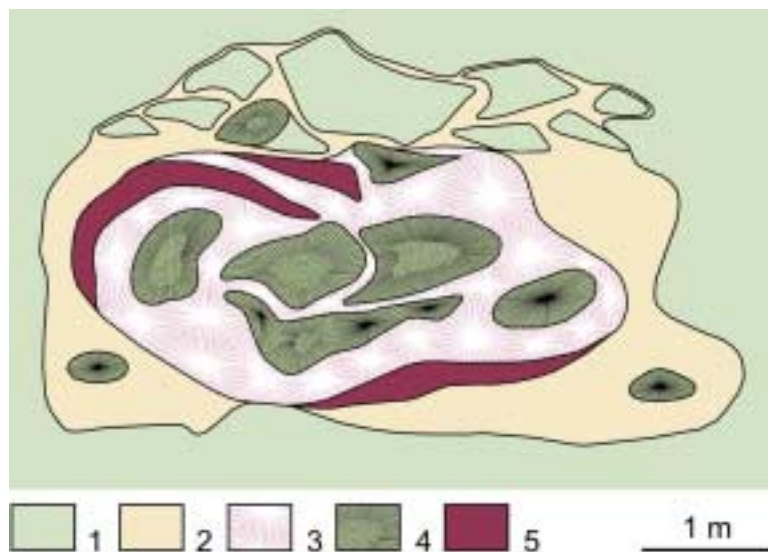


FIG. 1. Sketch of the chlorbarntonite-bearing microcline – pectolite – sodalite – aegirine vein. Legend: (1) host apatite–nepheline rocks, (2) marginal zone of microcline – nepheline – sodalite aggregate, (3) intermediate zone (snow-white radiating aggregates of pectolite), (4) aegirine-bearing zone, (5) lenses of dark red villiaumite containing crystals of chlorbarntonite, rasvumite, djerfisherite and sphalerite as inclusions within grains of light pink sodalite and light grey natrolite.

grains of natrite. When exposed to weathering, the natrite grains become covered with a crust of fine-grained thermonatrite and trona. Small flattened-prismatic crystals of rasvumite (up to 2 mm across), black-brown rounded grains of chlorbarntonite (up to 2 cm across), well-formed green crystals of burbankite (up to 5 mm long), elongate crystals of mosandrite (up to 4 cm long), and equant grains of djerfisherite and sphalerite (up to 2 mm across) occur as inclusions within light pink sodalite and light grey natrolite. Clusters (up to 4 mm in diameter) of elongate crystals of murunskite and well-formed cubic crystals of loparite-(Ce) (up to 3 mm across) occur at borders between villiaumite and microcline, sodalite and lomonosovite. Equant, apple-green grains and well-formed crystals of fluorcaphite and also grains of light brown sphalerite are common within the large blocks of villiaumite.

The core zone of the vein (zone 4 in Fig. 1) is formed of nodules of acicular aegirine (up to 1 m across) with inclusions of lamprophyllite and lomonosovite and cemented by villiaumite. Vitusite-(Ce), nacaphite, thorosteenstrupine-(Ce), natrophosphate, galena, mackinawite, djerfisherite and lemmleinite-K have also been observed in this zone.

Chlorbarntonite is a low-temperature hydrothermal mineral; it crystallized together with djerfisherite, rasvumite, natrolite and sodalite during the latest stages

TABLE 1. REFLECTANCE OF CHLORBARTONITE MEASURED IN AIR

λ (nm)	R (%)	λ (nm)	R (%)
420	9.8	580	14.8
440	9.9	600	15.6
460	10.2	620	16.4
480	10.8	640	17.1
500	11.5	660	17.8
520	12.3	680	18.4
540	13.1	700	19.0
560	14.0	720	19.5

of hydrothermal activity under conditions of high K activity (Dobrovolskaya *et al.* 1980).

