Eur. J. Mineral.
1994, **6**, 255-263

Dorallcharite, $Tl_{0.8}K_{0.2}Fe_3(SO_4)_2(OH)_6$, a new member of the jarosite-alunite family

Tonči BALIĆ ŽUNIĆ[1], Yves MOËLO[2], Željko LONČAR[3] and Harry MICHEELSEN[4]

[1)] Geological Institute, University of Copenhagen, Østervoldgade 10,
DK-1350 Copenhagen K, Denmark

[2)] C.N.R.S.-C.R.S.C.M., 1A rue de la Férollerie, F-45071 Orléans Cedex 2, France

[3)] Center for Marine Research, "Ruđer Bošković" Institute, G. Paliade 5,
52210 Rovinj, Croatia

[4)] Geological Museum, University of Copenhagen, Østervoldgade 5,
DK-1350 Copenhagen K, Denmark

Abstract: Dorallcharite, ideally $Tl^{+}Fe^{3+}_3(SO_4)_2(OH)_6$, is a Tl-Fe member of the alunite-jarosite family. Electron microprobe measurements and a crystal-structure determination show that K substitutes 8.3 to 29.5% (mean 18.6%) of the Tl atoms in the investigated sample. A complete solid-solution series is assumed to exist between dorallcharite and jarosite. The crystal structure was refined from powder X-ray diffraction data using the Rietveld method (Rw = 5.86%). The (hexagonal) unit cell parameters are: a = 7.3301(3) Å, c = 17.6631(7) Å, space group $R\bar{3}m$, $Z = 3$, ρ_{calc} = 3.85 g/cm³ (at 15°C). Structural data indicate a possible displacement of the Tl atom along the c axis direction (statistically distributed through the structure) owing to the lone-electron-pair effect. The strongest lines in the X-ray powder diffraction pattern are [d(Å), I, hkl] 5.974, 87, 101; 3.666, 34, 110; 3.112, 100, 021+113+015; 2.988, 22, 202; 2.577, 21, 024; 1.991, 29, 303+033+125; and 1.833, 23, 220. The mineral has a golden yellow colour and occurs in earthy and fine-grained aggregates of rhombohedral crystals under 10 µm in diameter with a distinct {0001} cleavage. It is uniaxial negative with n_ω = 1.822(3), n_ε = 1.768(2), with normal interference colours and no pleochroism. Dorallcharite is found in Allchar, Republic of Macedonia, a deposit known for Tl sulphides and sulphosalts, where it has formed in the oxidation zone of the ore body. It is often associated with an amorphous Fe-Mn sulphate-arsenate free of Tl. The observed paragenesis suggests that, in the oxidation zone of the sulphides, Tl concentrates preferentially in a material of jarositic composition.

Key-words: new mineral, jarosite-alunite group, thallium, Macedonia (Allchar deposit), dorallcharite.

Introduction

Sulphides represent the overwhelming majority (over 30 defined species) of known thallium minerals, according to the chalcophile geochemical nature of this element. Avicennite (Tl_2O_3, Konkova & Savelev, 1960; Radtke *et al.*, 1978) is the only known thallium oxide mineral. High contents of thallium were also found in carnotite, $K_2(UO_2)_2[V_2O_8]\cdot 2H_2O$ (Smyslova, 1972) (about 10 at% substitution of Tl for K), and in jarosite, $KFe_3(SO_4)_2(OH)_6$ (Mogarovskii, 1961) (about 5 at% substitution of Tl for K).

More recently, the formation of Tl-rich jarosite (up to 18 at% substituting for K) was recorded in material obtained by cleaning the gases from a sulphuric acid plant (Steffes-Tun *et al.*, 1989). The complete solid solution series between jarosite and the pure Tl end-member has been synthesized under laboratory conditions (SteffesTun, 1987).

0935-1221/94/0006-0255 $ 2.25

In the presently investigated natural occurrence, Tl represents the dominant large cation in the structure and this mineral can be regarded as a new species in the broader alunite-jarosite family. In the mineralogical literature there is only one earlier description of a Tl oxysalt mineral - monsmedite, described as a Tl,K sulphate-hydrate (Götz *et al.*, 1968). However, this presumed mineral was shown recently to correspond to voltaite ($K_2Fe^{2+}{}_5Fe^{3+}{}_3Al(SO_4)_{12}\cdot18H_2O$) with a questionable content of thallium (Zemann, 1993). Therefore, dorallcharite also represents the first sufficiently known Tl oxysalt mineral.

The new mineral originates from Allchar in the Republic of Macedonia (formerly Yugoslavia), a place known by the abundance of otherwise rare Tl minerals. It was found in a locality called Crven Dol, at the northern end of the ore body. The specimens were collected in the partly accessible mine entrance known as Potkop 21, during a field trip in 1988, as part of the project LOREX which planned to measure the solar neutrino flux by the use of lorandite ore (Pavićević, 1988).

The name of the new mineral is composed of a prefix designating its golden yellow colour ("doré" in French) and the name of the locality. The name "allcharite" has already been used in the mineralogical literature for a presumed new mineral species also found at Allchar together with vrbaite (Ježek, 1912a). It turned out that Ježek's specimens were, in reality, goethite (Čech & Johan, 1969) and this mineral name was discredited. Thus, a world famous mineral locality remained without a reference among the mineral names and so we felt appropriate to somehow revive this old name.

The mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA (vote 92-041). The type specimen is deposited in the Geological Museum of Copenhagen, under the number 1993.7.

