

## POSSIBLE STRUCTURAL AND CHEMICAL RELATIONSHIPS IN THE CYANOTRICHITE GROUP

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### ABSTRACT

The members of the cyanotrichite group, cyanotrichite, carbonate-cyanotrichite, camerolaite and khaidarkanite, are closely related in terms of their structures, although the single-crystal structure of the latter is the only one to have been determined. Powder X-ray-diffraction data for all members can be indexed on the basis of a common monoclinic cell with  $a \approx 10.2$ ,  $b \approx 2.9$ ,  $c \approx 12.6$  Å and  $\beta$  in the range 92.3–97.9° ( $a$  and  $c$  are interchanged in khaidarkanite owing to  $C$ -centering). The structures of cyanotrichite, carbonate-cyanotrichite and camerolaite can be rationalized in terms of that of khaidarkanite, with sulfate and carbonate taking the positions of  $\text{AlF}_3$  groups. Ordering and disordering of the sites yields  $P$ - and  $C$ -centered cells, respectively, depending on composition. The analytical data originally reported for carbonate-cyanotrichite are re-interpreted in terms of  $\text{Al}(\text{OH})_3$  taking the place of  $\text{AlF}_3$  groups in khaidarkanite. There is no evidence for solid solution between cyanotrichite and carbonate-cyanotrichite; it is evident that some carbonate-cyanotrichite specimens contain no sulfate. A range of other stoichiometries may be accommodated by the archetypical structural motif, and these remain to be discovered in nature. Other related species, including a Co-rich member of the group from the Grandview mine, Arizona, and a cyanotrichite-like phase from the Clara mine, Germany, have also been examined. These too conform to the structural relations that have been derived. Final resolution of the nature of individual members of the group awaits single-crystal structural studies, if and when suitable crystals become available, or if structure solution using powder X-ray diffraction data or *ab initio* methods becomes possible.

**Keywords:** cyanotrichite, carbonate-cyanotrichite, camerolaite, khaidarkanite, relationships, structure, composition, powder X-ray-diffraction data.

### SOMMAIRE

Les membres du groupe de la cyanotrichite, soient cyanotrichite, carbonate-cyanotrichite, camérolaïte et khaidarkanite, possèdent une relation structurale étroite, quoique la structure de la khaidarkanite est la seule à avoir été résolue par travaux sur monocristal. Il est possible d'indexer les données prélevées sur poudre pour tous ces membres avec une maille monoclinique ayant  $a \approx 10.2$ ,  $b \approx 2.9$ ,  $c \approx 12.6$  Å et  $\beta$  dans l'intervalle 92.3–97.9° ( $a$  et  $c$  sont interchangés dans la khaidarkanite à cause de la maille ayant  $C$  centré). On peut rationaliser les structures de la cyanotrichite, la carbonate-cyanotrichite et la camérolaïte en termes de celle de la khaidarkanite, avec sulfate et carbonate à la place des groupes  $\text{AlF}_3$ . Une relation ordre-désordre des sites mène aux mailles ayant  $P$  et  $C$  centrés, respectivement, dépendant de la composition. Nous ré-interprétons les données analytiques originelles pour la carbonate-cyanotrichite en termes de  $\text{Al}(\text{OH})_3$  à la place des groupes  $\text{AlF}_3$  dans la khaidarkanite. Nous ne trouvons aucune évidence en faveur d'une solution solide entre cyanotrichite et carbonate-cyanotrichite; il est évident que certains échantillons de carbonate-cyanotrichite ne contiennent pas de sulfate. Le motif structural de l'archetype peut accommoder une variété d'autres stoechiométries, qui pourraient bien exister comme minéraux. Nous avons aussi examiné un membre cobaltifère du groupe trouvé à la mine Grandview, en Arizona, et une phase semblable à la cyanotrichite trouvée à la mine Clara, en Allemagne. Ces phases se conforment aussi aux relations structurales que nous avons dérivées. Une résolution finale de la nature des membres individuels du groupe devra attendre des études fondées sur monocristaux, si et quand des cristaux convenables deviennent disponibles, ou si une solution structurale fondée sur la diffraction X sur poudre ou utilisant les méthodes *ab initio* deviennent possibles.

(Traduit par la Rédaction)

**Mots-clés:** cyanotrichite, carbonate-cyanotrichite, camérolaïte, khaidarkanite, relations, structure, composition, diffraction X sur poudre.

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## INTRODUCTION

Cyanotrichite was first recognized as a distinct species nearly two centuries ago (Werner 1808); the name was first recorded by Glocker (1839). Other early observations were summarized by Palache *et al.* (1951), together with properties and analytical data. The stoichiometry  $\text{Cu}_4\text{Al}_2\text{SO}_4(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$  is accepted on the basis of the latter, but the single-crystal structure of cyanotrichite remains to be determined. Powder X-ray-diffraction data are listed in the ICDD-PDF database (card no. 11-0131) and are indexed on the basis of an orthorhombic cell with  $a$  10.16,  $b$  12.61,  $c$  2.90 Å. However, two lines, one of low intensity and one with an  $I_{rel}$  of 50, could not be indexed. With this in mind, we have been prompted to re-examine the powder X-ray-diffraction data for cyanotrichite and other members of the cyanotrichite group (carbonate-cyanotrichite, camerolaite, khaidarkanite) and the results of this study are reported below. For this, we have made extensive use of powder X-ray-diffraction methods, supplemented by infrared absorption (IR) and thermogravimetric measurements. It is evident that all are related monoclinic phases and can be correlated to the khaidarkanite structure. In addition, it is apparent that other related species of subtly different stoichiometry probably exist in nature.

## BACKGROUND INFORMATION

In 1963, a new mineral, supposedly the carbonate analogue of cyanotrichite, was reported from several localities in northwestern Kara-Tau, Russia (Ankinovich *et al.* 1963). Carbonate-cyanotrichite is suggested to have the ideal end-member stoichiometry  $\text{Cu}_4\text{Al}_2\text{CO}_3(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$ , but the only composition available (in the original description) is not entirely satisfactory. The approximate formula,  $(\text{Cu,Zn})_{3.70}\text{Al}_{2.30}(\text{C}_{0.67}\text{S}_{0.33})_{\Sigma 1.00}[\text{O}_{2.98}(\text{OH})_{1.02}]_{\Sigma 4.00}(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$ , was obtained after allowance for the presence of quartz, dolomite and calcite. Powder X-ray-diffraction data also are listed in the ICDD-PDF database (card no. 16-0365), but are not indexed, and no single-crystal structure has been reported. Subsequently, Sarp & Perroud (1991) reported the mineral camerolaite,  $\text{Cu}_4\text{Al}_2[\text{HSbO}_4\cdot\text{SO}_4](\text{OH})_{10}(\text{CO}_3)\cdot 2\text{H}_2\text{O}$ , from the Cap Garonne mine, Var, France. They noted that camerolaite is crystallographically and chemically related to cyanotrichite and carbonate-cyanotrichite, and that the latter two species are isostructural. Again, no single-crystal structure for camerolaite is available, but a monoclinic unit-cell, space group  $P2_1$  or  $P2_1/m$ , with  $a$  10.765(6),  $b$  2.903(2),  $c$  12.527(8) Å,  $\beta$  95.61(4)°, was refined from powder X-ray-diffraction data. Camerolaite has been since reported from other localities (Cuchet 1995, Walenta 1995). Finally, in this connection, the mineral khaidarkanite,  $\text{Cu}_4\text{Al}_3(\text{OH})_{14}\text{F}_3\cdot 2\text{H}_2\text{O}$ , from the Khaidarkan deposit, Kyrgyzstan, has been reported

(Chukanov *et al.* 1999), and it was noted to be related to cyanotrichite. Its single-crystal X-ray structure had been previously described (Rastsvetaeva *et al.* 1997); khaidarkanite is monoclinic, space group  $C2/m$ , with  $a$  12.346(3),  $b$  2.907(3),  $c$  10.369(7) Å,  $\beta$  97.90(2)°.

Reported unit-cell dimensions of cyanotrichite, camerolaite and khaidarkanite are very similar and are characterized by one very short dimension of about 2.9 Å. This can be rationalized by an arrangement such that the metal-bearing octahedra are all edge-shared in the  $b$  direction. In khaidarkanite, the shared edges of the Al and Cu octahedra are perpendicular to  $b$  (see below). In the structure,  $C$ -centering is effected by an approximately half-occupied Al ion [Al(2)], which is the only metal ion coordinated to four symmetry-related fluoride ions with fractional occupancy. The octahedral coordination of Al(2) is completed by two symmetry-related and fully site-occupied  $\text{H}_2\text{O}$  molecules.