PHYSICAL AND OPTICAL PROPERTIES

Chlorbarntonite forms equant grains (up to 2 cm in diameter) within sodalite (Fig. 2). The mineral is opaque brown-black, with a black streak and submetallic luster, and brittle, with a conchoidal fracture. Cleavage and parting were not observed. The hardness VHN_{40} of chlorbarntonite is 203–212, with an average of 207 kg/mm^2 , which corresponds to 4 on the Mohs scale. The measured density is 3.70 g/cm^3 (average of three mea-

surements using heavy liquid); the calculated density is 3.65 g/cm³ based on the empirical formula and the measured unit-cell parameters. The mineral is weakly magnetic. It is barely soluble in hot concentrated hydrochloric acid.

In reflected light, chlorbartonite is isotropic, yellowish brown, and without internal reflections. Reflectance values obtained in air using metallic Si as a standard are given in Table 1.

CHEMICAL COMPOSITION

The composition of chlorbartonite was determined by wavelength-dispersion spectrometry using a Cameca MS-46 electron microprobe at 20 kV and 20 nA (Geological Institute, Apatity). The following standards were used: synthetic Fe₁₀S₁₁ (S, Fe), atacamite (Cl), wadeite (K), cobalt (Co) and copper (Cu) metals. Six different grains were analyzed, with 6–10 points for each grain. The chemical composition is quite uniform. In Table 2, we give the mean chemical composition, averaged from results of 45 electron-microprobe analyses, which was taken as the composition of the grain used for the single-crystal study. The empirical formula (Table 2), calculated on the basis of the structural data and K + Fe + Cu + Co + S + Cl = 57 atoms per formula unit (*apfu*), is K_{6.08}(Fe_{23.93}Cu_{0.22}Co_{0.01})_{Σ24.16}S_{26.00}(Cl_{0.69}S_{0.07})_{Σ0.76}, which corresponds to the ideal formula, K₆Fe₂₄S₂₆(Cl,S).

CRYSTAL STRUCTURE

Data collection

A fragment of chlorbartonite with no obvious crystal forms was selected for single-crystal structure study. The crystal was mounted on a Bruker PLATFORM goniometer equipped with a 1K SMART CCD detector, with a crystal-to-detector distance of 5 cm. A hemisphere of three-dimensional data was collected using MoK α X-radiation and frame widths of 0.3° in ω , with

10 s used to acquire each frame. The unit-cell dimensions were refined on the basis of 2169 reflections (Table 3). The systematic absences of reflections are consistent with the tetragonal space-group *I4/mmm*, which was also observed for bartonite by Evans & Clark (1981). 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. A total of 4884 intensities was measured; there were 508 unique reflections ($R_{\text{INT}} = 5.9\%$), with 447 classified as observed ($F_o \geq 4\sigma F_o$).

Structure refinement

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from the *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5.1 system of programs was used for the refinement of the crystal structure on the basis of F^2 . The structure was refined starting from a model given for bartonite by Evans & Clark (1981). Refinement of the occupancies of the atom positions indicate full ($\pm 2\%$) occupancy for all positions. Refinement of all atom-position parameters, allowing for the anisotropic displacement of all atoms, and the inclusion of a refinable weighting-scheme of the structure factors, resulted in a final agreement-index ($R1$) of 2.0%, calculated for the 447 unique observed reflections ($|F_o| \geq 4\sigma F_o$), and a goodness-of-fit (S) of 1.356. The final atom-parameters are listed in Table 4, and selected interatomic distances are in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Structure description

There are two symmetrically independent Fe positions in the structure of chlorbartonite. Each Fe atom is tetrahedrally coordinated by four S atoms. The average

TABLE 2. CHEMICAL COMPOSITION OF CHLORBARTONITE

Constituent		Range <i>n</i> = 45	Standard deviation	Standard
S wt.%	33.84	33.53 – 33.87	0.15	synthetic Fe ₁₀ S ₁₁
Cl	0.99	0.95 – 1.04	0.03	atacamite
K	9.62	9.05 – 9.61	0.07	wadeite
Fe	54.09	53.87 – 54.49	0.23	synthetic Fe ₁₀ S ₁₁
Co	0.04	0.00 – 0.08	0.03	Co metal
Cu	0.57	0.51 – 0.60	0.04	Cu metal
Total	99.15			

