BOHUSLAV CAMBEL, JÁN JARKOVSKÝ, HELENA GERTHOFFEROVÁ, JOZEF KRIŠTÍN, VLADIMÍR STREŠKO*

CONTRIBUTION TO GEOCHEMISTRY OF IRON AND MERCURY IN ANTIMONITES OF THE WEST CARPATHIANS

(Fig. 1—27)

Abstract: A team of authors presents in the article partial results of geochemical investigation of antimonites from various deposits and occurrences of the West Carpathians. The authors studied Fe contents established by the spectrochemical method and very low contents of Hg established by atomic absorption spectrometry. They also studied the modes of occurrences of iron on X-ray analyser and of mercury under electron microscope. Fe has been found to occur in antimonites heterogeneously on the one hand and homogeneously on the other hand (up to several hundredths %). Mercury occurs in antimonites heterogeneously, mainly as submicroinclusions of cinnabarite and metacinnabarite.

Резюме: Коллектив авторов представляет в статье частичные результаты геохимического изучения антимонитов из разных месторождений и местонахождений в Западных Карпатах. Авторы изучали содержание железа спектрохимическим методом и низкое содержание ртути методом абсорбционной спектрометрии. Изучались также формы проявления железа на рентгеновском анализаторе и ртути на электронном микроскопе. Было обнаружено, что железо проявляется в антимонитах как гетерогенный элемент но и как гомогенный в нескольких сотых долей %. Ртуть появляется как гетерогенный элемент, главным образом в виде субмикроинклюзий киновари.

The authors B. Cambel and J. Jarkovský were dealing with geochemistry of microelements in pyrite, pyrrhotite and chalcophyrite in the foregoing years (B. Cambel, J. Jarkovský, 1967, 1969, 1974). Similarly as in the quoted works, also in geochemical investigation of microelements in antimonites, the main intention of the authors was to determine crystallochemical relation of microelements in antimonites from deposits of the West Carpathians. It was necessary to determine their mode of occurrence and character of distribution, whether they are a component of the crystal structure of antimonite phase or are found in heterogeneous form in it.

For such a study cooperation with several specialists was requirable. The authors were based on the results of spectrochemical establishing of Fe with detection limit 10 ppm and on the results of determination of Hg by atomic absorption spectrometry for our investigations with the advantageous detection limit 0,05 ppm. The competent method of Hg determination in antimonites by means of the flameless technique by the so called method of cold vapour was worked out and the corresponding analyses

* Academician B. Cambel, DrSc., Geological Institute of Slovak Academy of Sciences, Obrancov mieru 49, 886 25, Bratislava; Doc. Dr. J. Jarkovský, CSc., Dept. of Geochemistry, Faculty of natural sciences, Comenius University, Pauliny-Tótha 1, 801 00, Bratislava; Dr. H. Gerthofferová, CSc., Geological Institute of Comenius University, Zadunajská 16, 801 00, Bratislava; Dr. J. Krištín, CSc., Chemical-technological faculty of Slovak Technical University, Microprobe Dept., Jánska 1, 801 00, Bratislava; Ing. V. Streško, CSc., Geological Institute of Comenius University, Zadunajská 15, 801 00, Bratislava.

Table 1

Results of HG determination in antimonites from various metallogenetic regions of the West Carpathians by the method of atomic absorption spectrometry (in ppm)