## EXPERIMENTAL

Powder X-ray-diffraction data were collected using a Philips PW1825-20 powder diffractometer ( $\text{CuK}\alpha$  radiation,  $\lambda = 1.5406$  Å, pure Si as internal standard,  $5 \leq 2\theta \leq 75^\circ$ , step size  $0.01^\circ$ , step time 1 s, no correction for preferred orientation) at room temperature. Unit-cell dimensions were refined using LAPOD (Langford 1973), based on indices derived from calculations using POWDERCELL (Kraus & Nolze 1996a, 1996b).

We used the following specimens in this study. Mr. Bill Pinch (Rochester, New York, USA) provided a specimen of carbonate-cyanotrichite from the Dachang (Qinglong) Sb-Au deposit, Guizhou Province, China. Cyanotrichite associated with the type specimen of grandviewite [ $\text{Cu}_3\text{Al}_9(\text{SO}_4)_2(\text{OH})_{29}$ ] from the Grandview mine, Coconino County, Arizona, USA, originally provided by Ray Grant (Mesa, Arizona, USA), was also examined (P. Leverett and P.A. Williams, unpubl. results). Further specimens of cyanotrichite from the Grandview mine that were investigated were donated by Malcolm Alter (Flagstaff, Arizona, USA; specimen GRAND) or purchased from George Stevens (George Stevens Minerals, Tucson, Arizona, USA; specimen PAWCYAN). A specimen of a Co-rich member of the cyanotrichite group from the Grandview mine was also provided for study by Malcolm Alter.

Thermogravimetric (TG) analyses for  $\text{SO}_3$  and  $\text{H}_2\text{O}$  for the sample from the Dachang deposit were made using a Netzsch STA 449C Jupiter simultaneous DSC-TGA thermoanalyzer (6 mg sample, PtRh crucible, heating rate  $10 \text{ K min}^{-1}$ ,  $\text{N}_2$  flow rate of  $50 \text{ cm}^3 \text{ min}^{-1}$ ). Volatile compounds formed during pyrolysis were transferred to an FTIR (Fourier-transform infrared) cell using a teflon transfer line 2 mm in internal diameter and 800 mm long. The transfer line and the head of the TG balance were heated at a constant temperature of  $200^\circ\text{C}$  to limit condensation of volatile products. The FTIR spectra were recorded using a Bruker VERTEX

70 spectrometer with an external mercury–cadmium telluride (MCT) detector. During the TGA–FTIR runs, spectra were collected at  $8\text{ cm}^{-1}$  resolution; 32 scans were co-added per spectrum.

The IR spectra (KBr pellets) were recorded on a PerkinElmer Spectrum One FTIR spectrophotometer. Atomic absorption analyses were performed using a PerkinElmer Analyst 100AAS spectrophotometer. A JEOL JXA–840 scanning electron microscope equipped with a light-element detector energy-dispersion system was used for semiquantitative analyses of the Co-rich cyanotrichite sample.

Samples of the specimens examined have been deposited in the collections of Museum Victoria (Geosciences Department, Museum Victoria, PO Box 666E, Melbourne, Victoria 3001, Australia). Specimen numbers are M50792 (Dachang deposit), M50793 (GRAND), M50794 (PAWCYAN) and M50795 (Co-rich member of the cyanotrichite group). The type specimen of grandviewite is deposited in the same collection (M50490).

## RESULTS AND DISCUSSION

### *Powder X-ray-diffraction data*

Powder X-ray-diffraction data for cyanotrichite are listed in Table 1. Published line-spacings for the mineral (ICDD–PDF card no. 11–0131) and all five specimens examined in this study can be successfully indexed on the basis of a monoclinic *P* unit cell with  $a\ 10.18$ ,  $b\ 2.90$ ,  $c\ 12.65\ \text{\AA}$ ,  $\beta\ 92.5^\circ$  (Table 2). All reflections in the ICDD–PDF card no. 11–0131 are now accounted for, save the weak reflection at  $d = 8.63\ \text{\AA}$ , also observed in one sample taken from specimen PAWCYAN. This reflection is, however, attributed to the  $I_{rel} = 100$  line of chalcoalumite ( $d = 8.502\ \text{\AA}$ ). The close association of cyanotrichite with chalcoalumite in the Grandview mine is well documented (Leicht 1971). In the type specimen of grandviewite from the Grandview mine, crusts of extremely acicular chalcoalumite fibers line vugs in gossan; these are coated for the most part by cyanotrichite and, in some cases, by radiating groups of acicular crystals of grandviewite. We note that the strong line in ICDD–PDF card no. 11–0131, with  $I_{rel}$  of 50 and that could not be indexed with the previously assumed orthorhombic cell, refines in a satisfactory way as the reflection  $10\bar{2}$ . Inspection of the indexed reflection record for cyanotrichite shows that it possesses a primitive Bravais lattice.

In ICDD–PDF card no. 11–0131, no unique lines for carbonate-cyanotrichite can be identified and, in the case of the samples taken from the type specimen of grandviewite and GRAND, negligible carbonate-cyanotrichite is present. In the remaining specimens, significant but variable amounts of carbonate-cyanotrichite were found to be admixed with the cyanotrichite, and these are visually indistinguishable.

This is at first sight a curious observation in that cyanotrichite and carbonate-cyanotrichite have been supposed to form a solid-solution series between ideal end-member stoichiometries  $\text{Cu}_4\text{Al}_2\text{SO}_4(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$  and  $\text{Cu}_4\text{Al}_2\text{CO}_3(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$ , respectively. If so, the solid solution must be highly lacunar. Alternatively, as we conclude below, cyanotrichite and carbonate-cyanotrichite in fact possess distinct formulae, and the solid solution of the kind hitherto assumed does not exist. Overlapping lines in the powder X-ray-diffraction records of mixed cyanotrichite and carbonate-cyanotrichite samples are identified in Table 1. Once this relationship was recognized, it was then possible to extract the appropriate data for both minerals and refine their unit cells independently. Unfortunately, we have been unable to locate a specimen of pure carbonate-cyanotrichite, and no method of synthesis for it is available.

Powder X-ray-diffraction data for carbonate-cyanotrichite are listed in Table 3, and the refined unit-cell data are shown in Table 2. The data used for the refinement are those that could be unambiguously assigned to carbonate-cyanotrichite. Inevitably, because the samples available for study contain significant (in some cases predominant) amounts of cyanotrichite, some reflections overlap with those of the latter. For example, the reflection 100 is present in both carbonate-cyanotrichite samples that we have investigated, and in the originally described material (Ankinovich *et al.* 1963), but was manifested as a shoulder on the virtually superimposed 100 reflection of cyanotrichite and could not be accurately measured. It was not included in the cell-refinement routines. Intensities for carbonate-cyanotrichite reflections were rescaled to be internally consistent, rather than to the dominant  $I_{rel} = 100$  line of cyanotrichite (the 100 reflection). Observed intensities for cyanotrichite and carbonate-cyanotrichite are seriously affected by preferred orientation and are not necessarily a useful guide to correlation. Refined unit-cell data for carbonate-cyanotrichite are remarkably similar to those of khaidarkanite, with a slightly larger  $\beta$  angle, and allowing for transposition of  $a$  and  $c$  in khaidarkanite because of *C*-centering on the  $10\ \text{\AA}$  axis (Table 2). The refined cell for the published data for carbonate-cyanotrichite (ICDD–PDF card no. 16–0365) is of lower precision, in line with the data being measured photographically, but is quite consistent with the results of other measurements. Only one reflection of weak intensity in the reported powder X-ray-diffraction data could not be indexed. It is attributed to the presence of brochantite as an impurity (Table 3). Inspection of the reflection record for carbonate-cyanotrichite shows that the strongest reflections show excellent correspondence in terms of indexing with those of cyanotrichite, as well as camerolaite (Sarp & Perroud 1991) and khaidarkanite (Chukanov *et al.* 1999). From the results, it is impossible to determine whether carbonate-cyanotrichite possesses a *P*- or a *C*-centered cell. The reflection 100

