

DISTRIBUTION OF THALLIUM AND THE ORE GENESIS AT THE CRVEN DOL LOCALITY IN ALŠAR

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Abstract: Crven Dol lies at the northern end of the Alšar deposit and, according to the general geological situation, represents the uppermost part of the body of ore with the lowest temperature of formation. The mineralogical and petrological investigations show pronounced oxidation effects at this locality. An influence of oxygenated meteoric waters was already present during the hydrothermal stage. Later on, it continued with the final formation of jarositic minerals. The first product of the hydrothermal solution was a transformation of dolomite in to ankerite. The first minerals deposited from solutions were siderite, pyrite and marcasite in a fine grained mixture. With a drop in temperature, realgar followed. Some of the realgar crystals include oxidation products (pharmacosiderite). When the temperature reached the stability field of lorandite, it appeared in a mixture with realgar. This was the last and the main stage in the hydrothermal event, characterized by large and well developed crystals. The last minerals in veins are the products of the following oxidation of sulphides. The most important are amorphous iron sulphate-arsenate and dorallcharite, Tl-member of the jarosite group. The content of thallium in hydrothermal solutions was high during all the stages. The siderite-pyrite-marcasite mixture contains 0.5-0.6, and realgar 0.4-0.5 wt% Tl. The two processes of Tl concentration in the solid phase were active in the deposit at Crven Dol. One was the crystallization of lorandite, as the main hypogene Tl mineral. The other occurred during the supergene enrichment, when Tl preferentially concentrated in jarositic minerals. Pharmacosiderite, which formed early, during the still active hydrotherms, contains 1.71 wt% Tl, and in dorallcharite $(\text{TlFe}_3(\text{SO}_4)_2(\text{OH})_6)$, Tl represents one of the main elements, being over 20 wt%.

Key words: Thallium, distribution, ore genesis, Alšar mine

INTRODUCTION

The investigations reported here were started as a part of the LOREX project (Pavićević, 1988) determined to measure the Solar-neutrino flux using the Tl ore from Alšar. They were made on specimens from the currently accessible part of the Tl-As mine, known as Potkop 21, which lies at the northern end of Alšar, Crven Dol, where the concentration of Tl in the ore is the highest (Ivanov, 1986).

A passage of about 100 m from the mine entrance to the opening which leads to lower galleries was cleaned for preliminary analyses of LOREX and is accessible today. Systematic sampling in this part of the mine was made, followed by detailed mineral and chemical analyses, and will be described here. The aim was to determine the local minerogenetic processes and Tl distribution between the various minerals.

ANALYTICAL METHODS

Beside microscopic observations of mineral textures and parageneses, X-ray diffraction of powdered samples and individual mineral grains, and

atomic absorption spectrometry of dissolved samples was made.

The mineral fractions for analysis were separated by hand picking under a microscope. For the X-ray

diffraction analysis the various methods were used both for powder and monocrystal measurements (the Guinier-camera, powder diffractometer, flat-plate camera, cylindrical camera and four-circle diffractometer).

For the analysis of thallium, a Perkin-Elmer Model 703 atomic absorption spectrophotometer was used equipped with D₂ background corrector and HGA-400 graphite furnace. Methods for these analyses are described in our earlier papers (Stafilov et al., 1988, 1993).

MINERALOGICAL AND PETROLOGICAL SITUATION

The entrance to Potkop 21 is in dolomite rock which at this point is white compact, coarsely grained and clear of visible inclusions. For about 80 m the passage traverses unchanged dolomite with only occasional tectonisation, the cracks filled by secondary minerals (limonitic substance and calcite crystals) but without any signs of hydrothermal alteration. After that it makes contact with a silicate rock where many signs of hydrothermal activity can be seen. They are present in the form of alterations in rocks and numerous veins filled with sulphide minerals. The accessible passage continues for about 20 m further along the contact of the rocks and into the silicate rock. The remnants of the old passages to the left, right, up and down are present in this part and still offer small galleries for sampling along the mineral veins.