Sample no.	Purity degree	Locality	Hg	Sample no.	Purity degree	Locality	Hg
Spišsko-gemerské rudohorie Mts.							
18	2	Poproč	2,85	212	0	Čučma	5,0
41	0	Poproč	18,0	28	0	Spišská Baňa	1,08
59	2	Poproč	2,0	30	1	Spišská Baňa	25,7
215	3	Poproč	6,92	168	1	Spišská Baňa	14,3
217	3	Poproč	3,2	57	2	Helcmanovce	3,6
50	2	Čučma	6,2	114	2	Helcmanovce	10,4
188	2	Čučma	32,4	149	3	Helcmanovce	80,0
204	3	Čučma	10,08	213	0	Helcmanovce	2,2
211	0	Čučma	2,85	19	1	Betliar	13,8
56	3	Švedlár	2,2	54	3	Betliar	3,6
66	2	Švedlár	8,9	26	3	Mníšek	25,5
24	3	Bystrý Potok	5,8	67	0	Mníšek	7,2
37	2	Bystrý Potok	2,2	68	3	Chyžné	2,74
134	2	Zlatá Ida	9,3	70	3	Chyžné	9,8
Nízke Tatry Mts.							
43	0	Dúbrava	2,8	39	1	Lom	13,27
49	0	Dúbrava	1,84	187	2	Lom	2,64
52	0	Dúbrava	0,96	23	0	Ľubela	2,74
61	2	Dúbrava	1,28	31	1	Kriváň	17,5
221	0	Dúbrava	4,5	46	3	Dve Vody	20,7
13	3	Medzibrod	1,96	51	2	Malé Železné	2,32
73	2	Medzibrod	2,8	143	0	Vajsková*	28,8
115	1	Medzibrod	1,0	180	2	Husárka	11,8
						Riavka	3,2
Malé Karpaty Mts.							
7b	3	Kuchyňa	2,2	12	3	Pezinok	7,3
14	3	Kuchyňa	18,0	117	3	Pezinok	6,7
				92	2	Cajla	5,3
Kremnica region							
107	0	Kremnica	41,0	174	0	Kremnica	21,4
111	0	Kremnica	49,6	203	0	Kremnica	22,5
152	1	Kremnica	16,8				

E x p l a n a t i o n s: Grading up of purity has been made according to the results of optical separation, further colouring test with KOH solution and at last according to the results of spectrochemical analysis.

* Sample from smelting works.

were carried out by Ing. V. S t r e š k o CSc. on the apparaturs Perkin-Elmer, model 303 (Tab. 1). The questions of homogeneity and heterogeneity of antimonite crystals mainly aimed at the occurrence of inclusions of various minerals of microscopic and submicroscopic dimensions were studied by Dr. H. G e r t h o f f e r o v á CSc. on the electron microscope TESLA B242 on fracture surface of crystals. Concerned were mainly disseminations and microaggregates of cinnabarite in antimonite, which could have been identified owing to the fact that the last named previously studied morphology of synthetic cinnabarite and metacinnabarite.

The character of distribution and modes od occurrence of other microelements but mainly of iron were studied by Dr. J. Krištín CSc., on X-ray microanalyser JXA-5A. Quantitative spectrochemical analyses were carried out by J. Chudý by the method worked out by Doc. E. Plško DrSc., on spectrograph PGS-2. To both the mentioned we express our thanks.

The authors of the work applied in evaluation of spectrochemical data a similar methodical approach as in geochemical investigation of chalcopyrite. Analysed were on the whole 208 samples of antimonite, divided according to the degree of purity (monominerality) into 4 categories:

Antimonite with a high degree of monominerality, i. e. the relatively purest samples (designated with zero-0) contain totally up to 0,1 % admixtures, predominantly isomorphous or such ones, which can have certain crystallochemical relation to antimonite (e. g. anomalous mixed crystals). Antimonites with considerable degree of monominerality (designated with one-1) contain totally up to 0,4 % admixtures, predominantly isomorphous but a certain proportion can be of the character of regular intergrowths or can also occur heterogeneously. Antimonites with a lower degree of monominerality (designated with two-2) have approximately up to 1 % heterogeneous admixtures. Antimonites with a very low degree of monominerality (designated with three-3) contain approximately 1—3 % heterogeneous admixtures of other minerals. Such a valuation of purity has been made according to the results of spectrochemical analysis, the results of optical separation, investigation by electron microscope and in many cases also according to data of X-ray microanalytical measurement of spectrochemically analysed powder samples as well as according to testing with KOH solution.

Whilst the samples designated „0" represent the relatively purest monomineralic fraction (50 analyses), the other ones have graved up higher admixtures of other minerals. Therefore the authors could use the contents of elements from samples designated „0" for calculation of average contents (mineral clarks) of the individual elements for antimonite. Concerned were the following elements: with the following average contents (ppm)-Mn 7; Pb 19; Au 3; Hg 11; As 87; Bi 0,2; Sn 2; 195
Mo 0,04; Fe 211; V 0,6; Ga 0; Cr 0; Cu 74; Ag 6; Ti 1; Zn 20; Ni 2; Co 0,02. It should be mentioned that the boundary between isomorphous (homogeneous) and nonisomorphous (heterogeneous) occurrence of elements cannot be unambiguously detectable as transitions exist when the mineral nucleus of arising inclusion can be so small that it may not be considered as evidence of heterogeneity yet. Another case can occur with unmixing of originally isomorphous element, which need not represent an own mineral phase yet since a certain crystallochemical relation to the mother mineral has remained as a consequence of incomplete individualization of the new mineral phase.