Occurrence

The locality Allchar (or Alšar, which is the phonetic version of the name in Macedonian) is named after the first letters of Allatini (from Thessaloniki), the one-time owners of the mining concession, and Charteaux, the French mining engineer who found the deposit (Ježek, 1912b). The mine of this name was opened in 1889, in the neighbourhood of the village Rožden. The first exploitation was of a stibnite ore which was exported to England. The first researches indicated that the ore body consists of an antimonian and an arsenic part. In the arsenic part signs of old mining were found, probably reaching back to the 12th or 13th century (the data about the beginning of Allchar are from Hofmann, 1891). That the ore is also rich in Tl was first noticed when Krenner (1895) found a new Tl mineral, lorandite, in the Allchar material.

The genesis of the ore is connected to an andesitic intrusion of Pliocene age (about 5 Ma, Pavićević, 1988) near the intersection of deep faults in a complex of Paleozoic sediments (Arsovski & Ivanov, 1977). The hydrothermal mineralization is developed at the contact with Paleozoic dolomites. The temperature of formation decreases from south to north with a change of the dominant ore mineral from stibnite to realgar and orpiment. The Tl content is higher in the northern part, also related to the temperature. A number of rare Tl minerals have been found in Allchar specimens: lorandite, $TlAsS_2$ (Krenner, 1895), vrbaite, $Tl_4Hg_3Sb_2As_8S_{20}$ (Ježek, 1912b), raguinite, $TlFeS_2$ (Laurent *et al.*, 1969), picotpaulite, $TlFe_2S_3$ (Johan *et al.*, 1970), parapierrotite, $TlSb_5S_8$ (Johan *et al.*, 1975), rebulite, $Tl_5Sb_5As_8S_{22}$ (Balić Žunić *et al.*, 1982), simonite, $TlHgAs_3S_6$ (Engel *et al.*, 1982) and bernardite, $TlAs_5S_8$ (Pašava *et al.*, 1989), most of which are still specific for this locality.

At the locality where dorallcharite was found, dolomite comes in contact with an argillaceous rock (composed of kaolinite, illite, and finely dispersed quartz). The latter most probably represents a totally altered andesite of a type widely observed in the Allchar area. The sulphide mineralization occurs at the contact of the two rocks and in veins along cracks within the dolomite. Around the veins, the dolomite is almost completely altered to ankerite. The first hydrothermally deposited minerals were siderite and a fine-grained mixture of pyrite and marcasite. Subsequently, a well-developed realgar was crystallized, forming euhedral crystals up to several millimeters long, occasionally with lorandite of similar grain size.

The mineral paragenesis is significantly influenced by oxidation in this part of the ore body. Sulphate and arsenate minerals are sometimes intimately mixed with realgar and sometimes form crystals and crusts in the open cavities of the rock, indicating an early oxidizing horizon during the hydrothermal event as well as recent oxidation due to water penetrating the porous rocks from the surface. The following accessory minerals were identified: gypsum, bassanite, rösslerite and pharmacosiderite. In an earlier investigation of the same part of the mine, melanterite and barite crystals were also described (Baric, 1958).

Dorallcharite forms yellow earthy masses occasionally associated with a colloform, more compact mass characterized by a shiny brownish surface. This colloform product is X-ray amorphous and represents hydrated Fe and Mn sulphate and arsenate (average of 11 microprobe measurements: 55.3% Fe_2O_3, 17.5% SO_3, 13.4% As_2O_5 and 9.5% MnO).

X-ray diffraction study

The first analysis of dorallcharite was made by X-ray powder diffraction. It suggested a new mineral. Some vague similarities to the diffraction pattern of beudantite (Walenta, 1966) led to an attempt to index the diffraction pattern assuming the same space group ($R\bar{3}m$) and similar crystal lattice dimensions. In this way, the whole pattern was successfully indexed.

The final X-ray diffraction study was performed with the Guinier technique, from which the refined hexagonal unit cell parameters are: $a = 7.3301(3)$ Å, $c = 17.6631(7)$ Å (at 15°C). The powder diffraction pattern of dorallcharite is given in Table 1. It is characterized by the virtual absence of the low-angle maxima 003 and 012, which are typically prominent in closely related minerals of the same family. The calculated patterns for jarosite (Menchetti & Sabelli, 1976) and beudantite (Szymanski, 1988) are also given in Table 1 for comparison.

Chemical analysis

The chemical analysis was made by electron microprobe on a finegrained aggregate. Qualitative analysis showed the presence of Fe, K, S and Tl as the major elements. Their contents, as well as that of As, were determined in a suite of 25 point analyses.

The substitution of K for Tl varies in the analysed sample from about 8.3 to 29.5 at%. The mean (18.6%) is comparable to the 13 at% substitution deduced from the crystal structure refinement. Substitution of As for S in the structure is not likely for the following reasons: (1) the chemical analysis does not give a deficit but a

Table 1. X-ray powder diffraction pattern for dorallcharite, compared with theoretical powder patterns of beudantite (Szymanski, 1988) and jarosite (Menchetti & Sabelli, 1976). Space group $R\bar{3}m$. Indices as for hexagonal lattice with unit cell parameters: $a = 7.3301(3)$ Å, $c = 17.6631(7)$ Å (at 15°C). For d < 1.7 only the observed reflections indicated. Unobserved have I_{calc} lower than 0.5.