The contact between dolomite and silicate rock is considered to be tectonic. On the one hand, dolomite is highly tectonized near the contact, and on the other the ascendance of hydrothermal solutions could be connected to the presence of an existing fault structure on the contact of two rocks.

Along the cracks in the dolomite at this point the hydrothermal alterations are present in the form of ankeritization, the extent of which depended on the porosity of the rock. Sometimes the larger portions of ankerite still include the "islands" of unaltered primary dolomite.

The alteration of the silicate rock was even more intensive and produced its complete kaolinitization. No preserved remnants of the primary rock could be found on the site. The altered rock is now a clay consisting of a mixture of kaolinite, quartz and some illite.

As the second step in the hydrothermal process, a fine grained mixture of siderite, pyrite and marcasite

had crystallized, representing the first hydrothermally deposited minerals in this part of the mine.

After this, realgar was crystallized and now forms the major part of hydrothermal veins. Some of the realgar crystals are dark, brownish-red in colour and clearly distinguishable from the bulk which is the bright red typical of this mineral.

In one of the veins, together with the larger crystals (several mm in diameter) of bright red realgar crystals of lorandite (sometimes larger than that of realgar) were found.

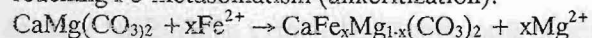
Besides products of hydrothermal activity numerous signs of intensive oxidation processes can be found in Potkop 21. They have continued to the present time and a still active formation of amorphous sulphates and arsenates of Fe and Mn can be observed on walls, caused by the dripping water. There is, however, evidence of a very early oxidation horizon in the deposit, synergetic with or even preceding the main hydrothermal phase. The crystals of pharmacosiderite have been overgrown by realgar. Some parts of the altered silicate rock, a mixture of pyrite, marcasite, kaolinite, illite, quartz and gypsum, also include pharmacosiderite.

Besides gypsum, the crystals of which are to be found in many places mixed with realgar, the most widespread supergene minerals in and around realgar veins are the previously mentioned amorphous mineral and dorallcharite, a recently discovered member of the jarosite-alunite family (Balić Žunić et al., in press). These two minerals are often found in close association, the translucent, shiny brownish-red crusts of the former passing to an earthy yellow mass of the latter.

THE CRYSTALLOGRAPHIC AND CHEMICAL PROPERTIES OF MINERALS

1. The dolomite rock

The hydrothermal solution produced a slow surface dissolution of dolomite, together with a deeper reaching Fe-metasomatism (ankeritization):



Fe can substitute for Mg in dolomite in various degrees up to approximately 70 at% (Goldsmith, 1983).

After the substitution reached its maximum, the further activity of hydrothermal solutions proceeded with the crystallization of FeCO₃ + FeS₂. A gradient of composition is preserved in ankerites and they pass continually to unaltered dolomite. The hand-picked specimens always contained some remnants of

dolomite, as well as some gypsum which is often present in the cavities of dolomite.

2. The clay

The specimens represent a mixture of finely grained kaolinite, quartz and illite which can be clearly identified by powder X-ray diffraction.

3. The first hydrothermal deposit

The gray microcrystalline aggregate is seen under the microscope as an intimate mixture of transparent siderite (FeCO_3) and opaque pyrite + marcasite (FeS_2). X-ray powder diffraction reveals in all investigated specimens the simultaneous presence of both pyrite and marcasite in comparable amounts. The two chemical analyses of samples from different parts of Potkop 21 yielded the content of Tl as 0.56 and 0.51 wt% respectively which suggests its homogeneous distribution in this hydrothermal stage.