Samples of purity degree 1, 2, 3 are characterized by increasing degree and dimensions of intergrowth with other minerals. Resulting from it are also the more difficult possibilities of obtaining pure fractions of antimonite. Samples of purity 1, 2, 3 show polymetalness of solutions, from which antimonite originated and are rather a reflection of the specific geochemical character of the individual antimonite deposits and characterize the genetic and paragenetic type as well as regional, metallogenetic and deposit particularities.

The character of Fe frequency of purity 0 and 1 and the character of Hg frequency regardless of the purity of samples we document by corresponding histograms on linear and logarithmical scale (Fig. 1, 2). This way we also traced the type of distribution of these elements (lognormal, normal). From the histograms and/or frequency curves it is possible also to find out, for the purpose of orientation, the mode of occurrence in these elements, in which it was not possible to trace by the microprobe because of inconvenient detection limit (Hg).

The most remarkable histogram from the mentioned ones is that of iron (Fig. 1). It proves namely that this element is present in antimonites in two forms, partly homogeneously (orderly in hundredths %) and partly heterogeneously (berthierite, Fe

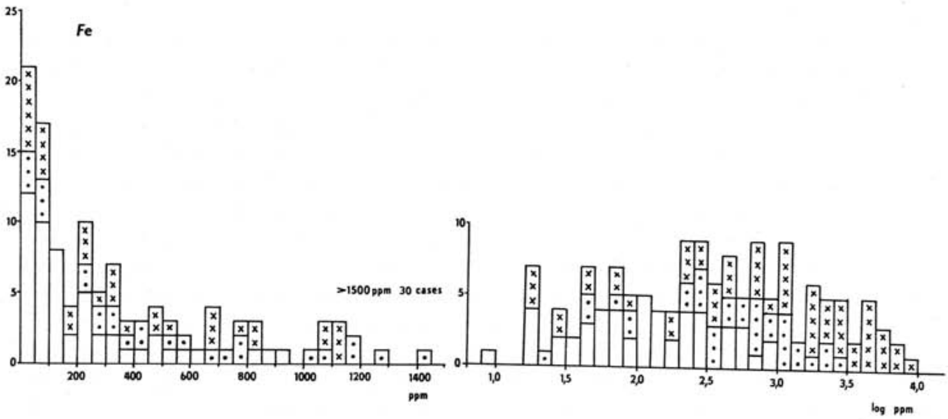

Fig. 1. Histograms of distribution of Fe content in antimonites on linear and logarithmical scale. Explanations: The graphs are compiled according to purity criterii of samples; the histograms without designation signify purity degree 0, histograms with point 1, with cross 2. Samples with Fe content > 1500 ppm, 30 cases of which are not plotted into the histograms. The values on the ordinate are the frequency.

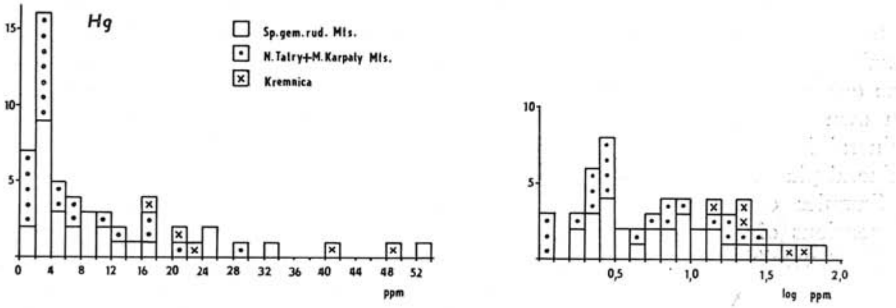

Fig. 2. Histograms of Hg content distribution in antimonites on the linear and logarithmical scale. Explanations: The graphs are compiled according to competence of samples to the individual metallogenetic regions and types of deposits of the West Carpathians. The values on the ordinate are the frequency.

oxides etc.) It is also evident from the line analysis of Fe on the microprobe (Fig. 3).