Empirical formula: K_{6.08}(Fe_{23.93}Cu_{0.22}Co_{0.01})_{Σ24.16}S_{26.00}(Cl_{0.69}S_{0.07})_{Σ0.76}
 Ideal formula: K₆Fe₂₄S₂₆(Cl,S)

TABLE 3. CRYSTALLOGRAPHIC DATA FOR CHLORBARTONITE

<i>a</i> (Å)	10.3810(8)	Crystal size (mm)	0.24 × 0.12 × 0.10
<i>c</i> (Å)	20.614(2)	Radiation	MoK α
<i>V</i> (Å ³)	2221.5(3)	Total reflections	4884
Space group	<i>I4/mmm</i>	Unique $F_o \geq 4\sigma F_o$	447
F_{000}	2342	$R1$	0.020
μ (cm ⁻¹)	94.14	$wR2$	0.049
D_{calc} (g/cm ³)	3.65	S	1.356

Note: $R1 = \Sigma F_o - F_c / \Sigma F_o$; $wR2 = \{\Sigma [w(F_o^2 - F_c^2)] / \Sigma [w(F_o^2)]\}^{1/2}$;
 $w = 1/[\sigma^2(F_o^2) + (0.0161P)^2 + 1.9P]$, where $P = (F_o^2 + 2F_c^2)/3$;
 $S = \{\Sigma [w(F_o^2 - F_c^2)] / (n - p)\}^{1/2}$, where n is the number of reflections,
 and p is the number of refined parameters.

TABLE 4. ATOM COORDINATES AND DISPLACEMENT PARAMETERS (Å²) FOR CHLORBARTONITE

Atom	x	y	z	U_{00}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	0.29581(16)	0	0	0.0233(4)	0.021(1)	0.026(10)	0.023(1)	0	0	0
K(2)	0	0	0.15318(11)	0.0235(6)	0.0241(9)	0.0241(9)	0.022(1)	0	0	0
Fe(1)	0.13076(5)	0.36801(5)	0.18394(2)	0.0159(2)	0.0174(4)	0.0161(4)	0.0143(3)	-0.0005(2)	-0.0004(2)	0.0000(2)
Fe(2)	0.36856(5)	0.36856(5)	0.06625(3)	0.0161(2)	0.0160(3)	0.0160(3)	0.0164(4)	-0.0001(2)	-0.0001(2)	-0.0001(3)
S(1)	0.22763(9)	0.22763(9)	0.11387(6)	0.0160(3)	0.0162(4)	0.0162(4)	0.0154(6)	0.0011(4)	0.0011(4)	0.0009(5)
S(2)	0	0.24716(12)	0.25142(6)	0.0158(3)	0.0166(8)	0.0164(8)	0.0146(7)	-0.0006(5)	0	0
S(3)	0.24677(17)	½	0	0.0157(4)	0.016(1)	0.017(1)	0.014(1)	0	0	0
S(4)	0	½	0.12252(8)	0.0158(4)	0.016(1)	0.016(1)	0.015(1)	0	0	0
S(5)	0	0	0.37261(12)	0.0161(6)	0.0170(9)	0.0170(9)	0.014(1)	0	0	0
Cl	0	0	0	0.0217(9)	0.021(1)	0.021(1)	0.024(2)	0	0	0

<Fe–S> bond lengths are 2.300 and 2.303 Å for Fe(1)S₄ and Fe(2)S₄ tetrahedra, respectively, whereas individual Fe–S distances are in the range of 2.285–2.313 Å. The FeS₄ tetrahedra share edges to produce two symmetrically independent Fe₈S₁₄ clusters shown in Figures 3a and 3b. The Fe(1)₈S₁₄ cluster is centered at (½ ½ 0), and its point-symmetry group is *4/mmm*, whereas the Fe(1)₈S₁₄ cluster is centered at (0 ½ ¼), and its point-symmetry group is *4m2*. The Fe₈S₁₄ clusters are linked by sharing the S(1) atoms to produce a Fe₂₄S₂₆ framework (Fig. 4). The framework has large cavities occupied by the ClK₆ octahedra, *i.e.*, octahedra formed by six K⁺ cations at the vertices and centered by a Cl⁻ anion. The symmetry of the ClK₆ octahedron is *4/mmm*, and the octahedron is slightly elongate along the *c* axis. The four equatorial Cl–K(1) bonds are symmetrically equivalent and 3.071 Å long, whereas two apical Cl–K(2) bonds are 3.158 Å long. The two symmetrically independent K atoms are coordinated by one Cl and eight S atoms each. The mean <K–φ> bond-lengths (φ: Cl, S) are 3.326 and 3.332 Å for K(1) and K(2), respectively.

