# 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

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## 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) Å$^3$, $Z = 2$. 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 – aegyrine 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

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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 $VHN_{40}$ est 203–212, en moyenne 207 kg/mm$^2$; la dureté de Mohs est 4. La densité est 3.70 g/cm$^3$ (mesurée) et 3.65 g/cm$^3$ (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 $K_{6.08}(Fe_{23.93}Cu_{0.22}Co_{0.01})_{\Sigma24.16}S_{26.00}(Cl_{0.69}S_{0.07})_{\Sigma0.76}$, ce qui mène à la formule idéale $K_6Fe_{24}S_{26}(Cl,S)$. Le minéral est tétragonal, $I4/mmm$, $a$ 10.3810(8), $c$ 20.614(2) Å, $V$ 2221.5(3) Å$^3$, $Z = 2$. Les huit raies les plus intenses du spectre de diffraction X [$d$ en Å ($I$)($hkl$)] 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 $R$1 de 0.020 (447 réflexions uniques observées avec $F_o \geq 4\sigma F_o$). La structure contient une trame de groupes $Fe_8S_{14}$ contenant huit tétraèdres $FeS_4$ à arêtes partagées. Cette trame possède des cavités volumineuses qu'occupent des octaèdres $ClK_6$. 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 $K_6Fe_{24}S_{26}(S,Cl)$, 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, $K_6Fe_{24}S_{26}(Cl,S)$. 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 villiaumite (up to 25 cm across). Villiaumite 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 villiaumite.

The border between the 2$^{nd}$ and 3$^{rd}$ zones is marked by extremely large lenses of dark red villiaumite 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
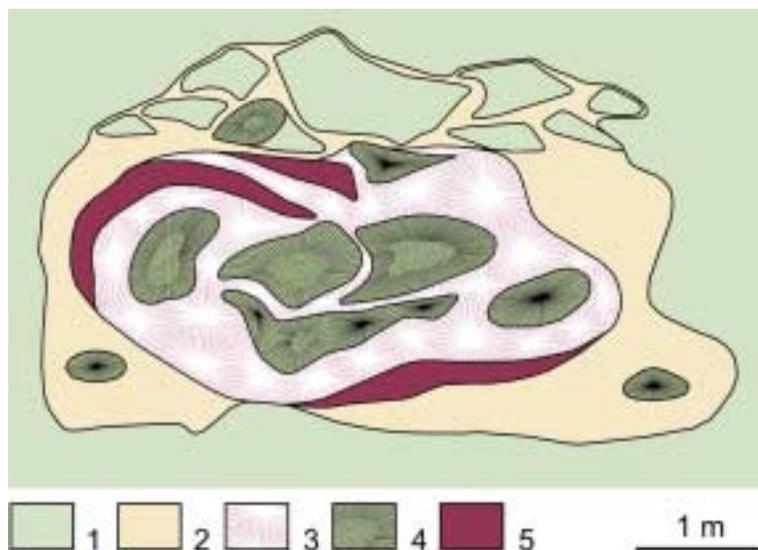
FIG. 1.   Sketch of the chlorbaronite-bearing microcline – pectolite – sodalite – aegirine vein. Legend: (1) host apatite–nepheline rocks, (2) marginal zone of microcline – nepheline – sodalite aggregate, (3) intermediate zone (snow-white radiating aggregates of pectolite), (4) aegirine-bearing zone, (5) lenses of dark red villiaumite containing crystals of chlorbartonite, 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 chlorbartonite (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.

Chlorbartonite 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

| $\lambda$ (nm) | $R$ (%) | $\lambda$ (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 (Dobrovol'skaya *et al.* 1980).