It may be read from Fe histograms that in no case zero concentrations of this element occur. The character of Fe distribution may be observed to approach the lognormal type of distribution as is to be seen from the total shape of histograms on linear and logarithmical scale. The polymodality of Hg distribution shown on the

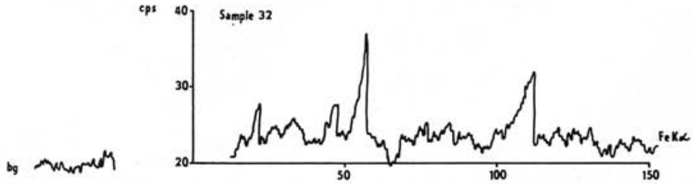

Fig. 3. Line analysis of Fe in antimonite sample from Spišská Baňa, sample 32. It is to be seen that iron is present in antimonite prevailingly heterogeneously in the form of very fine inclusions, however, partly is also found homogeneously but extremely unequably scattered. The values on the vertical scale (cps) indicate the number of pulses per sec., on the horizontal scale length in μm. The symbol „bg“ means the background.

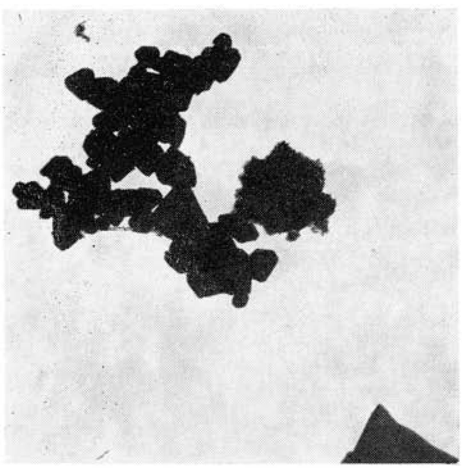

Fig. 4. Aggregate of synthetic metacinnabarite with proportion of cinnabarite. Magnif 7000 ×.

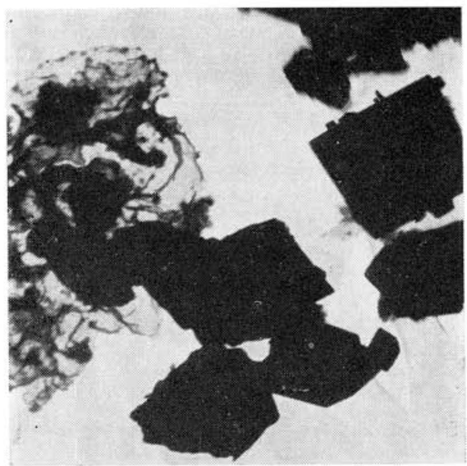

Fig. 5. Synthetic cinnabarite. Magnif. 7000 ×. Explanations: The irregular formation of rounded shapes, partly grey, ist probably cinnabarite in part altered into metallic mercury originated due to the heat from the beam of electrons.

logarithmical scale predominantly points to a heterogeneous position of this element in antimonites.

The authors also compiled histograms and competent frequency curves of contents of other elements (Pb, Zn, Cu, Ag, Mn), not mentioned because of lacking place. These

Fig. 6. Grained antimonite, sample 3, magnif. 7000 ×. Inclusions of cinnabarite (metacinnabarite) (black) of dimensions up to 1 μm. Explanations: Two-stage replica (Pt 80 %, Pd 20 %). The black places (impermeable for electrons) represent partly submicroinclusions of cinnabarite, partly parts of the fundamental mineral, which arose by their tearing off when making the preparation.

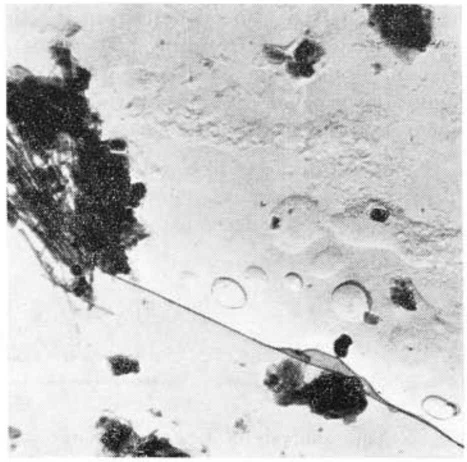

Fig. 7. Acicular antimonite, Kremnica, sample 223, magnif. 10 000 ×. Microinclusions of cinnabarite of irregular shapes of various dimensions (black). Visible are also needles of arsenopyrite 1—2 μm in size associated with cinnabarite — according to SPA there are 890 ppm As. Explanations ditto as in Fig. 6.