dorallcharite							beudantite		jarosite	
d_{obs}	d_{calc}	I_{obs}	I_{calc}	h	k	l	d	I	d	I
5.974	5.974	87	79.8	1	0	1	5.938	100	5.946	33
-	5.888	-	0.4	0	0	3	5.878	23	5.741	18
-	5.155	-	0.2	0	1	2	5.083	51	5.103	80
3.688	3.885	34	28.9	1	1	0	3.858	28	3.657	14
3.625	3.825	7	8.3	1	0	4	3.534	23	3.561	2
3.112	3.124	100	100.0	0	2	1	3.114	10	3.115	59
	3.111			1	1	3	3.075	44	3.085	100
	3.087			0	1	5	3.001	15	3.028	1
2.9877	2.9870	22	17.9	2	0	2	2.9889	17	2.9728	13
2.9438	2.9439	9	13.1	0	0	6	2.8392	7	2.8707	19
2.5773	2.5773	21	20.3	0	2	4	2.5418	12	2.5515	19
2.3781	2.3775	14	9.2	2	1	1	2.3711	14	2.3718	2
2.3620	2.3610	3	1.8	2	0	5	2.3199	6	2.3316	1
2.3446	2.3449	15	18.4	1	0	7	2.2718	11	2.2936	31
2.3159	2.3154	12	8.2	1	2	2	2.3051	13	2.3069	2
2.2954	2.2952	5	4.6	1	1	6	2.2428	13	2.2582	0
2.1175	2.1180	3	1.8	3	0	0	2.1117	4	2.1117	0
2.1082	2.1083	4	2.5	2	1	4	2.0872	9	2.0928	0
2.0858	2.0854	2	2.0	0	1	8	2.0185	5	2.0385	0
1.9912	1.9913	29	24.8	3	0	3	1.9793	4	1.9819	2
	1.9913			0	3	3	1.9793	6	1.9819	30
	1.9848			1	2	5	1.9590	8	1.9661	1
-	1.9752	-	0.1	0	2	7	1.9298	3	1.9432	7
-	1.9826	-	0.2	0	0	9	1.8928	1	1.9138	5
1.8329	1.8326	23	15.1	2	2	0	1.8288	5	1.8288	30
1.8124	1.8125	4	4.1	2	0	8	1.7872	4	1.7806	5
1.7523	1.7520	5	2.3	1	3	1	1.7478	4	1.7479	0
-	1.7488	-	0.1	2	2	3	1.7407	3	1.7425	4
1.7392	1.7388	4	4.2	2	1	7	1.7068	5	1.7180	3
1.7303	1.7301	4	3.9	1	1	9	1.6811	6	1.6957	2
-	1.7287	-	0.3	3	1	2	1.7208	3	1.7215	3
1.7180	1.7182	3	2.2	3	0	6				
				0	3	6				
1.7019	1.7017	1	0.9	1	0	10				
1.5758	1.5758	6	4.0	3	1	5				
1.5823	1.5820	6	2.9	0	4	2				
1.5558	1.5567	12	10.2	0	1	11				
	1.5557			2	2	6				
1.5435	1.5434	6	8.4	0	2	10				
1.4938	1.4935	6	2.7	4	0	4				
1.4518	1.4514	5	2.4	3	2	1				
1.4441	1.4439	4	3.2	1	3	7				
1.4390	1.4390	3	2.3	0	3	9				
				3	0	9				
1.4224	1.4224	1	1.0	2	1	10				
1.3854	1.3853	3	1.5	4	1	0				
1.3488	1.3485	9	8.7	4	1	3				
	1.3485			1	4	3				
	1.3464			2	3	5				
1.3358	1.3345	2	0.9	1	2	11				
1.3292	1.3288	1	1.3	1	0	13				
1.2884	1.2887	2	0.8	0	4	8				
1.2813	1.2813	4	2.8	3	2	7				
1.2533	1.2534	2	1.0	4	1	6				
				1	4	6				
1.2470	1.2470	2	1.3	1	3	10				
1.2217	1.2217	2	1.0	3	3	0				
1.1981	1.1982	2	1.8	3	3	3				
1.1888	1.1888	2	1.4	4	2	2				
	1.1884			3	1	11				
1.1809	1.1823	2	4.2	2	1	13				
	1.1805			4	0	10				
1.1577	1.1577	3	1.8	2	4	4				
1.1477	1.1478	1	1.1	2	2	12				

Experimental data: Guinier diffractometer with quartz monochromator (Huber G600), specimen on mylar, $CuK\alpha_1$, radiation, step width 0.01°2θ, counter time 8 s, receiving slit 0.2 mm, silicon standard for angular correction.

Table 2. Selected chemical analyses of dorallcharite compared to the composition obtained in the refinement of the structure. H_2O calculated according to ideal ratio in jarosite minerals ($6H_2O$ for one $(Tl,K)_2O$).

an.\wt%	Tl_2O	K_2O	Fe_2O_3	SO_3	As_2O_6	H_2O	Σox.
43	26.27	0.53	39.37	25.98	1.13	7.30	100.58
31	26.07	0.65	39.34	26.00	1.03	7.39	100.48
37	25.89	0.92	39.01	26.08	1.09	7.65	100.64
40	24.31	1.14	39.73	25.65	1.36	7.51	99.70
41	23.39	1.29	39.81	26.95	1.17	7.44	100.05
26	21.68	1.98	40.40	27.63	1.52	7.80	101.01
28	22.33	2.07	39.13	27.35	1.04	8.07	99.99
Mean	24.28	1.23	39.54	26.52	1.19	7.59	100.35
st.dev.	1.88	0.61	0.48	0.78	0.18	0.27	0.45
Structure	28.66	0.95	37.16	24.84	-	8.39	100.00

Analytical conditions: Automated CAMEBAX microprobe (BRGM-CNRS-University Orléans common laboratory). Analyst: O. Rouer (CNRS-CRSCM). Accelerating voltage: 15 kV; current: 15 nA; counting time: 10 s. Standards: $TlAsS_2$ (Tl $M\alpha$, As $L\alpha$); Fe_2O_3 (Fe $K\alpha$); $KAlSi_3O_8$ (K $K\alpha$); $BaSO_4$ (S $K\alpha$). Mn, Al, Ca: checked, not detected.

surplus of S; (2) there is no indication of a higher scattering factor in the S position in the structural analysis; (3) from a crystal-chemical point of view such a substitution is unlikely because of the difficulties in charge balance in the structure. Therefore, the small amount of recorded As is attributed to impurities, like the observed surplus of Fe and S. The deficit calculated from the microprobe analyses is considered to represent H_2O. The amount is just enough for six hydroxyl groups p.f.u., and substitution of the oxonium ion for the large cation was not assumed.