4. Realgar (AsS)

The reasons for the darker colour of some crystals could be found by the applied X-ray diffraction and chemical analysis which showed no important admixtures of crystallographic differences as compared to the normally coloured realgar. One possible explanation might come from the observation of Beran et al. (1990) that realgar heated to 250 °C changes its colour to dark red. This could mean that the darker realgar represents the first generation, which crystallized at a higher temperature. The X-ray powder data and the unit cell parameters for realgar are given in Table 1. The crystallographic parameters correspond well with that of the crystal structure refinement of realgar (Mullen and Novacki, 1972). The chemical analysis of one sample gave 0.44 wt% Tl.

5. Lorandite (TlAsS_2)

Lorandite and the last of the realgar seem to have formed syngenetically and represent the last hydrothermally deposited material. It can be noted that Krenner (1895) stated that lorandite from Alšar is a younger product, growing on realgar crystals, while Barić (1958) concludes from observations of material from Crven Dol that an older, as well as the younger lorandite can be found, the both minerals being present in mutual overgrowths. The X-ray powder data for lorandite are given in Table 2. The pattern is characterized by an extensive overlapping of many diffraction maxima. This is a consequence of the fact that its crystal lattice is based on a B-centered orthogonal one. However, the crystal structure has monoclinic symmetry and not orthorhombic, so the best choice for the unit cell is a monoclinic primitive, as standardly reported for lorandite. The relation between the orthogonal (primed) to the standard monoclinic

axes of lorandite is: $a' = 2a + c$; $b' = b$; $c' = c$. The overlapping of maxima makes a refinement of unit cell parameters from powder diffraction data inaccurate. One of the crystals was used for the crystal structure refinement (Balić Žunić et al., in preparation) and the unit cell parameters accurately determined on it by the four-circle diffractometer are also reported in Table 2.

6. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and rösselrit ($\text{MgHAsO}_4 \cdot 7\text{H}_2\text{O}$)

Rösselrit can be found in some cavities in aggregates of needle-like crystals always mixed with gypsum. It was identified by the X-ray powder diffraction. Gypsum is widespread in Potkop 21 and contained in almost every specimen. One specimen even contained bassanite (hemihydrate, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) as testified by the X-ray diffraction.

7. Dorallcharite ($(\text{Tl},\text{K})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$)

Dorallcharite appears as yellow earthy masses of submicroscopic crystals (Figure 1). This mineral is a member of the alunite-jarosite family and is isomorphous with jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$). The unit cell parameters are: $a = 7.330$; $c = 17.663$ (Å); space group R3m. The most prominent diffraction maxima on the X-ray powder diffractogram are (d (Å), 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; 1.833, 23, 220. The Tl:K proportion, as determined by 25 microprobe measurements, ranged from 71:29 to 92:8. The mean Tl content in the mineral is 23 wt%. The complete data on this newly defined mineral are to be published elsewhere (Balić Žunić et al., in press).

8. Amorphous Fe/Mn sulphate/arsenate

This mineral is X-ray amorphous. The average of 11 microprobe measurements is as follows (the minimum and maximum measured values are in parentheses): 55.3 (49.0-71.6) wt% FeO, 9.5 (5.0-11.6) wt% MnO, 14.6 (6.6-16.2) wt% SO_3 , 13.4 (0.9-17.8) wt% As_2O_3 , no Tl (T. Armbruster, personal communication). If the residual is attributed to water, its content is 7.2 wt% on average.

9. Pharmacosiderite ($\text{K}_2(\text{OH})\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot n\text{H}_2\text{O}$)

Pharmacosiderite can be found relatively often among the oxidation products in small, green crystals. It was also found together with pyrite and marcasite as inclusions in realgar, which shows that the oxidation in this part of the ore body began before the last hydrothermal phase. It is characteristic for the X-ray diffraction powder pattern otherwise prominent maximum at $d = 4.6$ Å appears very weak in the specimens from Alšar (Table 3). Chemically, this pharmacosiderite represents a Tl-rich variety,

Table 1. X-ray powder diffraction pattern of realgar. Guinier camera, $\text{CuK}\alpha$ radiation. Corrected using ZnO as internal standard. Refined unit cell parameters: $a = 9.340(8)$, $b = 13.587(3)$, $c = 6.595(5)$ Å; $\beta = 106.547(5)^\circ$. Calculated pattern as for these parameters, intensities from structural data of Mullen and Nowacki (1972). Observed intensities: w = weak, m = medium, s = strong.