Fig. 8. Coarse-grained antimonite, Malé Železné (Low Tatra region), sample 51, magnif. 15 000 ×. Microaggregate and individual cinnabarite (metacinnabarite) crystals (black). Explanations ditto as in Fig. 6.

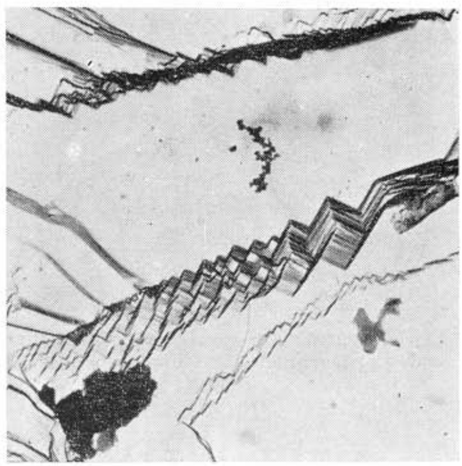

Fig. 9. Fine-grained antimonite, Medzibrod (Low Tatra region), sample 73, magnif. 7000 ×. Aggregate of cinnabarite (metacinnabarite) of submicroscopic dimensions. Block structure of the mineral on fissility plane with typical forms of crystal growth. Explanations in Fig. 6.

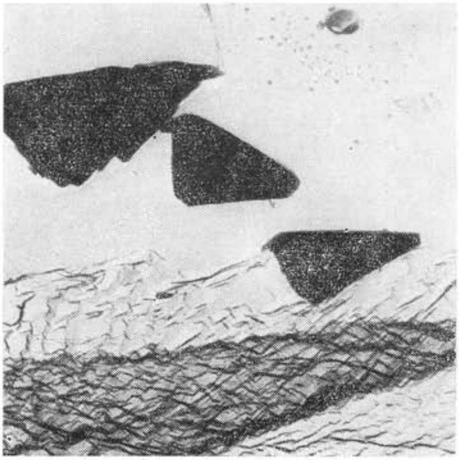

Fig. 10. Fine-grained antimonite, Dve Vody, sample 46 (Low Tatra region), magnif. 10 000 ×. Cinnabarite crystals (black). The inclusion of circular shape with dark points around it is probably a product of decomposition of cinnabarite (see Fig. 2).

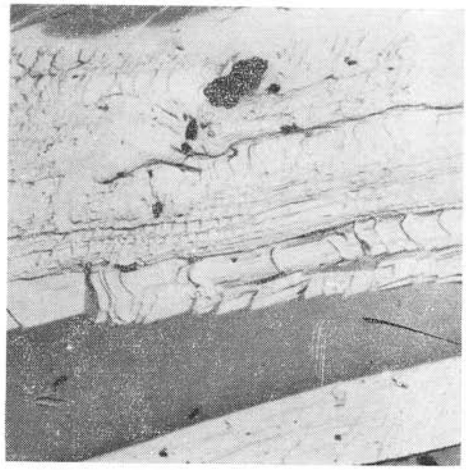

Fig. 11. Fine-grained antimonite, Dve Vody (Low Tatra region), sample 46, magnif. 7000 ×. Microaggregate of cinnabarite (black). Block structure disturbed by the affect of pressure in direction of transversal striation perpendicular to c axis.

graphical illustrations show the systematicity of the occurrence of the mentioned elements in very low concentrations at their analytical detection limit. As it is distinct, the higher content of these elements is conditioned by inclusions.

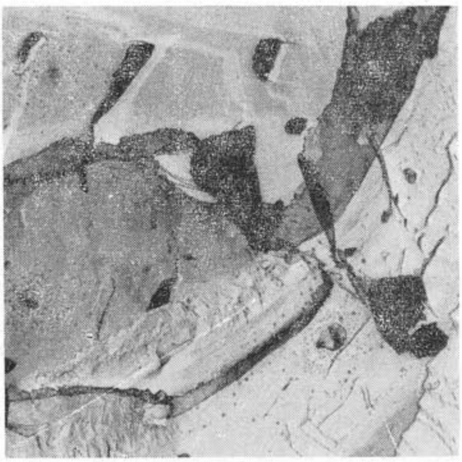

Fig. 12. Fine-grained antimonite, Dve Vody (Nízke Tatry region), sample 46, magnif. 7000 ×. Cinnabarite (black) with probable products of alteration (see Fig. 10).