The analyses show that, when the Fe/(Tl + K) atomic ratio increases (from 3.3 to 4.6), As contents increase and the correlated K and S contents decrease. These features indicate a mixture of finegrained dorallcharite with an amorphous product composed of Fe sulphates and arsenates. Table 2 selects the subgroup of seven analyses with the lowest Fe/(Tl + K) ratios (from 3.3 to 3.7). The final structural formula, after subtracting the minor As content and excess Fe, is: $(Tl_{0.81}K_{0.19})Fe_3(SO_4)_2(OH)_6$.

Physical properties

Dorallcharite is fine grained and forms earthy masses of golden yellow colour. The streak is yellow. Because of its appearance, it could be confused with fine-grained orpiment, which is also abundant in the mine though not in the part investigated in the present study. The calculated density of the mineral is 3.85 g/cm^3. Owing to the paucity of material, no density measurements were made. The aggregates are composed of crystals 1 to 8 µm in diameter with pseudocubic or pseudooctahedral habitus (Fig. 1). The former most probably corresponds to {01-12} rhombohedron, and the second to a combination of {10-11} with {0001}. The same forms and habitus types were observed for beudantite (Walenta, 1966) and are typical for this crystal family.

The small grain size prevented conoscopic optical measurements. Loose grains are colourless but aggregates 30-60 µm in size are brownish yellow without pleochroism. Assuming optic uniaxiality as for other members of the jarosite

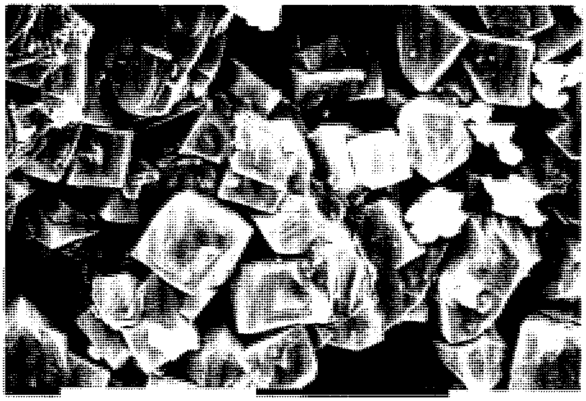

Fig. 1. SEM photograph of an aggregate of dorallcharite crystals. Scale bar represents 10 µm.

group, n_ω can be determined as that refractive index found in each grain and n_ε as the extreme value of the other index. Interference colours are normal and of the first order; most grains show a low grey colour but some exhibit yellow and orange when protruding from the aggregates. This corresponds to a distinct {0001} cleavage. The Becke line test showed that n_ω is above the highest R.I. liquid available ($n_D = 1.810$ at 18°C). Measurements were performed at 18°C. n_ω was determined by microinterferometry (Interphako, Jena) from the path difference Γ between light passing through the grain and the surrounding liquid; $\Gamma = t(n_x - n_{liq})$, where the subscript x stands for crystal and liq for liquid (Beyer, 1974). It was assumed that the average thickness (t) would be equal to the average widths and lengths of grains protruding from aggregates and in fact the measurements gave reasonably consistent values corresponding to $n_{\omega D} = 1.822 \pm 0.003$. Similar measurements on grains with the highest interference colours gave $n_{\varepsilon D} = 1.766 \pm 0.005$. Measurements of n_ε with liquids with $n_D = 1.744$ and 1.788 were then performed using the known n_ω as internal standard, largely removing the uncertainty in grain thickness. The results were $n_{\varepsilon D} = 1.769$ and 1.768, with an average of 1.768 ± 0.002.

It appears that n_ω of dorallcharite is surprisingly close to that of jarosite, and that the main difference is contained in n_ε. The compatibility index (Mandarino, 1981) is + 0.088 (poor) but the calculation gives a poor compatibility index for jarosite as well. If, however, the proposed Gladstone-Dale constant for Fe_2O_3 from silicates is used, and not that from oxides, the compatibility indices for both minerals calculate to superior (+ 0.011 for dorallcharite).

Crystal structure

The crystal structure of dorallcharite was refined by the Rietveld method, after the mineral was recognized as a member of the jarosite family whose structural characteristics are well established (Menchetti & Sabelli, 1976). The experimental data and the results of refinement are given in Table 3. The program used in the calculations was LHPM1 (Wiles & Young, 1981; Howard & Hill, 1986). In the course of refinement, the occupancy factor for the Tl position was refined and anisotropic displacement factors were introduced for this position. Anisotropic displacement factors for other positions did not improve the agreement factors, and isotropic factors were accordingly used for all atoms except Tl in the final refinement cycles. Table 4 gives the distances and angles in the coordination polyhedra of Tl, Fe and S, calculated using the CSU program (Vicković, 1988).

A projection of the crystal structure of dorallcharite is given in Fig. 2. It is crystal-chemically isotypic with alunite and jarosite and their well-known structural principles will not be repeated here (see, *e.g.*, Wang *et al.*, 1965). The general rule for crystal structures in this family predicts

Table 3. Results of structural analysis (powder X-ray diffraction, refined by Rietveld method).

Conditions:
$CuK_{\alpha 1}$ radiation, Guinier technique
2Θ range: 13.80 - 103.98°
Number of step intensities: 3007
Number of reflections: 143
Number of parameters varied: 25
Background fitted by a four-parameter function
Zero point correction.