			Measured			Calculated		
h	k	l	2Θ	$d(\text{Å})$	I	2Θ	$d(\text{Å})$	I/I ₀
1	0	-1	14.64	6.0504	m	14.672	6.0375	40
0	1	1	15.43	5.7424	m	15.459	5.7316	45
1	1	-1	16.04	5.5254	w	16.064	5.5173	25
1	2	0	16.35	5.4213	s	16.379	5.4118	100
2	1	-1	21.79	4.0786	w	21.808	4.0753	20
2	2	-1	24.58	3.6216	w	24.616	3.6164	9
2	3	0	28.03	3.1832	s	28.025	3.1838	31
1	4	0				28.097	3.1758	26
0	0	2	28.21	3.1633	s	28.232	3.1608	41
3	0	-1	29.22	3.0562	m	29.226	3.0556	33
0	4	1	29.89	2.9892	w	29.360	2.9921	19
1	2	-2	30.16	2.9631	w	30.188	2.9604	22
2	2	1	30.56	2.9252	m	30.540	2.9271	49
0	2	2	31.21	2.8657	w	31.209	2.8658	9
3	2	-1	32.13	2.7857	w	32.119	2.7867	12
3	2	0	32.79	2.7312	m	32.775	2.7324	12
1	4	1				32.812	2.7294	41
2	4	0	33.28	2.6921	w	33.105	2.7059	10
1	1	2				33.295	2.6908	14
2	4	-1	33.71	2.6587	w	33.710	2.6587	6
1	5	0	34.51	2.5989	w	34.492	2.6002	16
3	1	-2	35.63	2.5197	w	35.617	2.5206	13
3	3	0	36.06	2.4906	w	36.040	2.4920	13
1	5	-1	36.23	2.4793	w	36.252	2.4779	15
3	0	1	36.70	2.4487	w	36.780	2.4435	9
3	1	1	37.42	2.4032	w	37.392	2.4049	5
3	2	-2				37.476	2.3997	9
0	6	0	39.78	2.2659	w	39.807	2.2644	13
3	3	-2	40.37	2.2341	w	40.411	2.2320	10
1	0	-3	41.12	2.1951	m	41.115	2.1954	12
1	6	0				41.116	2.1953	9
1	1	-3	41.68	2.1669	w	41.673	2.1672	6
4	0	-2	42.34	2.1346	m	42.311	2.1360	9
2	1	-3				42.408	2.1313	11
1	2	3	49.05	1.8572	w	49.014	1.8584	9
2	6	1				49.062	1.8567	12
3	6	-1	50.14	1.8193	w	50.140	1.8193	11
5	2	-1	50.68	1.8012	w	50.681	1.8012	11
3	4	-3	52.88	1.7313	w	52.877	1.7314	5
1	4	3	54.67	1.6788	w	54.647	1.6794	12
5	4	-1	56.22	1.6361	w	56.194	1.6368	6

Table 2. X-ray powder diffraction pattern of lorandite. Guinier diffractometer (Huber G600), $\text{CuK}\alpha_1$ radiation, silicon standard for angular correction. Calculated pattern from the crystal structure refinement data (Balic Zunic et al, in preparation). Unit cell: $a = 12.296$, $b = 11.313$, $c = 6.114 \text{ \AA}$, $\beta = 104.206^\circ$. Space group: $P2_1/a$.