Bond-valence analysis and Fe–Fe bonding

The bond-valence sums for the atoms in the structure of bartonite were calculated using bond-valence parameters provided by Brese & O’Keeffe (1991). The bond-valence sums for the Fe(1) and Fe(2) atoms are 2.69 and 2.73 *vu* (valence units), respectively. Assuming the formula of chlorbartonite as K₆Fe₂₄S₂₆Cl, the Fe₂₄S₂₆ framework must have charge of –5. There are no indications of S–S bonding in the structure, and thus all sulfur should be considered as sulfide anions, S²⁻, and the oxidation state of the Fe cations should be +1.96, which is in contradiction with their bond-valence sums. This disagreement can be explained by the existence of metallic Fe–Fe bonding within the Fe₈S₁₄ clusters. The Fe atoms within the clusters are arranged at the vertices of a slightly distorted cube (Fig. 3c), with Fe–Fe dis-

TABLE 5. SELECTED BOND-LENGTHS (Å) FOR CHLORBARTONITE

K(1)–Cl	3.071(2)	Fe(1)–S(1)	2.285(1)
K(1)–S(4) _{a,b}	3.297(2) 2×	Fe(1)–S(2) _g	2.293(1)
K(1)–S(3) _{a,b}	3.325(2) 2×	Fe(1)–S(4)	2.307(1)
K(1)–S(1) _{b,c,d}	3.405(1) 4×	Fe(1)–S(2)	2.313(1)
<K(1)–φ>	3.326	<Fe(1)–S>	2.300
K(2)–Cl	3.158(2)	Fe(2)–S(1)	2.290(1)
K(2)–S(2) _{c,e,f}	3.269(2) 4×	Fe(2)–S(5) _h	2.305(2)
K(2)–S(1) _{c,e,f}	3.439(1) 4×	Fe(2)–S(3) _a	2.308(1) 2×
<K(2)–φ>	3.332	<Fe(2)–S>	2.303

a = –y + 1, x, z; b = y, –x, –z; c = y, –x, z; d = x, y, –z; e = –y, x, z;
f = –x, –y, z; g = –y + ½, x + ½, –z + ½; h = –x + ½, –y + ½, –z + ½.
* φ: Cl, S.

tances in the range 2.715–2.731 Å. Similar arrangements were observed in other iron sulfides containing M₈S₁₄ clusters (see below); the existence of metallic bonding within the M₈ cages has been confirmed by a variety of experimental and theoretical methods (Burdett & Miller 1987, Hoffmann *et al.* 1990). Other lines of evidence for this conclusion are the submetallic luster and weak magnetism of chlorbartonite.

The bond-valence sums for the S atoms are 2.45, 2.80, 2.96, 2.90 and 2.72 *vu* for S(1), S(2), S(3), S(4) and S(5), respectively. These values are in disagreement with the expected formal valence of the S²⁻ anions. We conclude that the metallic bonding within the Fe₈S₁₄ clusters strongly affects the bond-valence sums for the Fe and S atoms. We note that the deviations of calculated bond-valence sums from the expected valences are especially large (> 0.70 *vu*) for the S(2), S(3), S(4) and S(5) atoms, *i.e.*, those that cap the Fe₄ faces of the Fe₈ cubes (Fig. 3). In contrast, the deviation in the case of the S(1) atom (bridging between adjacent Fe₈S₁₄ clusters) is 0.45 *vu*. We attribute the observed deviations of bond-valence sums from the expected formal valences

observed for the atoms in the Fe_8S_{14} clusters to the shortening of the Fe–S bonds induced by the Fe–Fe metallic bonding.