Results:
Pearson VII profile function parameter = 2.7(1)
Peak full-width-half-maximum = 0.13(1)
Rietveld asymmetry parameter = 1.2(2)
Space group: $R\bar{3}m$
Unit cell parameters: a = 7.3301(3) Å, c = 17.6631(7) Å

Atomic coordinates, isotropic displacement factors and occupancies:

	x	y	z	B_{eq}	occ.
Tl	0.0	0.0	0.0	4.6(1)	0.87(2)
K	0.0	0.0	0.0	4.6(1)	0.13(2)
S	0.0	0.0	0.3104(9)	4.7(4)	1.0
Fe	0.0	0.5	0.5	4.4(3)	1.0
O(1)	0.0	0.0	0.389(1)	2.2(6)	1.0
O(2)	0.228(1)	-0.228(1)	0.938(1)	5.7(6)	1.0
OH	0.1372(9)	-0.1372(9)	0.1344(9)	3.4(5)	1.0

Anisotropic displacement factors for Tl(K): β_{11} $(=\beta_{22})$ $(=2\beta_{12})$ = 0.0165(8), β_{33} = 0.0069(3)

Agreement factors: R_p(profile) = 4.39, R_{wp}(weighted profile) = 5.86, R_B(Bragg) = 11.91

Table 4. Interatomic distances (in Å) and angles (in degrees) in the structure of dorallcharite.

Tl coordination polyhedron

O-Tl-O

Tl-O	oxygen	O(2)	O(2)^{1}	O(2)^{2}	O(2)^{3}	O(2)^{4}	O(2)^{5}	OH	OH^{1}	OH^{2}	OH^{3}	OH^{4}	OH^{5}
3.095(10)	O(2)	-	108.2(4)	108.2(4)	180.0	71.8(4)	71.8(4)	74.4(3)	124.2(3)	124.2(3)	105.6(3)	55.8(3)	55.8(3)
3.095(10)	O(2)^{1}	5.01(1)	-	108.2(4)	71.8(4)	180.0	71.8(4)	124.2(3)	74.4(3)	124.2(3)	55.8(3)	105.6(3)	55.8(3)
3.095(10)	O(2)^{2}	5.01(1)	5.01(1)	-	71.8(4)	71.8(4)	180.0	124.2(3)	124.2(3)	74.4(3)	55.8(3)	55.8(3)	105.6(3)
3.095(10)	O(2)^{3}	6.19(1)	3.63(2)	3.63(2)	-	108.2(4)	108.2(4)	105.6(3)	55.8(3)	55.8(3)	74.4(3)	124.2(3)	124.2(3)
3.095(10)	O(2)^{4}	3.63(2)	6.19(1)	3.63(2)	5.01(1)	-	108.2(4)	55.8(3)	105.6(3)	55.8(3)	124.2(3)	74.4(3)	124.2(3)
3.095(10)	O(2)^{5}	3.63(2)	3.63(2)	6.19(1)	5.01(1)	5.01(1)	-	55.8(3)	55.8(3)	105.6(3)	124.2(3)	124.2(3)	74.4(3)
2.937(15)	OH	3.65(2)	5.33(2)	5.33(2)	4.81(1)	2.83(2)	2.83(2)	-	61.7(5)	61.7(5)	180.0	118.3(5)	118.3(5)
2.937(15)	CH^{1}	5.33(2)	3.65(2)	5.33(2)	2.83(2)	4.81(1)	2.83(2)	3.01(1)	-	61.7(5)	118.3(5)	180.0	118.3(5)
2.937(15)	CH^{2}	5.33(2)	5.33(2)	3.65(2)	2.83(2)	2.83(2)	4.81(1)	3.01(1)	3.01(1)	-	118.3(5)	118.3(5)	180.0
2.937(15)	OH^{3}	4.81(1)	2.83(2)	2.83(2)	3.65(2)	5.33(2)	5.33(2)	5.87(2)	5.04(2)	5.04(2)	-	61.7(5)	61.7(5)
2.937(15)	OH^{4}	2.83(2)	4.81(1)	2.83(2)	5.33(2)	3.65(2)	5.33(2)	5.04(2)	5.87(2)	5.04(2)	3.01(1)	-	61.7(5)
2.937(15)	OH^{5}	2.83(2)	2.83(2)	4.81(1)	5.33(2)	5.33(2)	3.65(2)	5.04(2)	5.04(2)	5.87(2)	3.01(1)	3.01(1)	-

O-O

Fe coordination polyhedron

O-Fe-O

Fe-O	oxygen	O(2)^{6}	O(2)^{7}	OH^{8}	OH^{9}	OH^{10}	OH^{11}
2.006(16)	O(2)^{6}	-	180.0	88.7(5)	88.7(5)	91.3(5)	91.4(5)
2.006(16)	O(2)^{7}	4.01(2)	-	91.3(5)	91.4(5)	88.7(5)	88.7(5)
2.039(10)	OH^{8}	2.83(2)	2.89(2)	-	95.3(7)	180.0	84.7(7)
2.039(10)	OH^{9}	2.83(2)	2.89(2)	3.01(1)	-	84.7(7)	180.0
2.039(10)	OH^{10}	2.89(2)	2.83(2)	4.08(1)	2.75(1)	-	95.3(7)
2.039(10)	OH^{11}	2.89(2)	2.83(2)	2.75(1)	4.08(1)	3.01(1)	-

O-O

S coordination polyhedron

O-S-O

S-O	oxygen	O(1)	O(2)^{12}	O(2)^{13}	O(2)^{11}
1.395(40)	O(1)	-	117(1)	117(1)	117(1)
1.502(14)	O(2)^{12}	2.47(3)	-	101(1)	101(1)
1.502(14)	O(2)^{13}	2.47(3)	2.32(1)	-	101(1)
1.502(14)	O(2)^{11}	2.47(3)	2.32(1)	2.32(1)	-