TABLE 1. POWDER X-RAY-DIFFRACTION DATA FOR CYANOTRICHITE

Sample a			Sample b			Sample c			Sample d			Sample e			Sample f			
<i>h</i>	<i>k</i>	<i>l</i>	<i>I<sub>rel</sub></i>	<i>d<sub>obs</sub></i>	<i>d<sub>calc</sub></i>													
1	0	0	100	10.20	10.153	100	10.183	10.167	100	10.119	10.174	100	10.146	10.170	100	10.158	10.167	10.166
			5	8.63 <sup>h</sup>						8.492 <sup>a</sup>								
0	0	2	10	6.35	6.292	2	6.312	6.319	6	6.316	6.310	2	6.331	6.336	3	6.321	6.311	6.321
1	0	2	50	5.47	5.460	5	5.481	5.470	16	5.463	5.471	9	5.471	5.481	9	5.474	5.472	5.476
1	0	2	80	5.26	5.243	9	5.279	5.270	21	5.265	5.260	16	5.271	5.280	15	5.273	5.258	5.266
2	0	0	10	5.07	5.076	31	5.086	5.084	32	5.078	5.087	24	5.079	5.085	26	5.081	5.084	5.083
0	0	3				2	4.208	4.212	2	4.205	4.207							
1	0	3	4			4	3.949	3.950										
2	0	2	90	3.88	3.866	14	3.885	3.883	26	3.883	3.878	16	3.882	3.888	15	3.883	3.875	3.879
3	0	0	35	3.38	3.384	42	3.390	3.389	35	3.386	3.391	28	3.386	3.390	29	3.387	3.389	3.389
3	0	1	2			2	3.244	3.240										
2	0	3																
0	0	4	15	3.16	3.146	2	3.165	3.159	7	3.161	3.155	3	3.159	3.168	3	3.162	3.155	3.160
1	0	4																
3	0	2	40	3.04	3.038	9	3.043	3.040	15	3.042	3.043	8	3.098	3.042	6	3.042	3.043	3.042
3	0	2	10	2.935	2.926	3	2.936	2.936	6	2.935	2.934	2	2.934	2.939	2	2.935	2.932	2.934
0	1	1																
1	1	0																
4	0	0	25	2.539	2.538	20	2.542	2.542	18	2.540	2.544	12	2.540	2.542	11	2.541	2.542	2.542
1	1	2																
4	0	1				2	2.513	2.512	11	2.514	2.515							
4	0	1																
4	0	2	35	2.392	2.292	9	2.395	2.393	13	2.393	2.396	6	2.394	2.394	5	2.395	2.395	2.471
0	1	3																
4	0	2	25	2.318	2.318	6	2.325	2.325	9	2.325	2.324	4	2.325	2.326	3	2.325	2.324	2.323
2	1	2																
3	0	4	5	2.256	2.254	1	2.258	2.265										
4	0	3				1	2.221	2.217	5	2.215	2.220	1	2.217	2.219	1	2.216	2.220	2.263
1	0	6	5	2.071	2.072	1	2.081	2.080	5	2.080	2.078	1	2.084	2.085	1	2.080	2.078	2.220
1	1	4																
5	0	0	35	2.032	2.031	25	2.034	2.033	19	2.033	2.035	14	2.033	2.034	13	2.033	2.033	2.033
3	1	3	5	1.969	1.979	1	1.973	1.975	4	1.975	1.976							



TABLE 1. POWDER X-RAY-DIFFRACTION DATA FOR CYANOTRICHITE

<i>h k l</i>	Sample a			Sample b			Sample c			Sample d			Sample e			Sample f			
	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	
0 0 9						1.404													
7 0 2						1.403													
1 2 2	5	1.411	1.408	1	1.401	1.402	3	1.403	1.403	1	1.404	1.403	1	1.402	1.402	1	1.402	1.402	
1 0 9						1.400													
1 2 2						1.398													
1 1 8						1.381													
6 0 1						1.381													
5 0 7						1.379													
3 1 7	5	1.370	1.374	1	1.378	1.378													
7 0 4				1	1.341	1.341													
2 0 9						1.339													
5 0 7						1.323													
2 2 3				1	1.320	1.320													
0 2 4						1.318													
4 0 8						1.317													
4 2 0																			
8 0 1																			
0 2 5																			
4 2 1																			
8 0 2										1	1.257	1.256				1	1.256	1.256	
7 1 3																			
4 0 9																			
1 2 5																			
4 2 1																			

<sup>a</sup> Refined data ICDD—PDF card no. 11–0131 with indexing based on the monoclinic *P* cell; refined unit-cell constants are *a* 10.163(7), *b* 2.915(3), *c* 12.596(10) Å,  $\beta$  92.60(8)<sup>°</sup>. <sup>b</sup> This work; Grandview mine, from IMA 2007–004 type specimen; refined unit-cell constants are *a* 10.176(3), *b* 2.901(1), *c* 12.649(5) Å,  $\beta$  92.38(3)<sup>°</sup>; the variation in intensities is attributed to preferred orientation effects. <sup>c</sup> This work; Grandview mine, specimen PAWCYAN; material consists of dominant cyanotrichite plus minor admixed carbonate-cyanotrichite; refined unit-cell constants are *a* 10.184(5), *b* 2.903(2), *c* 12.632(8) Å,  $\beta$  92.51(6)<sup>°</sup>. <sup>d</sup> This work; Grandview mine, specimen PAWCYAN; refined unit-cell constants are *a* 10.178(2), *b* 2.903(1), *c* 12.684(4) Å,  $\beta$  92.38(3)<sup>°</sup>. <sup>e</sup> This work; Dachand (Qinglong) deposit, Guizhou Province, China; refined unit-cell constants are *a* 10.178(3), *b* 2.905(1), *c* 12.634(8) Å,  $\beta$  92.56(5)<sup>°</sup>. <sup>f</sup> This work; Grandview mine, specimen GRAND (from Malcolm Alter); refined unit-cell constants are *a* 10.176(2), *b* 2.903(1), *c* 12.654(6) Å,  $\beta$  92.50(4)<sup>°</sup>. <sup>h</sup> *I*<sub>rel</sub> = 100 line for chalcoculmrite; see text. Alternative indices are given for *d*<sub>calc</sub> values within 0.005 Å of those calculated for the refined unit-cell of the particular sample.

is clearly present, but no *Ok*l reflections are present in the reflection record, possibly because of preferred orientation effects.

The powder X-ray-diffraction data, together with derived unit-cell constants, provide convincing evidence for the long-assumed structural relationship in the cyanotrichite group. The question then remains as to just how substitution in the closely related monoclinic unit-cells of Table 2 gives rise to the various species that comprise the group. A careful examination of the khaidarkanite structure shows how this may be accomplished.

*Structural and chemical relationships*

Although the nature of the crystal structure of khaidarkanite has been well described by Rastsvetaeva *et al.* (1997), it is appropriate to reiterate the main structural features here. The three metal ion sites present, Cu, Al(1) and Al(2), each display octahedral coordination with varying degrees of distortion. Atom Al(1) is bonded to six OH<sup>-</sup> ions [OH(1) and OH(2)] with only minor variation in the bond lengths, whereas Al(2) is bonded

to four F<sup>-</sup> ions (in a plane) with two apical O(W) species (OH<sup>-</sup> or H<sub>2</sub>O) at a slightly longer distance. The Cu octahedron is significantly distorted, with the Cu atom at the center of four OH<sup>-</sup> ions [OH(2) and OH(3)], with Cu-O distances ~2.0 Å, plus two much longer bonds (~2.5 Å) to OW and an OH<sup>-</sup> ion [OH(1)]; the O(W)-Cu-OH(1) angle is ~150°. In the structure, each of the three different metal-ion octahedra link to like octahedra *via* shared edges to form columns in the *b* direction. In the case of Cu and Al(1), this occurs through shared OH<sup>-</sup> ions, and in the case of Al(2), it occurs *via* shared F<sup>-</sup> ions. Each Al(1)-centered column is then flanked by two Cu-centered columns and coupled to them by further edge-sharing *via* OH<sup>-</sup> ions to form a ribbon-like unit. These ribbons are then coupled edgewise by the Al(2)-centered columns *via* corner sharing of the O(W) species, to form a crenulated layer structure parallel to *ab*. These layers are strongly H-bonded to each other in the *a* direction. An (010) view of the structure is shown in Figure 1.