The bond-valence sums for the K(1), K(2) and Cl atoms are 1.24, 1.22 and 1.28 *vu*, respectively.

POWDER X-RAY DIFFRACTION

The powder X-ray-diffraction pattern of chlorbartonite (Table 6) was obtained using a DRON-2 diffractometer operated at 20 kV and 30 mA (Bragg–Brentano geometry, $\text{CuK}\alpha$ radiation). The strongest eight lines in the X-ray powder-diffraction pattern [d in Å (I)(hkl)] are: 9.25(33)(101), 5.97(65)(112), 3.121(45)(312), 2.986(100)(224), 2.380(38)(332), 2.374(57)(316), 1.834(51)(440), and 1.830(82)(408). Table 6 provides a comparison of the powder X-ray-diffraction patterns for chlorbartonite (measured and calculated) and bartonite (measured).

DISCUSSION

Comparison with bartonite

Chlorbartonite and bartonite are compared in Table 7. The unit-cell parameters for bartonite are slightly higher than those of chlorbartonite, which is in good agreement with the effective ionic radii for Cl^- and S^{2-} anions, equal to 1.81 and 1.84 Å, respectively (Shannon 1976).

Evans & Clark (1981) reported occupancies for the Fe(1) and Fe(2) positions in bartonite of 0.841 and 0.864, respectively. In contrast, both Fe positions in the structure of chlorbartonite are fully occupied. It is noteworthy that, despite the essential differences in chemical composition and site occupancies, structural parameters of bartonite and chlorbartonite differ only marginally (*e.g.*, the average $\langle\text{Fe-S}\rangle$ bond lengths in the FeS_4 tetrahedra differ by 0.01 Å).



FIG. 2. Black grains of chlorbartonite in sodalite–natrolite aggregates. The sample is approximately 1 cm across.

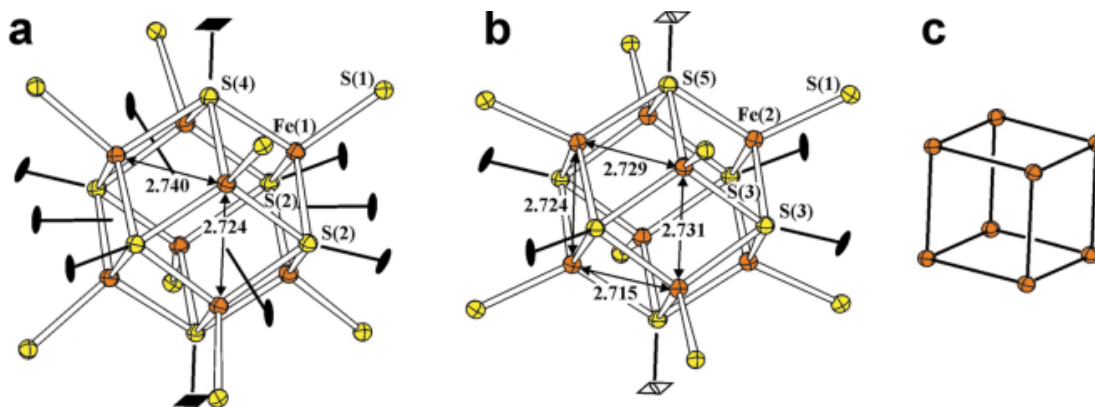


FIG. 3. Fe_8S_{14} clusters in the structure of chlorbartonite (symmetry axes are shown) (a and b). c. An Fe_8 cube stabilized by Fe-Fe metallic bonding is the core of the Fe_8S_{14} cluster.

Taking into account all the data available, the structural formula for bartonite and related phases may be written as $\text{K}_{6-a}\text{Fe}_{24-b}\text{S}_{26}\text{X}_{1-c}$ ($\text{X} = \text{S}, \text{Cl}$; $0 < a < 0.35$, $0 < b < 3.5$, $c < 0.25$). The small amounts of Cu, Ni and Co found (Table 2) are interpreted to substitute into the Fe sites.