O-O

Symmetry operations:

1: -y, x-y, z; 2: -x+y, -x, z; 3: -x, -y, -z; 4: y, -x+y, -z; 5: x-y, x, -z; 6: 1/3-x+y, 2/3-x, 2/3+z; 7: -1/3+x-y, 1/3+x, 1/3-z; 8: 1/3-x, 2/3-y, 2/3-z; 9: 1/3+y, 2/3-x+y, 2/3-z; 10: -1/3-y, 1/3+x-y, 1/3+z; 11: -1/3+x, 1/3+y, 1/3+z; 12: -1/3+x, 1/3+y, 1/3+z; 13: -1/3-y, -2/3+x-y, 1/3+z.

that replacement of small trivalent cations influences the extension of the octahedral layers parallel to (0001) and changes the *a* parameter, whereas the size of the large monovalent/divalent cation influences the interlayer spacing and the value of the *c* parameter (Menchetti & Sabelli, 1976). In agreement with this, dorallcharite has *a* similar to the other members of the family with Fe^{3+} (jarosite group) and a high *c*, corresponding to the largest known interlayer spacing in alunite-jarosite family. It should be noted that the layers are mutually connected *via* hydrogen bonding OH...O(1) as well as by large cations. Owing to the flexibility of the layers (Menchetti & Sabelli, 1976), a relatively large series of interlayer cations with crystal radii from 1.48 (Ca^{2+}) to 1.84 Å (Tl^{+}) (Shannon, 1976) can be incorporated without breaking the hydrogen bonding.

The bond distances and angles for Fe and S correspond to the values observed in the structures of jarosite, $KFe_3(SO_4)_2(OH)_6$ (Menchetti & Sabelli, 1976), plumbojarosite, $Pb[Fe_3(SO_4)_2(OH)_6]_2$ (Szymanski, 1985), and beudantite, $Pb(Fe,Al)_3[(As,S)O_4]_2(OH)_6$ (Szymanski, 1988; Giuseppetti & Tadini, 1989). In dorallcharite all distances in the Fe octahedron appear very simi-

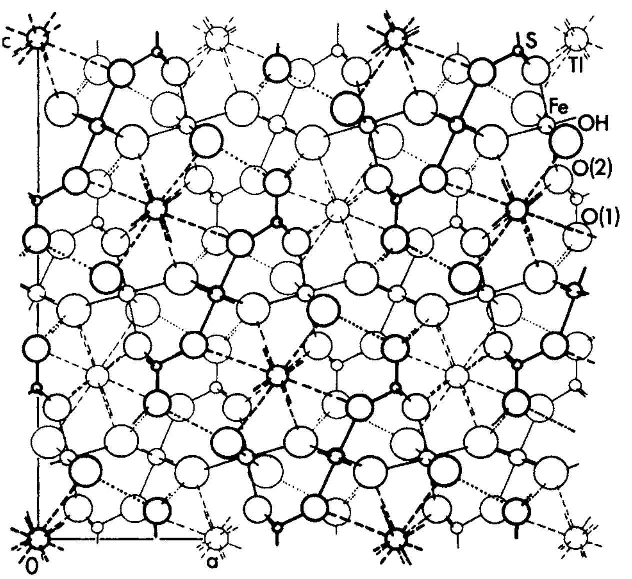

Fig. 2. The crystal structure of dorallcharite, viewed parallel to the *a* axis. Tl-O bonds indicated as stippled lines, hydrogen bonds OH...O(1) as dotted lines.

lar, with the Fe-O distances even somewhat shorter than the Fe-OH. In the other structures, Fe-OH distances are shorter than Fe-O. The SO_4 tetrahedron appears somewhat more distorted in dorallcharite than in any other related mineral, with S positioned closer to the apical O(1) atom. A very high standard deviation of positional coordinates for dorallcharite (compared with the other structural investigations which were made on single crystals and refined to significantly lower *R* values) prevents a definite conclusion about these peculiarities.

As a characteristic similar to Pb^{2+} the Tl^+ ion also has a $6s^2$ lone electron pair. For Pb^{2+} the effect of the lone electron pair is to displace the ion from the ideal position in the centre of the coordination polyhedron (Szymanski, 1988). In the dorallcharite structure Tl^+ shows a displacement ellipsoid elongated along the *c* axis (the r.m.s. displacement in this direction is 0.33 Å and, perpendicular to it, 0.18 Å). This could reflect the statistical displacement of Tl^+ through the structure in the direction of the *c* axis, as a consequence of the lone electron pair effect on its coordination. This effect is either not as well expressed as for Pb or the quality of the data does not allow its examination in detail. An attempt to refine the structure with isotropic displacement factors and removal of the restriction on the *z* coordinate for Tl did move the atom from the central position, but it moved back again when the anisotropic displacement factors were introduced, without changing the agreement factors.

If the elongated displacement ellipsoid of Tl^+ arises from the influence of the lone electron pair on coordination, then its effect is somehow different from that of Pb^{2+}. The large cation in the alunite-jarosite family occupies an icosahedron formed by six oxygens (O(2)) and six hydroxyl groups. The two $(OH)_3$ triplets form opposite faces viewed along the *c* axis. Whereas an alkali cation occupies the centre of the coordination polyhedron (site symmetry $\bar{3}m$), Pb^{2+} is displaced from the centre in the *x-y* plane (site symmetry 2) (Szymanski, 1988). In contrast, Tl^+ seems to be displaced along the *c* axis (site symmetry $3m$). This would bring Tl closer to one of the $(OH)_3$ triplets, thus lengthening the distance to the other triplet. In other words, the $6s^2$ lone electron pair is displaced towards the more distant $(OH)_3$ group. Such a displacement could also influence the hydrogen bonding in the structure. The hydrogens from hydroxyls facing the lone electron pair of Tl^+ experience a weaker cation repulsion from that side. If they were displaced in that direction, this would loosen the hydrogen bonding to the neighbouring O(1) apex of the SO_4 tetrahedron and thus explain the observed shortening of the S-O(1) bond. A similar displacement has been documented in plumbojarosite where the positions of hydrogens in the structure could be experimentally determined (Szymanski, 1985). There, the hydroxyls are displaced towards the highly ordered vacancies in Pb positions, so lengthening their bonds to apical oxygens of some of the SO_4 groups. At the same time, however, the Pb vacancies produce underbonding of the other oxygens from the same SO_4 groups and thus a significant distortion of sulphur coordination as in dorallcharite is not produced.