In the structure, space group *C2/m* (Rastsvetaeva *et al.* 1997; *R* = 0.029), all atoms save one of the hydrogen atoms lie in special positions (Table 4). It should be noted that the O(W) site is occupied by an H<sub>2</sub>O molecule or an OH<sup>-</sup> ion (occupancy for each

TABLE 2. REFINED UNIT-CELL DATA AND LITERATURE VALUES FOR MEMBERS OF THE CYANOTRICHITE GROUP

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)
<b>Cyanotrichite</b>				
1 <sup>a</sup>	10.163(7)	2.915(3)	12.596(10)	92.60(8)
2	10.178(3)	2.901(1)	12.649(5)	92.38(3)
3	10.184(5)	2.903(2)	12.632(8)	92.51(6)
4	10.178(2)	2.903(1)	12.684(4)	92.38(3)
5	10.178(3)	2.905(1)	12.634(8)	92.56(5)
6	10.176(2)	2.903(1)	12.654(6)	92.50(4)
<b>Carbonate-cyanotrichite</b>				
7	10.13(2)	2.87(2)	12.41(3)	98.9(4)
8	10.166(6)	2.833(4)	12.551(6)	98.61(8)
9	10.149(6)	2.832(5)	12.549(9)	98.48(10)
<b>Camerolaite</b>				
10	10.765(6)	2.903(2)	12.527(8)	95.61(4)
<b>Co-rich member of the cyanotrichite group</b>				
11a	10.136(4)	2.885(2)	12.714(8)	95.52(6)
11b	10.204(3)	2.914(2)	12.421(9)	98.69(7)
<b>Khaidarkanite</b>				
12	12.326(3)	2.907(3)	10.369(7)	97.90(2)
13	12.33	2.90	10.37	97.8

<sup>a</sup> 1: ICDD-PDF card no. 11-0131 (original orthorhombic cell given as *a* 10.16, *b* 12.61, *c* 2.90 Å); 2: this work, from IMA 2007-004, Grandview mine; 3: this work, specimen PAWCYAN, Grandview mine; 4: this work, specimen PAWCYAN, Grandview mine, separate hand-picked sample; 5: this work, Dachang (Qinglong) deposit, Guizhou Province, China; 6: this work, specimen GRAND, Grandview mine; 7: ICDD-PDF card no. 16-0365; 8: this work, Grandview mine, Arizona, specimen PAWCYAN; 9: this work, Dachang (Qinglong) deposit, Guizhou Province, China; 10: Cap Garonne mine, Var, France, Sarp & Perroud (1991); 11: this work, Grandview mine, Co-rich member of the cyanotrichite group; 11a and 11b refer to cells refined based on camerolaite- and carbonate-cyanotrichite-like cells, respectively; 12: Khaidarkan deposit, Kyrgyzstan, refined single-crystal X-ray data, Rastsvetaeva *et al.* (1997); space group *C2/m* requires the interchange of *a* and *c* as compared to other members of the group; 13: Khaidarkan deposit, Kyrgyzstan, refined from powder X-ray-diffraction data, Chukanov *et al.* (1999).

TABLE 3. POWDER X-RAY-DIFFRACTION DATA FOR CARBONATE-CYANOTRICHITE

<i>h k l</i>	1 <sup>a</sup>			2			3		
	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>
1 0 0	95	10.1	10.004						
1 0 2	45	5.63	5.628	44	5.641	5.673	60	5.640	5.666
2 0 0	60	5.03	5.002	95	5.030	5.026	100	5.035	5.019
1 0 2				30	4.944	4.958	41	4.946	4.962
2 0 2	100	4.21	4.207	63	4.208	4.227	70	4.215	4.219
		6	3.89 <sup>c</sup>						
2 0 2	16	3.65	3.611	11	3.632	3.647	26	3.636	3.648
3 0 0	60	3.33	3.335	100	3.351	3.350	72	3.353	3.346
2 0 3	2	2.93	2.949						
3 0 2	45	2.77	2.756	26	2.779	2.779	24	2.780	2.779
4 0 0	50	2.51 <sup>c</sup>	2.501	67	2.515	2.513	47	2.515	2.510
4 0 2	45	2.45	2.452	18	2.457	2.461	24	2.456	2.456
2 1 1	8	2.38	2.402						
1 1 3				25	2.325	2.321	47	2.325	2.319
1 1 3				5	2.234	2.235			
4 0 2				7	2.217	2.216			
2 1 3				2	2.197	2.192			
3 0 4				3	2.130	2.124			
5 0 0	55	2.01	2.001	51	2.011	2.010	35	2.010	2.008
4 1 1				5	1.826	1.829	11	1.825	1.828
2 1 5				2	1.818	1.818			
6 0 2	2	1.67	1.676	5	1.680	1.682	12	1.678	1.679
6 0 4				5	1.578	1.578			
2 0 8	2	1.529	1.533	3	1.549	1.549	15	1.548	1.548
3 1 7	2	1.441	1.436						
1 0 10				3	1.254	1.255			

<sup>a</sup> 1: ICDD-PDF card no. 16-0365; refined unit-cell constants are *a* 10.13(2), *b* 2.87(2), *c* 12.41(3) Å, β 98.9(4)°; 2: this work, Grandview mine, Arizona, specimen PAWCYAN; refined unit-cell constants are *a* 10.166(6), *b* 2.833(4), *c* 12.551(6) Å, β 98.61(8)°; 3: this work, Dachang (Qinglong) deposit, Guizhou Province, China; refined unit-cell constants are *a* 10.149(6), *b* 2.832(5), *c* 12.549(9) Å, β 98.48(10)°. The intensities for 2 and 3 are rescaled to 100 rather than to the strongest line at *d* = *ca.* 10.1 Å (see text). <sup>b</sup> Observed to overlap with *I*<sub>rel</sub> = 100 line of cyanotrichite (see text); data are rescaled to 100 rather than to the strongest line at *ca.* 10.1 Å (see text). <sup>c</sup> The *d* = 3.89 Å line is attributed to the *I*<sub>rel</sub> = 85 line of brochantite (*d* = 3.90 Å), and the *I*<sub>rel</sub> = 100 of brochantite (*d* = 2.521 Å) overlaps that at *d* = 2.51 Å.

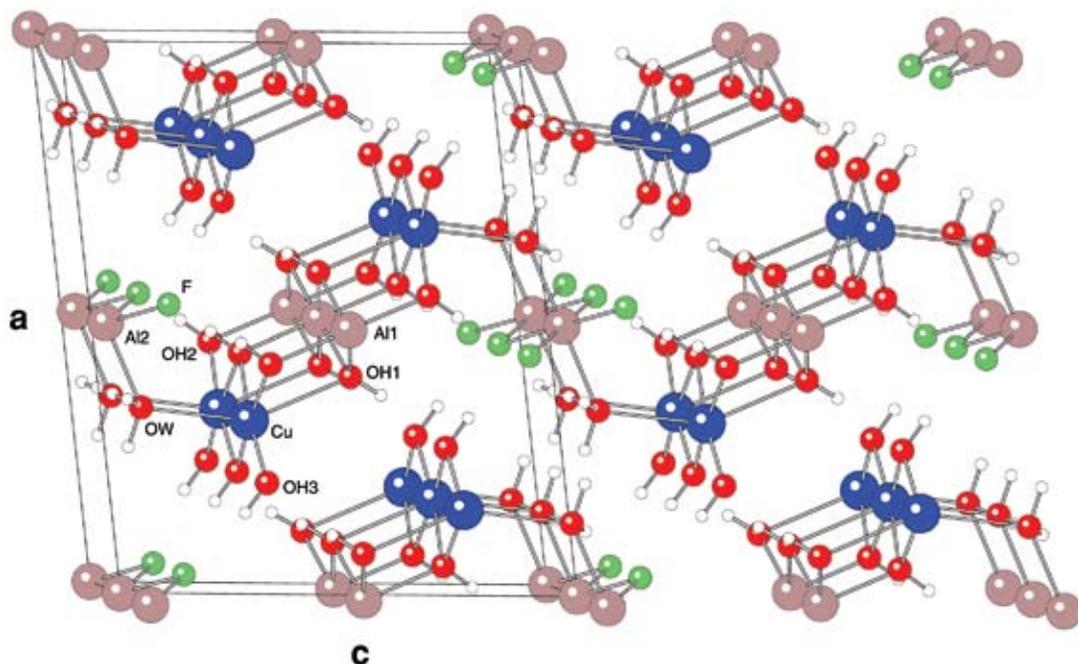


FIG. 1. Projection of the structure of khaidarkanite looking down  $b$ . Symmetry-related atoms are not labeled, and hydrogen bonds are omitted for clarity. The O(W) and F sites are only fractionally occupied (see text).

exactly 0.5). Furthermore, it is evident from the data in the table that both the site-occupancy factor (sof) and the thermal parameters were refined for Al(2) and F, but the site occupancies are interdependent. If the sof of Al(2) were exactly 0.5, and that of F were 0.75, the stoichiometry of the mineral would be precisely  $\text{Cu}_4\text{Al}_3(\text{OH})_{14}\text{F}_3 \cdot 2\text{H}_2\text{O}$ ; adoption of these sof values would have a negligible bearing on the structure analysis. We also note that the structure is entirely consistent with results of electron-microprobe and wet-chemical analyses of the mineral (Table 5; bulk analyses at least for composition 1). Nevertheless, although it is accepted that the structure is essentially correct, there are some subtle points evident in both it and the analytical data that warrant further comment.