Comparison to other minerals based upon Fe_8S_{14} clusters

Bartonite (Czamanske *et al.* 1981, Evans & Clark 1981) and its Cl-bearing analogue, chlorbartonite, are members of a group of minerals based upon Fe_8S_{14} clusters. The other minerals of this group are pentlandite, $(\text{Fe}, \text{Ni})_9\text{S}_8$ (Rajamani & Prewitt 1973), argentopentlandite, $\text{Ag}(\text{Fe}, \text{Ni})_8\text{S}_8$ (Hall & Stewart 1973, Rudashevskii *et al.* 1977), cobalt pentlandite, Co_9S_8 (Rajamani & Prewitt 1973), djerfischerite, $\text{K}_6\text{Na}(\text{Fe}, \text{Cu})_{24}\text{S}_{26}\text{Cl}$ (Dmitrieva & Ilyukhin 1975), thalfenisite, $\text{Tl}_6(\text{Fe}, \text{Ni}, \text{Cu})_{25}\text{S}_{26}\text{Cl}$ (Rudashevskii *et al.* 1979) and owensite, $(\text{Ba}, \text{Pb})_6(\text{Cu}, \text{Fe}, \text{Ni})_{25}\text{S}_{27}$ (Laflamme *et al.* 1995, Szymański 1995). Whereas pentlandite, cobalt pentlandite and argentopentlandite contain additional octahedrally coordinated positions inside the frameworks of Fe_8S_{14} clusters only, djerfischerite, thalfenisite, and owensite contain also A_6X octahedral clusters (A : K, Tl, Ba, Pb; X : Cl, S) in the framework cavities. Contrary to the latter group, no octahedral voids for additional cations exist in chlorbartonite and bartonite, and only A_6X groups are present in the framework cavities. The $\text{Cl} \rightleftharpoons \text{S}$ substitution at the X site is quite common in minerals of the djerfischerite and bartonite structure-types.

Chlorine-poor djerfischerite was first described by the late N.L. Balabonin and co-authors (Balabonin *et al.*

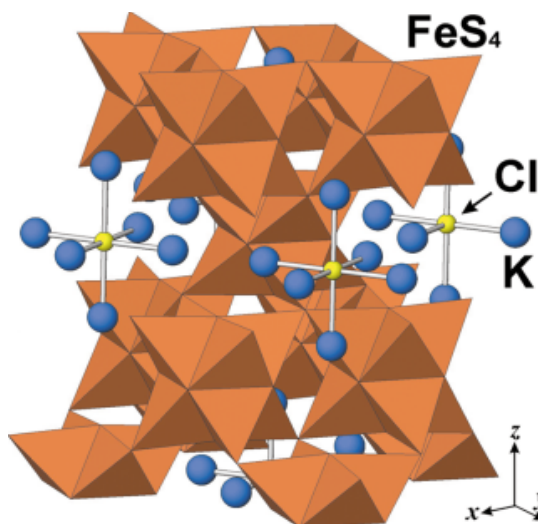


FIG. 4. Crystal structure of chlorbartonite. Legend: FeS_4 polyhedra are brown, whereas Cl and K atoms are yellow and blue, respectively.

1980). Barkov *et al.* (1997) reported chlorine-poor analogues of the djerfischerite–thalfenisite series that form subhedral inclusions in chalcopyrite from the Oktyabrsk deposit, Noril'sk, Siberia, and Salmagorsky alkaline complex, Kola Peninsula. Thus, $\text{Cl} \rightleftharpoons \text{S}$ substitution is well known in this mineral group, and confirms the existence of a complete solid-solution between bartonite and chlorbartonite.