PHYSICAL AND OPTICAL PROPERTIES

Chlorbartonite 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 chlorbartonite 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/cm$^3$ 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 $Fe_{10}S_{11}$ (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 $K_{6.08}(Fe_{23.93}Cu_{0.22}Co_{0.01})_{\Sigma24.16}S_{26.00}(Cl_{0.69}S_{0.07})_{\Sigma0.76}$, which corresponds to the ideal formula, $K_6Fe_{24}S_{26}$ (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 Mo$K\alpha$ 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 *I*4/*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 ($R_{INT}$ = 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 (±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 n = 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: $K_{6.08}(Fe_{23.93}Cu_{0.22}Co_{0.01})_{\Sigma24.16}S_{26.00}(Cl_{0.69}S_{0.07})_{\Sigma0.76}$
Ideal formula: $K_6Fe_{24}S_{26}(Cl,S)$

TABLE 3.  CRYSTALLOGRAPHIC DATA FOR CHLORBARTONITE

| | | | |
|---|---|---|---|
| *a* (Å) | 10.3810(8) | Crystal size (mm) | 0.24 × 0.12 × 0.10 |
| *c* (Å) | 20.614(2) | Radiation | Mo$K\alpha$ |
| *V* (Å$^3$) | 2221.5(3) | Total reflections | 4884 |
| Space group | *I*4/*mmm* | Unique $F_o \geq 4\sigma_F$ | 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:  $R1 = \Sigma|F_o - F_c| / \Sigma F_o$;  $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2) + (0.0161P)^2 + 1.9P]$, 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 ($\mathring{A}^2$) FOR CHLORBARTONITE

| Atom | $x$ | $y$ | $z$ | $U_{iso}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 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)S$_4$ and Fe(2)S$_4$ tetrahedra, respectively, whereas individual Fe–S distances are in the range of 2.285–2.313 Å. The FeS$_4$ tetrahedra share edges to produce two symmetrically independent Fe$_8$S$_{14}$ clusters shown in Figures 3a and 3b. The Fe(1)$_8$S$_{14}$ cluster is centered at (½ ½ 0), and its point-symmetry group is 4/mmm, whereas the Fe(1)$_8$S$_{14}$ cluster is centered at (0 ½ ¼), and its point-symmetry group is $\bar{4}m2$. The Fe$_8$S$_{14}$ clusters are linked by sharing the S(1) atoms to produce a Fe$_{24}$S$_{26}$ framework (Fig. 4). The framework has large cavities occupied by the ClK$_6$ octahedra, i.e., octahedra formed by six K$^+$ cations at the vertices and centered by a Cl$^-$ anion. The symmetry of the ClK$_6$ 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 K$_6$Fe$_{24}$S$_{26}$Cl, the Fe$_{24}$S$_{26}$ 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, S$^{2-}$, 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 Fe$_8$S$_{14}$ 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 $M_8$S$_{14}$ clusters (see below); the existence of metallic bonding within the $M_8$ 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 S$^{2-}$ anions. We conclude that the metallic bonding within the Fe$_8$S$_{14}$ 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 Fe$_4$ faces of the Fe$_8$ cubes (Fig. 3). In contrast, the deviation in the case of the S(1) atom (bridging between adjacent Fe$_8$S$_{14}$ 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, Cu*K*α 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 <Fe–S> bond lengths in the $FeS_4$ tetrahedra differ by 0.01 Å).



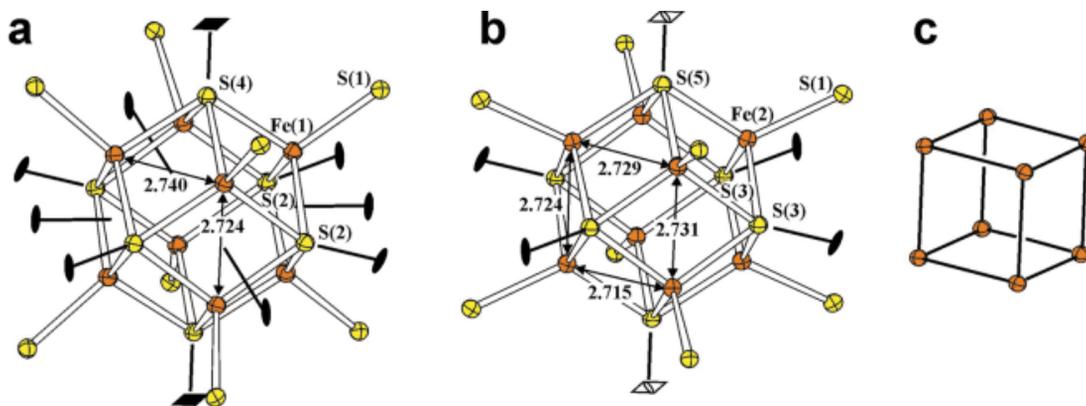FIG. 2.    Black grains of chlorbartonite in sodalite–natrolite aggregates. The sample is approximately 1 cm across.