First, the  $B_{\text{eq}}$  values for Al(2), F and O(W) are rather high compared to those of the other non-hydrogen atoms. This must arise in part from the fact that F and O(W) are the only atoms coordinated to Al(2); O(W) bridges Al(2) and Cu (Fig. 1). Where the Al(2) site is vacant, O(W) remains, as does one third of the total fluoride. In this case, O(W) is coordinated solely to Cu, and F is hydrogen-bonded to OH(2) and OH(3) groups. Thus it is inevitable that the coordinates for O(W) and F actually represent averages for the two situations, as separate coordinates cannot be resolved

by the single-crystal data, and higher  $B_{\text{eq}}$  values would be expected. Indeed, the O(W) position, for the reason that it does bond to both Al(2) and Cu, may also subtly vary depending on whether or not it is occupied by  $\text{H}_2\text{O}$  or  $\text{OH}^-$ . However, this possible variation may be very slight, although it may contribute to the larger  $B_{\text{eq}}$  value for Al(2) sited in a variable coordination environment [nearly three times larger than the value for Al(1)].

A list of structure factors for khaidarkanite was kindly provided by Dr. Nikita Chukanov, one of the authors of the papers describing the mineral and its structure. Starting with the coordinates of the non-H atoms and sof values of Rastsvetaeva *et al.* (1997), the structure was re-refined using the original data with SHELXL-97 (Sheldrick 1997). The H atoms were located in a difference map at positions close to those reported. In subsequent refinements, non-H atoms were refined anisotropically, and the positions of H atoms were restrained in the same manner as described by Rastsvetaeva *et al.* (1997). For all 485 reflection data, an  $R1$  of 0.035 was obtained. Final atomic coordinates (essentially the same as those previously reported), anisotropic thermal parameters and  $U_{\text{eq}}$  values are listed in Table 6. Site-occupancy factors are somewhat different, as discussed below. As anticipated, the thermal ellipsoid for F is significantly elongate along  $b$ ,

and that of O(W) is flattened in the *ab* plane. A consequence of this analysis is that the alternative F and O(W) coordinates associated with the presence or absence of Al(2) lie across the mirror in space group *C2/m*; the true space-group of the mineral may be *C2*. The data are not of sufficient quality to enable this possibility to be tested, although the “average” structure does conform to space group *C2/m*.

Alternatively, and in conjunction with the above, it may be the case that sof values for Al(2), F and O(W) are somewhat lower than those reported. Attempts to refine the structure with a reduced sof for Al(2) sent this atom non-positive definite when the occupancy of the two-fold site was less than about 40% and the Al:F ratio was maintained at 1:3. Under the above condition, the  $U_{eq}$  values for Al(2) and F fell to 0.026(2) and 0.048(3) from 0.038(2) and 0.064(3), respectively. The relatively high  $U_{eq}$  value of O(W) of 0.057(2) reduced to 0.036(2) when its site occupancy was lowered to 75%, and *R1* increased slightly to 0.041 for all data. For charge-balance reasons, the O(W) site must then accommodate two OH<sup>-</sup> ions and one H<sub>2</sub>O molecule. The  $U_{eq}$  value for F may be further lowered by reducing its sof, but this reduces the Al:F ratio of 1:3. In this case, the OH<sup>-</sup> component of the O(W) site must vary sympathetically to maintain charge balance. It is therefore possible that the particular crystal used for the data collection had a slightly different composition from that used for chemical analysis. This would be in line with analytical variations, but only single analyses of F and H<sub>2</sub>O were carried out. Notwithstanding this possibility, we re-emphasize that the reported structure is consistent with bulk contents of CuO, Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O and F, taking the Na value to arise from impurities and ignoring the minor amounts of SO<sub>3</sub> and SiO<sub>2</sub>. This may not be the case, as set out below, but before this possibility is dealt with, the possible range of composition of khaidarkanite is worthy of exploration.

There is no compelling reason for the composition of khaidarkanite to be simply Cu<sub>4</sub>Al<sub>3</sub>(OH)<sub>14</sub>F<sub>3</sub>•2H<sub>2</sub>O.

TABLE 4. COORDINATES, SITE MULTIPLICITIES, SITE OCCUPANCIES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS OF ATOMS IN KHAIDARKANITE<sup>a</sup>

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	multiplicity	occupancy	$B_{eq}$ , Å <sup>2</sup>
Cu	0.1747(1)	0	0.7085(1)	4	1	1.21(3)
Al(1)	0.5000	0	0.5000	2	1	1.01(5)
Al(2)	0	0	0	2	0.49(1)	2.9(1)
OH(1)	-0.0949(2)	0	0.5228(3)	4	1	1.3(1)
OH(2)	0.5630(2)	0	0.6813(3)	4	1	1.3(1)
OH(3)	0.7780(3)	0	0.7160(3)	4	1	1.5(1)
F	0.5446(5)	0	0.1108(5)	4	0.73(1)	4.8(2)
O(W)	-0.1528(6)	0	0.0569(5)	4	1	4.6(2)
H(1)	0.1460(90)	0	0.4160(90)	4	1	
H(2)	0.4740(90)	0	0.2590(90)	4	1	
H(3)	0.1550(90)	0	0.2200(90)	4	1	
H(4)	0.1680	0.2630	0.9980	8	0.5 <sup>b</sup>	
H(5)	0.2350	0	0.9560	4	0.5 <sup>b</sup>	

<sup>a</sup> Fixed occupancy. <sup>b</sup> Rastsvetaeva *et al.* (1997).

If each of the Al(2), F and O(W) sites is fully occupied, the latter must contain only OH<sup>-</sup> ions to give a formula of Cu<sub>4</sub>Al<sub>4</sub>(OH)<sub>16</sub>F<sub>4</sub>. Similarly, the Al:F ratio can vary with sympathetic variation of the H<sub>2</sub>O:OH<sup>-</sup> ratio at the O(W) site and appropriate adjustment of Al and F sof values. It is also possible to envisage replacement of F<sup>-</sup> by OH<sup>-</sup> to give possible stoichiometries that could be devoid of any fluoride. The importance of this is addressed below in a consideration of the possible nature of carbonate-cyanotrichite. Variation of the sof of O(W) would lead to a range of hydration states. Further

TABLE 5. ANALYTICAL DATA FOR KHAIDARKANITE

	1 <sup>a</sup>	2	3	4	5	6
Na <sub>2</sub> O wt%		1.20	1.96	1.58		
CuO		46.27	45.91	46.09	46.27	47.76
Al <sub>2</sub> O <sub>3</sub>		23.34	21.36	22.35	23.34	22.95
SiO <sub>2</sub>	0.50	0.47	1.10	0.785 <sup>c</sup>	0.47	
SO <sub>3</sub>	4.7	0.10	4.55	2.325 <sup>c</sup>	0.10	
H <sub>2</sub> O	22.30				22.30	24.34
F	8.05				8.05	8.55
Total		101.73 <sup>b</sup>	105.23 <sup>b</sup>	103.48 <sup>f</sup>	100.53	103.60
Less O=F		3.39 <sup>e</sup>	3.39 <sup>e</sup>	3.39 <sup>e</sup>	3.39 <sup>g</sup>	3.60
Total		98.34 <sup>d</sup>	101.84 <sup>d</sup>	100.09 <sup>d</sup>	97.14 <sup>d</sup>	100.00

<sup>a</sup> 1: Wet-chemical analyses for SiO<sub>2</sub> and SO<sub>3</sub>, F by ion-selective electrode, H<sub>2</sub>O by absorption pipe method (Chukanov *et al.* 1999); 2, 3: electron-microprobe analyses except for F and H<sub>2</sub>O (Chukanov *et al.* 1999); 4: average of 1 and 2; 5: analytical data taken from Rastsvetaeva *et al.* (1997); 6: calculated for Cu<sub>4</sub>Al<sub>4</sub>(OH)<sub>16</sub>F<sub>4</sub>•2H<sub>2</sub>O with F rounded from 8.555 to 8.55; an error is present in the similar calculation of Rastsvetaeva *et al.* (1999). <sup>b</sup> Including F and H<sub>2</sub>O from analysis 1. <sup>c</sup> Given in error as 3.30% in Chukanov *et al.* (1999). <sup>d</sup> Correct sum taking into account an error in O=F. <sup>e</sup> Given as 0.78 and 2.32%, respectively, in Chukanov *et al.* (1999). <sup>f</sup> Correct sum from averaging of SiO<sub>2</sub> and SO<sub>3</sub> analytical results. <sup>g</sup> Given in error as 3.03% in Rastsvetaeva *et al.* (1999).