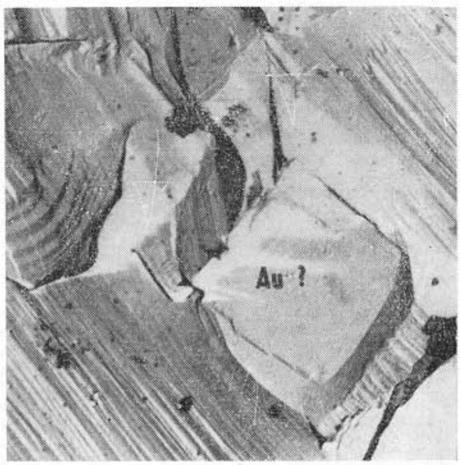

Fig. 13. Fine-grained antimonite, Kuchyňa (Malé Karpaty region), sample 7b, magnif. 7000 ×. Aggregates of cinnabarite of submicroscopic dimensions (black) and microinclusion (3 μm) of cubic habit, probably gold.

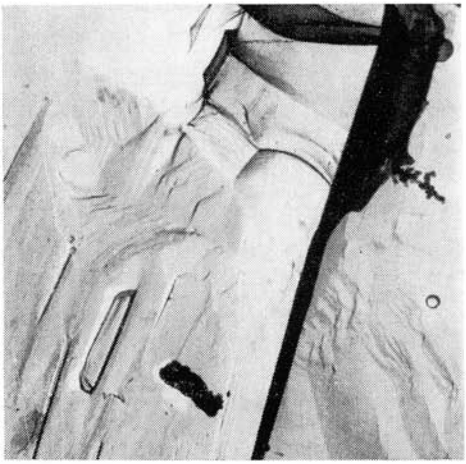

Fig. 14. Fine-grained antimonite, Spišská Baňa (Spišsko-gemerské rudohorie Mts. region), sample 27, magnif. 7000 ×. Aggregates of cinnabarite (metacinnabarite) (black) about 1 μm in size. Visible are also inclusions of elongated shape about 2 μm in size (arsenopyrite, jamesonite?).

Fig. 15. Grained antimonite, Kremnica, sample 3, magnif. 7000 ×. Aggregates of cinnabarite of minute dimensions and individual crystals. Inclusions of other minerals (grey) are also to be seen.

In the next we present photographic documentation from the investigation of antimonite samples on the electron microscope (Figs. 4—15) and X-ray microanalyser (Figs. 16—27).

This documentation makes clear that Hg in antimonites, also in spite of its systematic low contents, is present as fine disseminations of cinnabarite or metacinnabarite of the

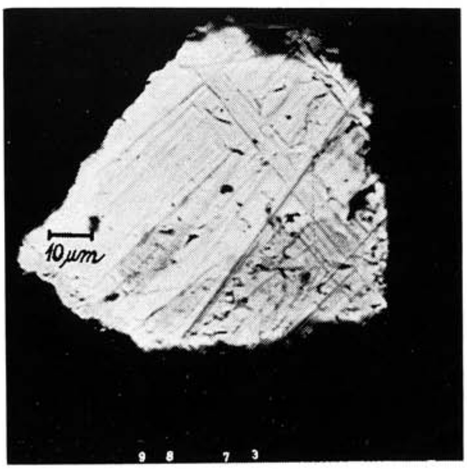

Fig. 16. Poproč, sample 36, magnif. 600 ×. Composition of antimonite (litghter-coloured) with berthierite (darker).

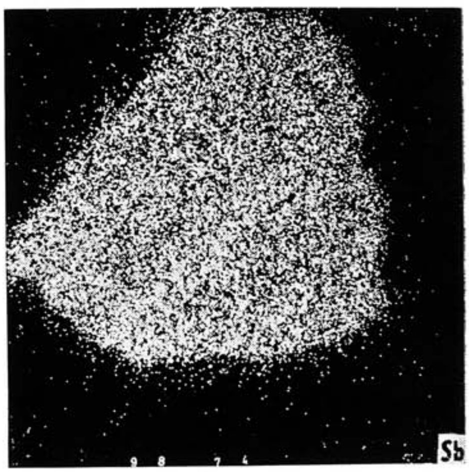

Fig. 17. Distribution of Sb.