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 $K_{6-a}Fe_{24-b}S_{26}X_{1-c}$ ($X = S$, 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, $(Fe,Ni)_9S_8$ (Rajamani & Prewitt 1973), argentopentlandite, $Ag(Fe,Ni)_8S_8$ (Hall & Stewart 1973, Rudashevskii *et al.* 1977), cobalt pentlandite, $Co_9S_8$ (Rajamani & Prewitt 1973), djerfisherite, $K_6Na(Fe,Cu)_{24}S_{26}Cl$ (Dmitrieva & Ilyukhin 1975), thalfenisite, $Tl_6(Fe,Ni,Cu)_{25}S_{26}Cl$ (Rudashevskii *et al.* 1979) and owensite, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$ (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, djerfisherite, 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 Cl $\rightleftharpoons$ S substitution at the X site is quite common in minerals of the djerfisherite and bartonite structure-types.

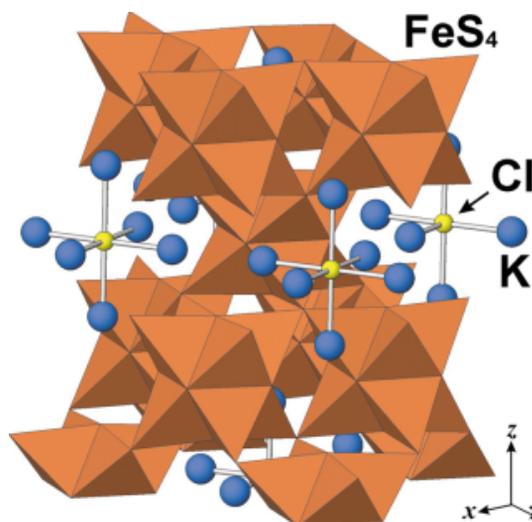Chlorine-poor djerfisherite was first described by the late N.L. Balabonin and co-authors (Balabonin *et al.*



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 djerfisherite–thalfenisite series that form subhedral inclusions in chalcopyrite from the Oktyabrsky deposit, Noril'sk, Siberia, and Salmagorsky alkaline complex, Kola Peninsula. Thus, Cl $\rightleftharpoons$ 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) | | |
|---|---|---|---|---|---|---|
| $I/I_o$ | $d_{obs}$ | $d_{calc}$ | $h\,k\,l$ | $I/I_o$ | $d_{obs}$ | $h\,k\,l$ |
| 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 | | | |

TABLE 7. COMPARATIVE DATA FOR CHLORBARTONITE AND BARTONITE

| Parameters | Chlorbartonite | Bartonite* |
|---|---|---|
| Chemical formula | $K_6Fe_{24}S_{26}(Cl,S)$ | $K_{6-x}Fe_{24-b}S_{26}(S,Cl)_{1-c}$ $a \approx 0.32$, $b \approx 3.73$, $c \approx 0.07$ |
| System | Tetragonal | Tetragonal |
| Space group | $I4/mmm$ | $I4/mmm$ |
| $a$, Å | 10.3810(8) | 10.424(1) |
| $c$, Å | 20.614(2) | 20.626(1) |
| $Z$ | 2 | 2 |
| Density (g/cm³) | | |
| measured | 3.70 | 3.305 |
| calculated | 3.65 | 3.286 |

* Evans & Clark (1981).

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