Conclusion

Geochemical studies on the behaviour of Tl in oxidation zones (Vlasov, 1966) show that Tl is removed from the ore during the earliest oxidation processes and that its content is distinctly low in the resulting products (simple sulphates). It accumulates in jarositic minerals if they form during the second stage of the process and is dissolved and removed again in the last stage when iron gossan (mostly iron hydroxides) is formed. A final accumulation of Tl in oxidation zones sometimes takes place in association with manganese oxide; oxidation to Tl^{3+} is assumed to take place and the Tl mineral avicennite can appear.

Observations at Allchar very convincingly demonstrate the concentration of Tl in jarositic minerals. It is completely absent from the amorphous iron and manganese sulphates which form as the first oxidation products, but then appears as the main large cation in closely associated dorallcharite. The formation of this unique Tl-dominant mineral is evidently promoted by high Tl concentrations in the hypogene minerals, concentrations which are unmatched by other known sulphide deposits.

Concerning the high primary Tl contents in the Allchar area, the formation of dorallcharite has an important environmental effect. It immobilizes Tl and almost certainly greatly reduces its concentration in the groundwater. A similar effect was observed in the waste deposits of a sulphuric acid plant (SteffesTun *et al.*, 1989).

The role of Tl^+ in structures of the alunite-jarosite family is similar to the other large cations. From the data on synthetic analogues (SteffesTun, 1987), a complete solid solution series is expected between K-free dorallcharite and jarosite. The large cation in alunite-jarosite structures is situated between the tetrahedral-octahedral-tetrahedral layers parallel to (0001). In dorallcharite we have the largest recorded interlayer spacing in this family, and this is in good agreement with Tl^+ having the largest crystal radius (Shannon, 1976) among the known interlayer cations. The lone electron pair $6s^2$ of Tl^+ is supposed to induce the high anisotropy of Tl displacement factors obtained in the crystal structure refinement.

Although the finally investigated material consisted of a relatively small sample, it could be assumed that dorallcharite is widespread at Allchar. It was recorded on various samples collected during the field trip and later deposited in the Institute of Mineralogy and Petrology in Zagreb. The members of the dorallcharite-jarosite solid solution series, because of their resemblance to earthy orpiment, may well have been overlooked or ignored in previous studies at Allchar, as well as in other Tl deposits.

Acknowledgements: The authors are grateful to Dr. Thomas Armbruster, Berne, for microprobe data on the amorphous mineral and suggestions during the preparation of manuscript. We are also indebted to Drs. John Bailey and Emil Makovicky, Copenhagen, for critically reading the finished manuscript, to Dr. Trajče Stafilov, Skopje, for the preliminary determination of Tl in the sample and to Dr. Hans Jørgen Hansen, Copenhagen, for the SEM photographs. We thank Mr. D. Tibljaš and Dr. V. Bermanec, Zagreb, for the help in some preliminary analyses and Dr. E. Leonardsen, Copenhagen, for the help in preparing the figures and tables for publication. The suggestions of referees Prof. J. Zemann, Vienna, and Dr. A.-M. Fransolet, Liege, helped very much in preparing the final version of the typescript.

Some of the investigations were made in the Institute of Mineralogy and Petrology, Faculty of Science, Zagreb with financial help from the Research Council of a one-time Socialist Republic of Croatia and Institute of Mineralogy and Crystallography, University of Göttingen, with financial help from the Humboldt Foundation. The completion of the work was supported by grants of the Natural Science Council (SNF) of Denmark as part of the cooperation with CNRS (France).

References

Arsovski, M. & Ivanov, T. (1977): Neotectonics, magmatism and metallogeny on the territory of Yugoslavia. *in* "Metallogeny and plate tectonics in the northeastern Mediterranean", S. Janković ed.

Faculty of Mining and Geology, University of Belgrade, 471-482.

Balic Žunic, T., Šcavničar, S., Engel, P. (1982): The crystal structure of rebulite, $Tl_5Sb_5As_8S_{22}$. *Zeit. Krist.*, **160**, 109-125.

Baric, Lj. (1958): Neuuntersuchung des LoranditVorkommens von Mazedonien und Vergleich der Mineralvergesellschaftungen in den beiden bisher bekannten Fundorten des Lorandits. *Schweizer. Mineral. Petrogr. Mitt.*, **38**, 247-253.

Beyer, H. (1974): Theorie und Praxis der Interferenzmikroskopie. Akademische Verlagsgesellschaft, Gest & Portig K.-G., Leipzig.

Čech, F. & Johan, Z. (1969): Identité de l'allcharite et de la goethite. *Bull. Soc. fr. Minéral. Cristallogr.*, **92**, 99-100.

Engel, P., Nowacki, W., Balic Žunic, T., Šcavničar, S., (1982): The crystal structure of simonite, $TlHgAs_3S_6$. *Zeit. Krist.*, **161**, 159-166.