			Measured			Calculated		
h	k	l	2θ	$d(\text{\AA})$	I/I_0	2θ	$d(\text{\AA})$	I/I_0
1	1	0	10.78	8.2057	11	10.78	8.2057	9
2	0	0	14.86	5.9600	15	14.86	5.9600	14
2	1	0	16.88	5.2501	31	16.80	5.2730	22
1	1	-1	18.32	4.8380	8	16.90	5.2436	20
2	0	-1	18.32	4.8380	8	18.32	4.8380	3
1	1	1	19.90	4.4579	10	19.88	4.4604	5
2	1	-1	19.90	4.4579	10	19.94	4.4483	3
2	2	0				21.64	4.1028	5
0	2	1	21.71	4.0889	30	21.70	4.0920	11
1	2	-1				21.72	4.0889	28
2	0	1	23.64	3.7604	23	23.60	3.7659	11
3	1	0				23.72	3.7488	8
1	2	1	24.17	3.6792	83	24.14	3.6834	88
2	2	-1				24.18	3.6766	61
1	3	0				24.74	3.5954	64
2	1	1	24.86	3.5786	100	24.90	3.5731	65
3	1	-1				24.98	3.5628	100
3	2	0				27.40	3.2514	3
0	3	1	27.99	3.1851	32	28.02	3.1816	41
2	2	1				28.44	3.1347	7
3	2	-1	28.50	3.1293	12	28.52	3.1277	5
4	0	0				29.96	2.9800	23
1	3	1				29.98	2.9778	17
2	3	-1				30.02	2.9742	8
0	0	2	30.15	2.9617	56	30.14	2.9635	43
2	0	-2				30.18	2.9588	11
1	1	-2				30.26	2.9511	25
4	1	0				31.00	2.8817	64
3	1	1				31.02	2.8812	24
0	1	2	31.09	2.8742	63	31.18	2.8668	8
2	1	-2				31.22	2.8625	63
1	4	0				32.52	2.7519	85
3	3	0	32.53	2.7502	62	32.72	2.7352	8
2	3	1				33.60	2.6647	5
3	3	-1				33.66	2.6604	5
1	1	2				33.82	2.6480	7
3	1	-2	33.92	2.6413	29	33.92	2.6413	5
4	2	0				33.98	2.6365	16
3	2	1				33.98	2.6361	6
4	2	-1				34.06	2.6303	22
4	0	1				36.90	2.4335	7
2	0	2	37.04	2.4250	17	37.02	2.4268	17
4	0	-2				37.14	2.4190	10
4	1	1				37.78	2.3791	10
1	3	-2	37.88	2.3736	17	37.86	2.3747	7
4	1	-2				38.00	2.3655	14
4	3	-1				38.54	2.3338	8
2	3	-2	38.64	2.3278	15	38.64	2.3278	6
3	4	0	39.05	2.3047	27	39.06	2.3041	45
4	2	1				40.32	2.2354	13
5	2	-1	40.43	2.2292	15	40.40	2.2309	3
1	5	0				40.54	2.2229	5