TABLE 6. COORDINATES OF THE NON-HYDROGEN ATOMS, ANISOTROPIC DISPLACEMENT PARAMETERS,  $U_{ij}$ , AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS,  $U_{eq}$ , IN KHAIDARKANITE

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}$
Cu	0.1748(1)	0	0.7085(1)	0.0016(1)
Al(1)	0.5000	0	0.5000	0.0012(1)
Al(2)	0	0	0	0.0038(2)
OH(1)	0.0947(4)	0	0.4773(4)	0.0015(1)
OH(2)	0.5631(4)	0	0.6811(4)	0.0014(1)
OH(3)	0.7779(4)	0	0.7157(5)	0.0018(1)
F	0.5443(7)	0	0.1108(8)	0.0064(3)
O(W)	0.1527(8)	0	0.9423(7)	0.0057(2)

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cu	0.0015(1)	0.0014(1)	0.0018(1)	0	0.0002(1)	0
Al(1)	0.0013(1)	0.0013(1)	0.0009(1)	0	0.0001(1)	0
Al(2)	0.0035(4)	0.0030(4)	0.0040(4)	0	-0.0026(3)	0
OH(1)	0.0015(2)	0.0017(2)	0.0013(2)	0	0.0006(2)	0
OH(2)	0.0017(2)	0.0018(2)	0.0008(2)	0	0.0003(2)	0
OH(3)	0.0014(2)	0.0016(2)	0.0023(3)	0	0.0002(2)	0
F	0.0042(5)	0.0120(10)	0.0032(4)	0	0.0015(4)	0
O(W)	0.0085(6)	0.0052(5)	0.0032(4)	0	0.0008(4)	0

These values were calculated using the starting coordinates of Table 4, and re-refined using the original data (see text). The exponent of the anisotropic displacement factor takes the form  $-2\pi^2[h^2a^2U_{11} + \dots + 2hkab^2U_{12}]$ , and  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The values of  $U_{ij}$  are expressed in Å<sup>2</sup>.

elaboration of these possibilities is rather hypothetical, but we note in passing that if the  $\text{H}_2\text{O}:\text{OH}^-$  ratio at the O(W) site is maintained at 1:1 and F is fully occupied, the maximum sof of Al(2) is 2/3, and the formula  $\text{Cu}_4\text{Al}_{3.33}(\text{OH})_{14}\text{F}_4 \cdot 2\text{H}_2\text{O}$  is obtained.

The situation is made somewhat more complex if the  $\text{SO}_3$  content of khaidarkanite is taken into account, in conjunction with other reported data. In all of the reported compositions of khaidarkanite,  $\text{SO}_3$  is present. In fact, Chukanov *et al.* (1999) noted that the sulfur content of most samples examined is significant. The presence of sulfate was mentioned in passing in the structure determination by Rastsvetaeva *et al.* (1997). What is most telling in this connection is the comparison of the IR spectra of khaidarkanite and cyanotrichite presented by Chukanov *et al.* (1999). All modes in the 400 to 1650  $\text{cm}^{-1}$  region of khaidarkanite (1630, 1560, 1135, 1101, 1036, 930, 885, 744, 658, 574, 508, 452  $\text{cm}^{-1}$ ) are duplicated in the spectrum of cyanotrichite, except for the 930 and 885  $\text{cm}^{-1}$  bands of the former, which appear as a rather more broad band in cyanotrichite. Aside from intensity variations, the spectra are virtually identical, and the authors explicitly referred to S–O modes being present in khaidarkanite. Bands at 1135, 1101 and 1036  $\text{cm}^{-1}$  can be identified as antisymmetric S–O stretching modes (Nakamoto 1997, Frost *et al.* 2004). The inescapable conclusion is that sulfate is present in the khaidarkanite structure and is not present as a contaminant. Similarly, the small amount of  $\text{SiO}_2$  reported may be viewed in the same light, with  $\text{SiO}_2(\text{OH})_2^{2-}$  also present in the structure, but this possibility is more speculative. We note that the small amount of Na reported by Chukanov *et al.* (1999) was ignored by Rastsvetaeva *et al.* (1997). The radius of the  $\text{Na}^+$  ion is too large to be sensibly accommodated by any of the Cu and Al sites. We attribute the Na reported to impurities or, possibly, an artefact of the electron-microprobe analyses. To be fair, Chukanov *et al.* (1999) proposed the formulae  $\text{Na}_{0.26}\text{Cu}_{4.00}\text{Al}_{3.12}(\text{OH})_{14.51}\text{F}_{2.89}(\text{SO}_4)_{0.19}(\text{SiO}_4)_{0.05} \cdot 1.19\text{H}_2\text{O}$  and  $\text{Na}_{0.44}\text{Cu}_{4.00}\text{Al}_{2.90}(\text{OH})_{12.90}\text{F}_{2.94}(\text{SO}_4)_{0.39}(\text{SiO}_4)_{0.13} \cdot 2.12\text{H}_2\text{O}$ , on the basis of compositions 2 and 3 in Table 5, respectively, and ideally  $\text{Cu}_4\text{Al}_3(\text{OH})_{14}\text{F}_3 \cdot 2\text{H}_2\text{O}$ .

There is only one site in the structure that can accommodate sulfate, and this concerns the special positions 0,0,0 and  $\frac{1}{2}, \frac{1}{2}, 0$ . If the S atom is placed at the origin [*i.e.*, the Al(2) site], two oxygen atom sites must be present in space group  $C2/m$  in general positions to generate a tetrahedral array that is then itself disordered over two positions. At the level of substitution of sulfate indicated by the analytical results, electron density in the Fourier projection corresponding to sulfate oxygen atoms would be low (of the order of  $1.5 \text{ e } \text{Å}^{-3}$ ), and this would render its exact location difficult to discern. Available single-crystal X-ray data do not allow a resolution of this matter, but the general conclusion remains valid.

### Common structural features in the cyanotrichite group

Knowledge of the structure of khaidarkanite makes it possible to suggest structures for other members of the cyanotrichite group. The unifying structural motif for the group is the structure generated by the ribbon-like unit built from Cu, Al(1), OH(1), OH(2) and OH(3), with a formula of  $[\text{Cu}_4\text{Al}_2(\text{OH})_{12}^{2+}]$ . The O(W) site may be occupied by  $\text{H}_2\text{O}$  or  $\text{OH}^-$ , or may be vacant. Sites at or near 0,0,0 and  $\frac{1}{2}, \frac{1}{2}, 0$  may be occupied by a variety of charge-balancing chemical constituents, and these need not be identical in both positions. Thus, as noted above, in khaidarkanite, each of the four symmetrically equivalent O(W) sites is occupied by  $[(\text{H}_2\text{O})_{0.5}(\text{OH})_{0.5}]$  and an  $\text{AlF}_3$  [Al(2)] fragment with reduced site-occupancy is centered at 0,0,0 and at  $\frac{1}{2}, \frac{1}{2}, 0$ . Cyanotrichite itself would simply comprise the basic structural motif above, a half-occupied O(W) site containing only  $\text{H}_2\text{O}$ , and a sulfate ion centered at the origin. As a consequence, the  $\frac{1}{2}, \frac{1}{2}, 0$  site is vacant, and the lattice is primitive, in line with the powder X-ray-diffraction data. In this case, the space group is likely to be  $P2/m$ , which would necessitate the coordinates of Cu, Al(1), OH(1), OH(2) and OH(3) to be duplicated at sites close to, but not exactly at,  $\frac{1}{2}+x, \frac{1}{2}+y, 0$ . This situation may be elaborated by vacancies at the O(W) site, protonation of two of the remaining  $\text{OH}^-$  groups (probably disordered over the lattice), and incorporation of a carbonate ion near  $\frac{1}{2}, \frac{1}{2}, 0$  to give the stoichiometry ascribed to camerolaite,  $\text{Cu}_4\text{Al}_2[\text{HSbO}_4, \text{SO}_4](\text{OH})_{10}(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ , where the mole fraction of  $\text{HSbO}_4^{2-}$  exceeds that of  $\text{SO}_4^{2-}$  (although the exact position of the  $\text{Sb}^{5+}$  center is not known). It is immediately apparent that a potentially new mineral could exist where the reverse is true. It would have the ideal end-member stoichiometry  $\text{Cu}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{10}(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ , and it is tempting to speculate that this would possibly represent the formula of the most enigmatic member of the group, carbonate-cyanotrichite. However, in light of the multiple solid-solution complications that now present themselves, this possibility is far from clear. It is true that carbonate-cyanotrichite may be the carbonate-substituted analogue of cyanotrichite, based on the above structural relationship. Both of these possibilities would require carbonate-cyanotrichite to possess a  $P$  cell, but it is also possible that a carbonate group could occupy 0,0,0 and  $\frac{1}{2}, \frac{1}{2}, 0$  with fractional occupancy. On the other hand, this would be at odds with the fact that there is no definitive evidence for a solid solution between cyanotrichite and carbonate-cyanotrichite; on the contrary, the minerals (on the basis of powder X-ray-diffraction measurements) are present in many specimens as two separate phases. A re-examination of the reported analytical data for type carbonate-cyanotrichite gives rise to an intriguing alternative formulation that serves in part to explain these observations.