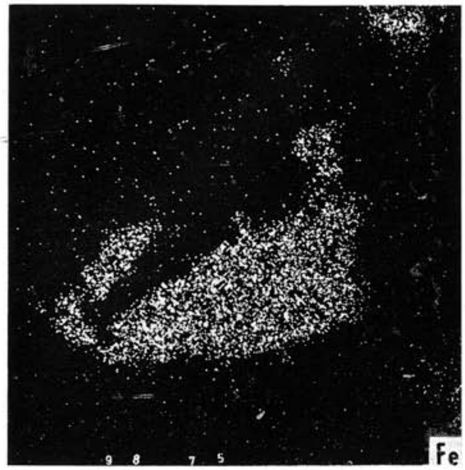

Fig. 18. Distribution of Fe.

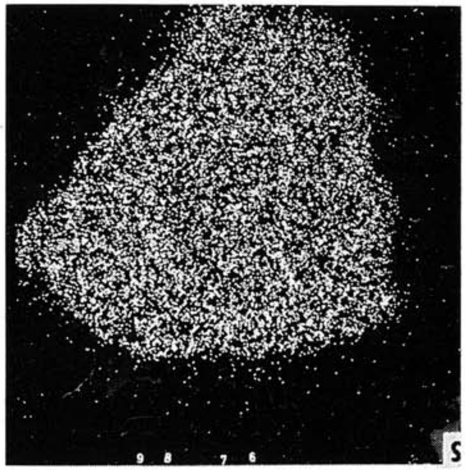

Fig. 19. Distribution of S.

dimensions of several hundredths to several μm. Regarding to the unfavourable detection limit of Hg (about 500 ppm) it was not possible to trace this element on the microprobe.

In spite of that, however, iron, with detection limit $1-3.10^{-3}$ % on the microprobe, is also present in homogeneous from, approximately up to 0,02 % (Figs. 3, 23, 27).

Similarly also in the case of Pb and As in some antimonite samples manifestations of homogeneous occurrence of these elements have been found (Figs. 21, 26), however,

Fig. 20. Dve Vody, sample 26, magnif. 600 ×. Composition of berthierite (somewhat darker) with antimonite (lighter-coloured).

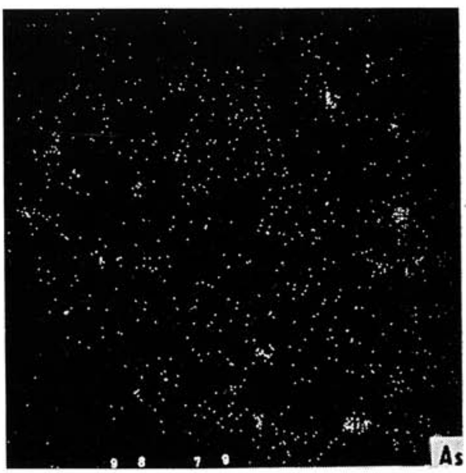

Fig. 21. Distribution of As in berthierite and antimonite.

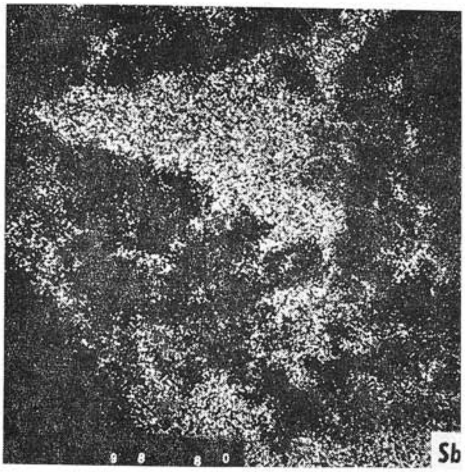

Fig. 22. Distribution of Sb in berthierite and antimonite.

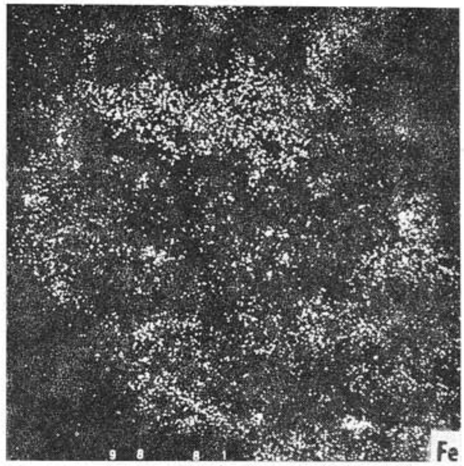

Fig. 23. Distribution of Fe in berthierite and antimonite.

because of overlapping of the main analytical lines of Pb and As and insufficient detection limit of these elements according of subsidiary analytical lines (about 0,1 %) this question remains open so far.