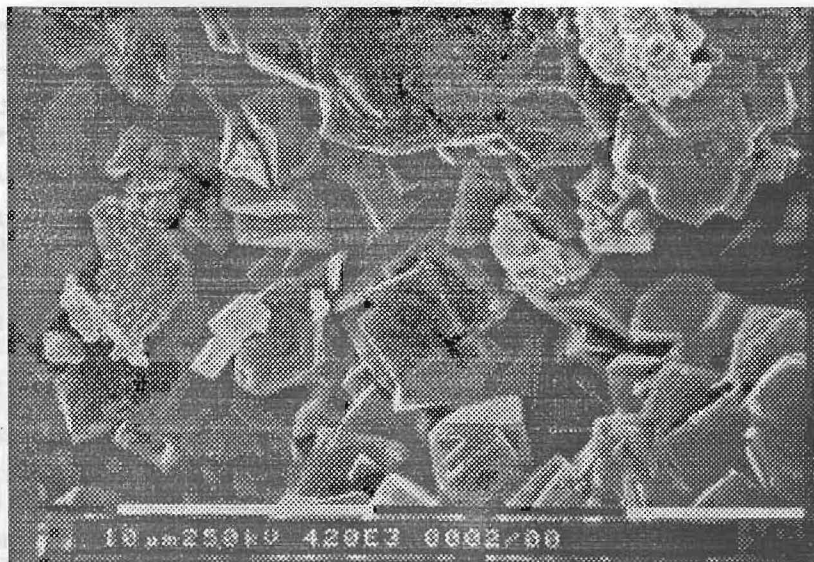


Fig. 1. SEM photograph of dorallcharite crystals (darker) in association with amorphous Fe-Mn sulphate-arsenate (brighter). A division on the scale corresponds to 10 mm.

registered for the first time. The Tl content, as determined by atomic absorption spectrometry is 1.71 wt%. Pharmacosiderite has a zeolite character and alkali cations and water with some of the hydroxyl groups from channels in the structure can be exchanged and show variable contents (Mutter et al., 1984).

Therefore, it is hard to determine the extent of Tl/K replacement in our specimen without detailed chemical analyses. Not enough clean specimen could be obtained up to now for this purpose. From the present result, it can be estimated that most probably Tl replaces K in quantities over 5 wt%.

THE ORE GENESIS

Mineral parageneses show that the first result of hydrothermal activity on the contact of dolomite and silicate rock in Crven Dol was the ankeritization of dolomite and kaolinization of the silicate rock.

The first hydrothermally deposited minerals were iron sulphides and iron carbonate. The presence of siderite and marcasite suggests that the initial temperature of solutions did not exceed 400 °C. Marcasite also testifies to the acidic character of the solutions (the same is documented by the formation of kaolinite).

The main hypogene mineral in the Crven Dol locality is realgar, which crystallized in the next hydrothermal stage.

The observed paragenesis suggests that lorandite did not appear immediately with the first realgar, but crystallized together with the youngest one, forming with it the last hydrothermal stage. The reason could be in the temperature of solutions. There are indications that the first realgar crystallized at a temperature of 250 °C. For the crystallization of lorandite from

hydrothermal solutions the experiments indicate lower temperatures (Edenharter and Peters, 1979). The content of Tl in the hydrothermal solutions was, however, high all the time from the beginning of the hydrothermal activity, as testified by its pyrite + marcasite and realgar content. The formation of lorandite, as a Tl-mineral, produced a peak of Tl concentration in the solid phase. Until then, it was only included as an admixture in non-thallium minerals. The crystallization of iron and arsenic sulphides as the first hydrothermal minerals probably increased the relative concentration of Tl versus that of Fe and As in the solutions. The relative concentration of Tl was so increased at the end of the hydrothermal event that finally crystallization of a Tl-As-sulphide (lorandite) together with As-sulphide (realgar), occurred as the last stage. Potkop 21 lies in the uppermost part of Crven Dol locality, where the oxidation occurred already during the hydrothermal activity and has continued to the present time. This suggests that already at the time of ore formation this horizon was lying relatively close

Table 3. X-ray powder diffraction pattern of inclusions in realgar. Ma = marcasite, Ph = pharmacosiderite, Py = pyrite, Re = realgar. Experimental conditions as for Table 1.