Giuseppetti, G. & Tadini, C. (1989): Beudantite: $PbFe_3(SO_4)(AsO_4)(OH)_6$, its crystal structure, tetrahedral site disordering and scattered Pb distribution. *N. Jb. Mineral. Mh.*, **1989**, 27-33.

Götz, A., Mihalka, St., Ionita, I., Toth, Z. (1968): Monsmedite, a new thallium mineral from Baia Sprie. *Rev. Minelor*, **19**, 154-159. (Cited in *Am. Mineral.*, **54**, 1496.)

Hofmann, R. (1891): Antimon und Arsen-Erzbergbau "Allchar" in Macedonien. *Österreichische Zeitschrift für Berg und Hüttenwesen*, **16**, 167-173.

Howard, C.J. & Hill, R.J. (1986): A computer program for Rietveld analysis of fixed wavelength X-ray and neutron powder diffraction patterns. AAEC report No.M112.

Ježek, B. (1912a): Allcharit, ein wahrscheinlich neues Mineral. *Zeit. Krist.*, **51**, H. III, 275-278.

— (1912b): Vrbait, ein neues Thalliummineral von Allchar in Mazedonien. *Zeit. Krist.*, **51**, 365-378.

Johan, Z., Pierrot, R., Schubnel, H.J. (1970): La picotpaulite $TlFe_2S_3$, une nouvelle espèce minérale. *Bull. Soc. fr. Minéral. Cristallogr.*, **93**, 545-549.

Johan, Z., Picot, P., Hak, J., Kvaček, M. (1975): La parapierrotite, un nouveau minéral thallifère d'Allchar (Yougoslavie). *Tschermaks Mineral. Petrogr. Mitt.*, **22**, 200-210.

Konkova, E.A. & Savelev, V.F. (1960): Novyj mineral talliya - avicennit. *Zap. Vsesojuzn. Miner. Obshch.*, **89**, 316-320.

Krenner, J.S. (1895): Lorandit, uj thallium-ásvány Allcharról Makedoniában. *Mathematikai és Természettudományi Értesitö*, **13**, 1895, 258-263.

Laurent, Y., Picot, P., Pierrot, R., Permingeat, F., Ivanov, T. (1969): La raguinite, $TlFeS_2$, une nouvelle espèce minérale et le problème de l'allcharite. *Bull. Soc. fr. Minéral. Cristallogr.*, **92**, 38-48.

Mandarino, J.A. (1981): The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Can. Mineral.*, **19**, 441-450.

Menchetti, S. & Sabelli, C. (1976): Crystal chemistry of the alunite series: crystal structure refinement of alunite and synthetic jarosite. *N. Jb. Mineral. Mh.*, **1976**, 406-417.

Mogarovskii, V.V. (1961): K geokhimii talliya v zone okisleniya sul'fidnogo mestorožhdeniya Daraiso (Srednyaya Aziya). *Geokhimiya*, **9**, 771-774.

Pašava, J., Pertlik, F., Stumpfl, E.F., Zemann, J. (1989): Bernardite, a new thallium arsenic sulphosalt from Allchar, Macedonia with a determination of the crystal structure. *Mineral. Mag.*, **53**, 531-538.

Pavićevic, M.K. (1988): Lorandite from Allchar - a low energy solar neutrino dosimeter. *Nuclear Instrum. Methods Phys. Res.*, **A271**, 287-296.

Radtke, A.S., Dickson, F.W., Slack, J.F. (1978): Occurrence and formation of avicennite, Tl_2O_3, as a secondary mineral at the Carlin gold deposit, Nevada. *Journal of Research USGS*, **6**, 241-246.

Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, **A32**, 751-767.

Smyslova, I.G. (1972): O talliyevoy raznovidnosti karnotita. *Zap. Vsesojuzn. Miner. Obshch.*, **101**, 87-90.

Steffes Tun, W. (1987): Der Weg des Thalliums in Schwefelkies- Abbränden vom Erz zur Deponie. Diploma work, University of Münster.

Steffes-Tun, W., Bambauer, H.U., Krause, Ch. (1989): Jarosit als Thallium-Träger in einer Deponie von Schwefelkiesabbränden. Envirotech Vienna 1989, 2.2 Aktuelle Entwicklungen in der Umwelschutztechnik, Umweltbundesamt (Vienna), 316-320.

Szymanski, J.T. (1985): The crystal structure of plumbojarosite $Pb[Fe_3(SO_4)_2(OH)_6]_2$. *Can. Mineral.*, **23**, 659-668.

— (1988): The crystal structure of beudantite, $Pb(Fe,Al)_3[(As,S)O_4]_2(OH)_6$. *Can. Mineral.*, **26**, 923-932.

Vicković, I. (1988): CSU, a highly automatic and selective program for the calculation and presentation of geometrical parameters and their e.s.d.'s. *J. Appl. Cryst.*, **21**, 987-990.

Vlasov, K.A. (editor) (1966): Geochemistry and mineralogy of rare elements and genetic types of their deposits. Vol. 1, Geochemistry of rare elements. Israel Program for Scientific Translations, 491-524.

Walenta, K. (1966): Beiträge zur Kenntnis seltener Arsenatmineralien unter besonderer Berücksichtigung von Vorkommen des Schwarzwaldes. *Tschermaks Mineral. Petrogr. Mitt.*, **11**, 121-164.

Wang, R., Bradley, W.F., Steinfink, H. (1965): The crystal structure of alunite. *Acta Cryst.*, **18**, 249-252.

Wiles, D.B. & Young, R.A. (1981): A new computer program for Rietveld analysis of Xray powder diffraction patterns. *J. Appl. Cryst.*, **14**, 149-151.

Zemann, J. (1993): What is monsmedite? *Rom. J. Mineralogy*, **76**, 1, 97-98.

Received 13 July 1993
Accepted 7 December 1993