TABLE 6. COMPARATIVE POWDER X-RAY-DIFFRACTION DATA FOR CHLORBARTONITE AND BARTONITE

Chlorbartonite				Bartonite (ICDD no. 35-476)		
I/I_0	d_{obs}	d_{calc}	hkl	I/I_0	d_{obs}	hkl
14	10.31	10.31	002	15	10.31	002
33	9.25	9.27	101	25	9.31	101
12	7.31	7.34	110	8	7.38	110
65	5.97	5.98	112	75	5.99	112
7	5.72	5.73	103	8	5.74	103
9	3.82	3.83	105			
9	3.43	3.44	006			
18	3.41	3.41	301	12	3.428	301
10	3.28	3.28	310	15	3.296	310
45	3.121	3.128	312	25	3.139	312
100	2.986	2.989	224	100	2.998	224
7	2.863	2.865	206	8	2.863	206, 321
8	2.851	2.851	321			
13	2.831	2.833	107	6	2.837	107
5	2.592	2.595	400			
9	2.511	2.516	402			
		2.508	226			
10	2.497	2.499	411	6	2.510	411
38	2.380	2.380	332	17	2.389	332
57	2.374	2.373	316	25	2.379	316
13	2.063	2.066	431, 501	8	2.075	501
		2.061	0.0.10			
13	1.993	1.993	336	6	2.000	512, 336
6	1.985	1.985	1.1.10	6	1.987	1.1.10
4	1.919	1.919	521			
7	1.910	1.910	309			
9	1.852	1.854	505	4	1.860	505
51	1.834	1.835	440	25	1.841	440
82	1.830	1.828	408	40	1.833	408
4	1.774	1.774	338			
9	1.751	1.751	516			
10	1.746	1.746	525			
8	1.694	1.694	419	8	1.698	419
4	1.576	1.577	615			
		1.576	3.3.10			
10	1.562	1.564	624	12	1.570	624
7	1.554	1.556	2.2.12	4	1.557	2.2.12
5	1.451	1.453	552, 712	2	1.459	712
4	1.442	1.442	3.0.13			
4	1.348	1.348	725			
		1.347	5.3.10			
4	1.296	1.298	800	2	1.302	800
4	1.287	1.288	0.0.16	2	1.288	0.0.16
5	1.265	1.267	736	2	1.272	736
		1.266	743, 813			
		1.265	655			
3	1.135	1.135	7.2.11, 5.3.14			
10	1.057	1.057	2.1.19			
6	1.054	1.054	4.4.16			

ACKNOWLEDGEMENTS

Thanks are due to Andrew Locock for many important discussions of the first draft of the manuscript. We are grateful to T. Balić-Zunić, Y. Močlo, J.A. Mandarino, Associate Editor N.J. Cook and R.F. Martin for useful comments that improved the manuscript. We thank Dr. H.R. Wilke, who provided a specimen of bartonite from California. This work is supported by a grant to V.N.Ya., Ya.A.P., Yu.P.M. and G.Yu.I. by the INTAS (project 97-0722). S.V.K. is grateful to the INTAS for a post-doctoral fellowship (YSF 01/1-192).

TABLE 7. COMPARATIVE DATA FOR CHLORBARTONITE AND BARTONITE

Parameters	Chlorbartonite	Bartonite*
Chemical formula	$K_6Fe_{24}S_{26}(Cl,S)$	$K_{6-x}Fe_{24-x}S_{26}(S,Cl)_{1-c}$ $a \approx 0.32, b \approx 3.73,$ $c \approx 0.07$
System	Tetragonal	Tetragonal
Space group	$I4/mmm$	$I4/mmm$
$a, \text{Å}$	10.3810(8)	10.424(1)
$c, \text{Å}$	20.614(2)	20.626(1)
Z	2	2
Density (g/cm^3)		
measured	3.70	3.305
calculated	3.65	3.286

* Evans & Clark (1981).