2 θ	d(Å)	I	Minerals
11.04	8.0140	w	Ph
14.66	6.0422	w	Re
15.46	5.7313	w	Re
16.06	5.5185	w	Re
16.39	5.4081	m	Re
19.00	4.6707	w	Ph
21.83	4.0712	w	Re
22.20	4.0042	w	Ph
24.62	3.6158	w	Re
25.85	3.4465	w	Ma
27.27	3.2701	m	Ph
28.05	3.1810	m	Re
28.20	3.1644	m	Re
28.47	3.1350	w	Py
29.24	3.0542	m	Re
29.89	2.9892	w	Re
30.15	2.9640	w	Re
30.53	2.9280	m	Re
31.56	2.8347	w	Ph
32.14	2.7849	w	Re
32.79	2.7312	m	Re
32.96	2.7175	m	Ma Py
33.24	2.6952	w	Ph Re
34.51	2.5989	w	Re
35.46	2.5314	w	Ph
35.62	2.5204	w	Re
36.05	2.4913	w	Re
37.00	2.4295	w	Py
37.21	2.4163	w	Ph Ma
40.69	2.2173	w	Py
41.11	2.1956	w	Re
42.39	2.1322	w	Re Ph
47.38	1.9186	w	Py Ma Ph
49.09	1.8557	w	Re Ph
50.70	1.8005	w	Re
51.01	1.7903	w	Ma Ph
54.70	1.6779	w	Re
56.19	1.6369	s	Py Ph
57.72	1.5971	w	Ph Ma
61.68	1.5038	w	Py
64.15	1.4517	w	Py Ph
65.85	1.4183	w	Ph

to the surface and was influenced by meteoric waters. As regards the Tl content the oxidation process had a complex influence. The geochemical behaviour of Tl during the oxidation of sulphides generally takes the following course (Vlasov, 1966): In the first stage of the process Tl is removed from sulphide minerals and is not retained in the first solid products, the simple sulphates. However, it can accumulate in jarositic minerals if they are formed as the next stage. When the process develops further and a gossan (consisting mostly of limonite) is formed from jarosites, Tl is leached from the solids and re-enters the water cycle again. The final possibility for the concentration of Tl is in the case of its oxidation to Tl^{3+} when it could be included as a solid solution in manganese oxides or crystallize as Tl-oxide (avicennite).

We were able to confirm the existence of the described process in Alšar up to the stage of jarosite crystallization. It is significant that Tl is completely absent from the amorphous sulphates and arsenates of iron and manganese, while it forms one of the main constituents of the jarositic mineral which is in close association with them. This clearly shows that the formation of jarositic minerals enables the capture of Tl from solution and its concentration in the solid phase. The concentration of Tl in Alšar is so great that a Tl-dominated member of the jarosite group (dorallcharite) is formed. The conditions in the investigated locality (especially the acidity of the circulating water) remained such that the formation of jarositic minerals represents here the final stage of the oxidation. However, in the greater Alšar region a further development of gossan and even the formation of Tl-oxides may probably also be found in future mineralogical investigations.

Another interesting question is the formation of arsenate minerals and Tl concentration in them. A high content of As in the Alšar ore makes them an important part of the oxidation products. Arsenate can isomorphously replace sulphate in minerals from the alunite-jarosite family. However, this is connected with the substitution of a divalent or trivalent cation (e.g. Pb^{2+} , Ca^{2+} or Ce^{3+}) for alkalis, because of the charge balance in the structure. In dorallcharite no arsenate is present, although it is abundant in the environment, which can be connected to the fact that it contains only monovalent cations (Tl^+ and K^+) in 12-fold coordination position. There is an arsenate mineral, pharmacosiderite, which appears as the second carrier of Tl in the oxidation zone. The Tl content of pharmacosiderite is caused, as in dorallcharite by Tl-K isomorphous replacement. However, it appears to be much lower. From the point of crystal-chemical properties there seem to be no hindrance to a complete Tl-K solid solution in pharmacosiderite, although we lack the experimental data. The reason for a much lower relative Tl content than in dorallcharite could be in that pharmacosiderite was formed during the first oxidation

processes which were active somewhere between the pyrite-marcasite-siderite and realgar-lorandite phases, when the content of Tl in sulphides was still much lower than the final one (after the crystallization of lorandite). Pharmacosiderite is also, in contrast to dorallcharite and jarosite, a poor immobilizer for Tl^+ . It has a zeolitic character and alkalis (or other big cations) which

occupy the channels in the structure together with water molecules can easily be exchanged (Mutter et al., 1984). The full crystal and chemical characteristics of Tl-rich pharmacosiderite from Alšar still remain an open question until more clean material can be obtained for analysis.

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