In the original description of carbonate-cyanotrichite (Ankinovich *et al.* 1963), analytical results were interpreted as reflecting the presence of some impurities. Thus quantities corresponding to 2.98% quartz, 0.88% dolomite, 0.50% calcite and 0.80% adsorbed H<sub>2</sub>O were deducted. The remaining values were used to calculate the formula [(Cu<sub>3.63</sub>Zn<sub>0.05</sub>V<sub>0.01</sub>Mg<sub>0.01</sub>)<sub>Σ3.70</sub>Al<sub>2.30</sub>](C<sub>0.67</sub>S<sub>0.33</sub>)[O<sub>2.98</sub>(OH)<sub>1.02</sub>]<sub>Σ4.00</sub>(OH)<sub>12</sub>•2H<sub>2</sub>O. The simplified formula Cu<sub>3.70</sub>Al<sub>2.30</sub>(C<sub>0.67</sub>S<sub>0.33</sub>)[O<sub>2.98</sub>(OH)<sub>1.02</sub>]<sub>Σ4.00</sub>(OH)<sub>12</sub>•2H<sub>2</sub>O also was given. This has been quoted as (Cu,Zn)<sub>3.70</sub>Al<sub>2.30</sub>(C<sub>0.67</sub>S<sub>0.33</sub>)[O<sub>2.98</sub>(OH)<sub>1.02</sub>](OH)<sub>12</sub>•2H<sub>2</sub>O elsewhere (see, for example, Anthony *et al.* 2003) and is cast in allusion to the cyanotrichite formula in that Cu+Al = 6, CO<sub>3</sub><sup>2-</sup> + SO<sub>4</sub><sup>2-</sup> = 1, with 12 lattice OH<sup>-</sup> ions and two structurally bound H<sub>2</sub>O molecules. If, however, the Cu site is taken to be fully occupied, the formula may be cast as (Cu,Zn)<sub>Σ4.00</sub>Al<sub>2.486</sub>(CO<sub>3</sub>)<sub>0.724</sub>(SO<sub>4</sub>)<sub>0.357</sub>(OH)<sub>13.320</sub>•2.54H<sub>2</sub>O, with no change to the originally proposed elemental ratios. Taking into account the unifying structural motif identified above, this formula can be re-arranged to give [Cu<sub>4</sub>Al<sub>2</sub>(OH)<sub>12</sub>]Al<sub>0.486</sub>(CO<sub>3</sub>)<sub>0.724</sub>(SO<sub>4</sub>)<sub>0.357</sub>(OH)<sub>1.320</sub>•2.54H<sub>2</sub>O or, more ideally, [Cu<sub>4</sub>Al<sub>2</sub>(OH)<sub>12</sub>][Al(OH)<sub>3</sub>]<sub>0.49</sub>(CO<sub>3</sub>)<sub>0.7</sub>(SO<sub>4</sub>)<sub>0.3</sub>•2H<sub>2</sub>O. Therefore, carbonate-cyanotrichite can be viewed as being analogous to khaidarkanite with Al(OH)<sub>3</sub> replacing AlF<sub>3</sub>. The O(W) site is 50% occupied by H<sub>2</sub>O, and sulfate is located at 0,0,0. Carbonate may be located near ½,½,0, or this site may be occupied by both carbonate or sulfate; all such arrangements give a *P* cell. Alternatively, Al(OH)<sub>3</sub>, SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> may be disordered over 0,0,0 and ½,½,0 to give an average *C* cell, as discussed previously for khaidarkanite.

In any event, it is now clear that whereas one-for-one substitution in the cyanotrichite group could be entertained, a series of more complex substitutions can take place. These change the stoichiometry of the particular species being considered in a more fundamental way. The Cu<sup>2+</sup>:Al<sup>3+</sup>:OH<sup>-</sup> proportions will vary depending upon subtle variations in the activity of constituent ions and pH in the solutions from which the minerals crystallize. Further, this variation may act in concert with changes in stoichiometry due to the relative activities of SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup> and F<sup>-</sup> in solution. Because it is inevitable that these quantities evolve with time in the supergene setting, various members of the cyanotrichite group would likely be present in the same deposit, as we have found. In this connection, we draw attention to an Austrian deposit that hosts (*inter alia*) the three species cyanotrichite, carbonate-cyanotrichite and khaidarkanite (Schnorrer & Bacher 2000). It is also worth pointing out in passing that cyanotrichite containing small amounts of F<sup>-</sup> (up to 0.16 *apfu*) has been reported by Sejkora *et al.* (2006).

It is now obvious that other new minerals of the cyanotrichite group with subtly different stoichiometries and either *P* or *C* face-centered cells remain to be described. This became evident in this study with

respect to the mixed samples of cyanotrichite and carbonate-cyanotrichite from the Grandview mine and the Dachang deposit, data for which are given in Tables 1–3. A TGA analysis of the Dachang specimen, which contains significant amounts of carbonate-cyanotrichite, gave 22.57% H<sub>2</sub>O and 12.00% SO<sub>3</sub> [Cu<sub>4</sub>Al<sub>2</sub>SO<sub>4</sub>(OH)<sub>12</sub>•2H<sub>2</sub>O, cyanotrichite, requires 22.37% H<sub>2</sub>O and 12.43% SO<sub>3</sub>]. No mass loss that could be attributed to CO<sub>2</sub> evolution was identified. The FTIR spectra of the material show it to be devoid of carbonate, with no hint of a C–O stretch around 1400 cm<sup>-1</sup> (Fig. 2). A similar result was obtained for specimens PAWCYAN and GRAND. Thus among the family of stoichiometries that can be imagined for carbonate-cyanotrichite-like minerals, a carbonate-free species must exist. This may have a stoichiometry of Cu<sub>4</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>10</sub>•*n*H<sub>2</sub>O (*n* in the range 2–4), akin to that of camerolaite, but an evaluation must await the results of further studies if suitable specimens come to light.

Other patterns of substitution are possible. A further specimen of dark brown, Co-rich carbonate-cyanotrichite from the Grandview mine was provided for study by Malcolm Alter. Exceedingly acicular brown crystals up to 5 mm in length and up to 3 μm in diameter are associated with brochantite, and are perched on blue cyanotrichite and chalcoalumite in turn. Small amounts of antlerite were noted also to be present in matrix of the specimen. An SEM examination of isolated needles showed that they were liberally coated with minute crystals of antlerite or brochantite, thus rendering accurate analyses impossible. A hand-picked sample was dissolved in dilute aqueous HNO<sub>3</sub>, and the solution was analyzed by AAS to give Co ≈ Cu. This was confirmed by semiquantitative SEM (WDS) analyses of a sample embedded in epoxy and hand-polished to give a flat surface. A Co-dominant analogue of cyanotrichite or one or other of its congeners could thus exist, and substitution at the Cu site can obviously be significant. Powder X-ray-diffraction data are listed in Table 7. The data could not be indexed on the basis of the cyanotrichite cell with β ≈ 92.5°. However, if peaks corresponding to brochantite save for a shoulder at *d*<sub>obs</sub> = 6.384 Å and antlerite are ignored, a fit to a camerolaite-like cell is possible, with refined unit-cell constants *a* 10.136(4), *b* 2.885(2), *c* 12.714(8) Å, β 95.52(6)° (Table 2). Alternatively, a fit to a carbonate-cyanotrichite-like cell also is possible (Table 7). In this case, two further reflections that are close to those of antlerite and one close to a strong reflection of brochantite can be indexed (assuming overlap) with a carbonate-cyanotrichite-like cell that refines to give *a* 10.204(3), *b* 2.914(2), *c* 12.421(9) Å, β 98.69(7)° (Table 7). Unfortunately, the data to hand are not of sufficiently high quality to resolve this particular issue, and not enough material is available free of brochantite to fully characterize the sample. As with cyanotrichite, carbonate-cyanotrichite and camerolaite, further under-