C o n c l u s i o n s: Hg in antimonites has been found to occur in the form of submicroscopic inclusions of cinnabarite or metacinnabarite of the dimensions of hundredths μm to several μm. These occurrences have also been confirmed in samples, in which Hg was neither recorded by microprobe nor by spectrochemical analysis.

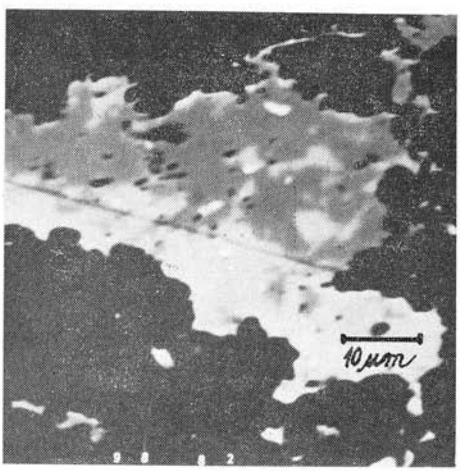

Fig. 24. Dve Vody, sample 46, magnif. 1200 ×. Composition of berthierite (darker) with antimonite (lighter-coloured).

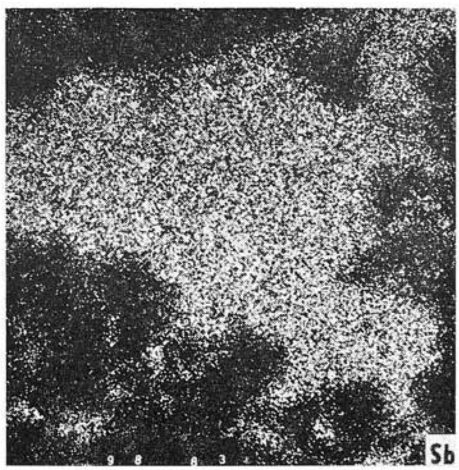

Fig. 25. Distribution of Sb in berthierite and antimonite.

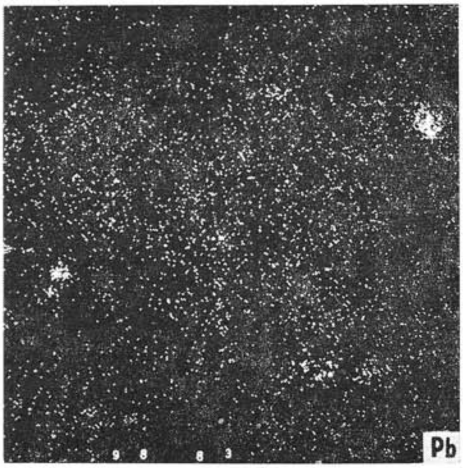

Fig. 26. Distribution of Pb in berthierite and antimonite.

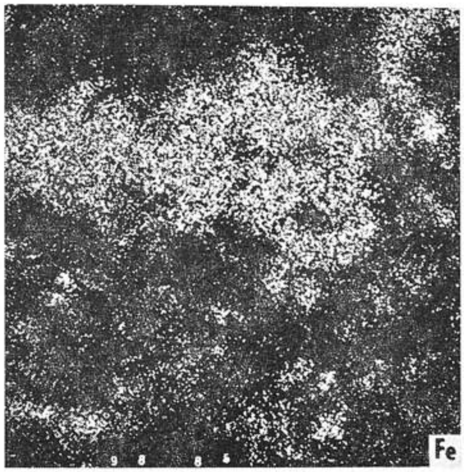

Fig. 27. Distribution of Fe in bethierite and antimonite.

Only by the method of atomic absorption also very low Hg contents could be recorded. Iron in antimonites is found prevailingly as a component of heterogeneous admixtures of other minerals, mainly of berthierite, Fe oxides etc., but on the basis of determination by the microprobe it may be found also in homogeneous form, up to the content of several hundredths %. The authors B. Cambel and J. Jarkovský are preparing a more complex geochemical evaluation also of other microelements in antimonite.

Translated by J. PEVNÝ

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