REFERENCES

- BALABONIN, N.L., VOLOSHIN, A.V., PAKHOMOVSKIY, YA.A. & POLYAKOV, K.I. (1980): The composition of djerfisherite from alkaline complexes, Kola Peninsula. *Mineral. Zh.* **2**(1), 90-99 (in Russ.).
- BARKOV, A.Y., LAAJOKI, K.V.O., GEHÖR, S.A., YAKOVLEV, Y.N. & TAIKINA-AHO, O. (1997): Chlorine-poor analogues of djerfisherite-thalfenisite from Noril'sk, Siberia and Salmagorsky, Kola Peninsula, Russia. *Can. Mineral.* **35**, 1421-1430.
- BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.
- BURDETT, J.K. & MILLER, G.J. (1987): Polyhedral clusters in solids. The electronic structure of pentlandite. *J. Am. Chem. Soc.* **109**, 4081-4091.
- CZAMANSKE, G.K., ERD, R.C., LEONARD, B.F. & CLARK, J.R. (1981): Bartonite, a new potassium iron sulfide mineral. *Am. Mineral.* **66**, 369-375.
- DMITRIEVA, M.T. & ILYUKHIN, V.V. (1975): Crystal structure of djerfisherite. *Dokl. Akad. Nauk SSSR* **223**, 343-346 (in Russ.).
- DOBROVOL'SKAYA, M.G., SOKOLOVA, M.N., KHOMYAKOV, A.P. & TSEPIN, A.I. (1980): Potassium- and sodium-containing sulfides as indicators of mineral formation conditions in alkali rocks and kimberlites. *Geokhimiya* **1980**, 199-205 (in Russ.).
- EVANS, H.T., JR. & CLARK, J.R. (1981): Crystal structure of bartonite, a potassium iron sulfide, and its relationship to pentlandite and djerfisherite. *Am. Mineral.* **66**, 376-384.
- HALL, S.R. & STEWART, J.M. (1973): Crystal structure of argentic pentlandite $(Fe,Ni)_8AgS_8$, compared with the refined structure of pentlandite $(Fe,Ni)_9S_8$. *Can. Mineral.* **12**, 169-177.

- HOFFMAN, G.G., BASHKIN, J.K. & KARPLUS, M. (1990): Electronic structure of icosahedral cobalt–sulfur clusters. *J. Am. Chem. Soc.* **112**, 8705–8714.
- IBERS, J.A. & HAMILTON, W.C., eds. (1974): *International Tables for X-ray Crystallography IV*. The Kynoch Press, Birmingham, U.K.
- KAMENEV, E.A., MINEEV, D.A., NECHAEVA, O.S., PESHEV, N.G., BELYAKOV, A.YU. & KRAVCHENKO, S.M. (1982): *New Khibiny apatite deposits*. Nedra, Moscow, Russia (in Russ.).
- LAFLAMME, J.H.G., ROBERTS, A.C., CRIDDLE, A.J. & CABRI, L.J. (1995): Owensite, $(\text{Ba,Pb})_6(\text{Cu,Fe,Ni})_{25}\text{S}_{27}$, a new mineral species from the Wellgreen Cu–Ni–Pt–Pd deposit, Yukon. *Can. Mineral.* **33**, 665–670.
- RAJAMANI, V. & PREWITT, C.T. (1973): Crystal chemistry of natural pentlandites. *Can. Mineral.* **12**, 178–187.
- RUDASHEVSKII, N.S., KARPENKOV, A.M., SHIPOVA, G.S., SHISHKIN, N.N. & RYABKIN, V.A. (1979): Thalfenisite: the thallium analog of djerfisherite. *Zap. Vses. Mineral. Obshchest.* **108**, 696–701 (in Russ.).
- _____, MITENKOV, G.A., KARPENKOV, A.M. & SHISHKIN, N.N. (1977): Silver-containing pentlandite $\text{Ag}(\text{Fe,Ni})_8\text{S}_8$: the independent mineral species, argentopentlandite. *Int. Geol. Rev.* **21**, 695–698.
- SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751–767.
- SZYMAŃSKI, J.T. (1995): The crystal structure of owensite, $(\text{Ba,Pb})_6(\text{Cu,Fe,Ni})_{25}\text{S}_{27}$, a new member of the djerfisherite group. *Can. Mineral.* **33**, 671–677.
- YAKOVENCHUK, V.N., IVANYUK, G.YU., PAKHOMOVSKY, YA.A. & MEN'SHIKOV, YU.P. (1999): *Minerals of the Khibina massif*. Zemlya, Moscow, Russia (in Russ.).

Received August 17, 2002, revised manuscript accepted February 8, 2003.