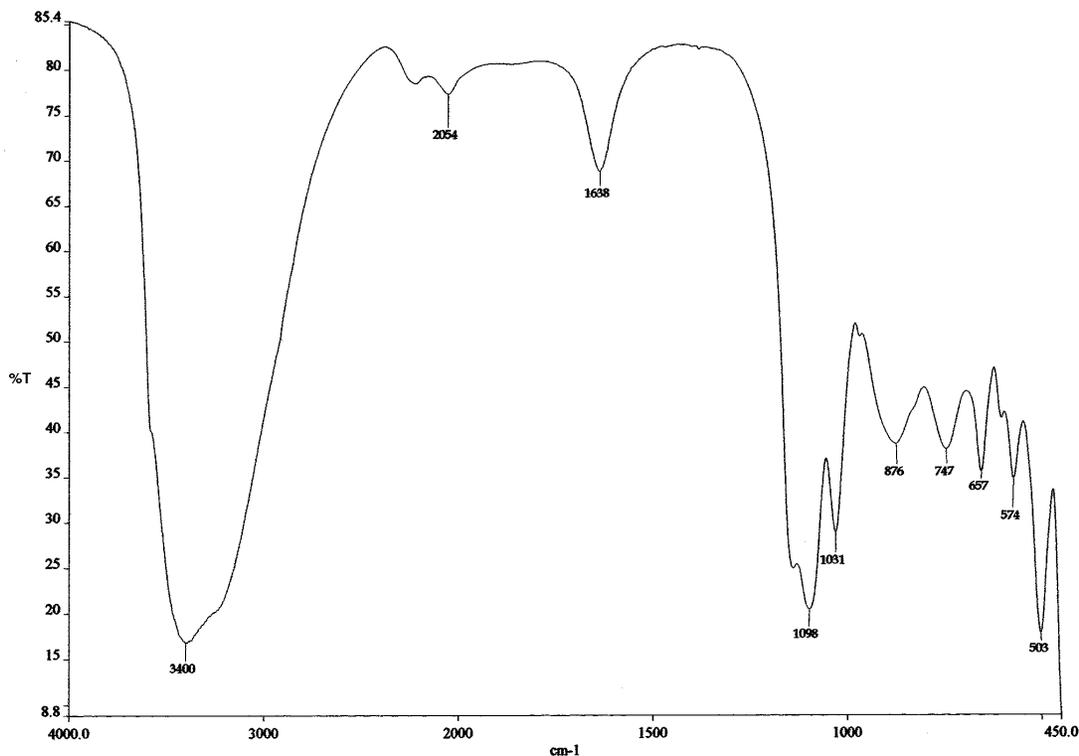


FIG. 2. The FTIR spectrum of a sample of cyanotrichite which is, according to powder X-ray-diffraction data, mixed with significant amounts of carbonate-cyanotrichite. The sample is from the Dachang (Qinglong) Sb–Au deposit, Guizhou Province, China. A C–O mode around  $1400\text{ cm}^{-1}$  is not observed.

standing is limited by the lack of crystals suitable for single-crystal studies of the structure.

Finally, attention is drawn to another cyanotrichite-like phase reported from the Clara mine, Germany (Walenta 2001). Qualitative analyses indicated the significant presence of Cu, Al and S; carbonate is not present, as shown by dissolution of the mineral in acid. Walenta (2001) discussed possible relationships between the mineral and cyanotrichite, carbonate-cyanotrichite and camerolaite, and concluded, correctly in our view, that cyanotrichite is a monoclinic phase. Powder X-ray-diffraction data (FeK $\alpha$  radiation) were given for nine unindexed lines. We have been unable to index these on the basis of cells related to cyanotrichite or carbonate-cyanotrichite. However, it has been possible to find a cell related to khaidarkanite (Table 8), and given the number of data points, the errors are surprisingly small; refined unit-cell constants are  $a$  10.388(16),  $b$  2.907(8),  $c$  12.349(22) Å,  $\beta$  97.98(19)°. We note in passing that other related cells can be derived if the indexing of the reflexions is different, but these have somewhat higher errors associated with cell constants. This material probably represents another chemical variant of the

cyanotrichite group in terms of patterns of substitution discussed above. Again, elucidation of the intimate structural details of this phase awaits a single-crystal investigation of the structure.

#### SUPPLEMENTARY DATA

Full lists of crystallographic data excluding tables of structure factors for the re-refined structure of khaidarkanite have been deposited with the Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum, Karlsruhe, Germany; CRYSDATA@FIZ-Karlsruhe.DE. Any request to the ICSD for this material should quote the full literature citation and the CSD number 419513. This information, together with lists of observed and calculated structure-factors, is available from the Depository of Unpublished Data on the MAC website [document Khaidarkanite CM47\_635].

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TABLE 7. POWDER X-RAY-DIFFRACTION DATA FOR THE CO-RICH MEMBER OF THE CYANOTRICHITE GROUP

1 <sup>a</sup>				2 <sup>a</sup>			
<i>h k l</i>	<i>I<sub>rel</sub></i>	<i>d<sub>obs</sub></i> (Å)	<i>d<sub>calc</sub></i> (Å)	<i>h k l</i>	<i>I<sub>rel</sub></i>	<i>d<sub>obs</sub></i> (Å)	<i>d<sub>calc</sub></i> (Å)
1 0 0	100	10.074	10.089	1 0 0			10.087
0 0 2	32	6.384	6.327 <sup>b</sup>				
1 0 2	48	5.640	5.609	1 0 2			5.636
2 0 0	32	5.041	5.044	2 0 0			5.044
				1 0 2	29	4.921	4.924 <sup>c</sup>
0 0 3	75	4.223	4.218	2 0 2			4.223
				2 0 2	15	3.635	3.637 <sup>d</sup>
3 0 0	33	3.359	3.363	3 0 0			3.362
				1 0 2	7	3.071	3.069 <sup>e</sup>
0 1 1	5	2.816	2.813	2 0 2			2.818
1 1 0	24	2.776	2.774	3 0 2			2.777
1 1 1	2	2.725	2.725				
4 0 0	26	2.519	2.522	4 0 0			2.522
4 0 2	3	2.266	2.269	1 1 3			2.267
0 1 4	3	2.131	2.132	3 1 1			2.131
4 0 3	3	2.080	2.079	2 1 3			2.079
2 0 6	24	2.016	2.016	5 0 0			2.017
3 1 3	3	1.994	1.995				
6 0 0	2	1.682	1.681	6 0 0			1.681

<sup>a</sup> 1: Data indexed on a camerolaite-like cell; 2: data indexed on a carbonate-cyanotrichite-like cell. <sup>b</sup> Shoulder on brochantite peak ( $d = 6.38$  Å,  $I_{rel} = 40$ ); omitted in the cell refinement based on the carbonate-cyanotrichite-like cell as it could not be indexed satisfactorily. <sup>c</sup> This line may be due to the presence of antlerite ( $d = 4.848$  Å,  $I_{rel} = 100$ ), and could not be indexed on the camerolaite-like cell. <sup>d</sup> This line may be due to the presence of antlerite ( $d = 3.596$  Å,  $I_{rel} = 64$ ), and could not be indexed on the camerolaite-like cell. <sup>e</sup> Overlapped with a brochantite reflection ( $d = 2.923$  Å,  $I_{rel} = 20$ ). <sup>f</sup> Low-intensity line that could not be indexed on the basis of a carbonate-cyanotrichite-like cell.

Nikita Chukanov kindly provided a list of  $F_{obs}$  and  $F_{calc}$  data for khaidarkanite. We thank Dr. Adriyan Milev for translation of Russian publications. Dr. Uwe Kolitsch is thanked for a thorough review of the manuscript and thoughtful suggestions that have strengthened it considerably.

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TABLE 8. POWDER X-RAY-DIFFRACTION DATA FOR A CYANOTRICHITE-LIKE MINERAL FROM THE CLARA MINE, GERMANY

<i>h k l</i>	<i>I<sub>rel</sub></i>	<i>d<sub>obs</sub></i> (Å)	<i>d<sub>calc</sub></i> (Å)	<i>h k l</i>	<i>I<sub>rel</sub></i>	<i>d<sub>obs</sub></i> (Å)	<i>d<sub>calc</sub></i> (Å)
1 0 0	10	10.34	10.288	1 1 1	½	2.75	2.750
1 0 2	2	5.72	5.609	4 0 1	2	2.59	2.590
2 0 0	3	5.15	5.144	4 0 1	4	2.45	2.449
1 0 4	½	3.04	3.048	1 0 5	3	2.31	2.309
				4 0 3	6	2.05	2.051

Values of  $I_{rel}$  and  $d_{obs}$  are those of Walenta (2001). Refined unit-cell constants (Langford 1973) are  $a$  10.388(16),  $b$  2.907(8),  $c$  12.349(22) Å,  $\beta$  97.98(19)°.

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