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CONTRIBUTION TO THE MINERALOGY OF MALÉ KARPATY ORES

(Fig. 1—47)

Abstract: The chemical composition of Sb minerals was studied and checked by X-ray microanalysis method in order to decide whether some Sb and Ni ore minerals are present in the hydrothermal deposits of Malé Karpaty. Especially such minerals where "wet" chemical analysis could not be done by B. Cambel (1959) because of the small size, rare occurrence and difficult separation were studied. The same ore specimens were chosen for X-ray microanalysis as for chalcographic study. The results of Cambel's study were published in his monography in 1959. The following minerals were studied: andorite, freislebenite (unconfirmed identity), bertierte, bournonite, goudmundite, jamesonite, ullmanite, gersdorffite, chalcopyrite and elementary antimony.

Резюме: Авторы попытались изучить и проверить химический состав сурьмяных минералов помощью рентгенового микроанализа и решить присутствие некоторых сурьмяных и никелевых минералов, а также точно определить в рудах гидротермальных месторождений Малых Карпат. Изучались минералы, которые нельзя было до сих пор достаточно точно изучить (Б. Цамбел 1959), сделать их химический анализ из-за небольшого количества, редких находок и из-за невозможности их сепарации. Эти рудные образцы были изучены раньше халкографически и результаты опубликованы в монографии Б. Цамбеля (1959) Изучались минералы: андорит, фрейслебенит (неподтвержден), далее бертьерит, гудмундит, джемсонит, самородная сурьма и коринит в ассоциации с минералами ульманит, герсдорфит и халкопирит.

The electron microprobe (V-ray microanalyzer) study of the Malé Karpaty ores is brought in this paper. The X-ray microanalysis was used in order to solve the question of the determination of the minerals which were not surely identified in B. Cambel's monograph (1959) because of lack of information about their chemical composition. The minerals were either very small (not sufficiently separated) or very rare. The electron microprobe research had to prove the identification of chosen minerals and therefore the same specimens which had already been chalcographically studied by B. Cambel (1959) were used. At this occasion it must be emphasized that during specimen preparation there is a danger the desired mineral will not be found on the surface because the cross-section is randomly chosen. Therefore sometimes it is impossible to obtain new information about the mineral.

Following minerals had to be identified:

1. Andorite and freislebenite. Both minerals were studied on the polished blocks BH_2, BH_6 and $B\acute{H}_7$ (B. Cambel 1959, pages 170, 171, tab. XVIII, fig. 1). These minerals were described from the Pb-Zn mineralization „Pod Babou".
2. Bertierite, goudmundite and jamesonite.
3. Pure antimony. It occurs in the Sb deposit of Kuchyňa and Pezinok. This

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mineral was originally identified by A. K o c h (1925) as allemontite (an alloy of the type Sb-As). Later it was proved (by B. C a m b e l) with an optical analysis to be pure antimony without As. (B. C a m b e l 1959, pages 143–146, fig. 2, 4, 5, 6; tab. VI).

4. Glaucodot. This mineral was described as glaucodot with question mark: because chemical analysis could not be done (B. C a m b e l 1959, p. 130).
5. Corynite. This mineral occurs in the deposit of Častá as a mixture formed by unseparable minerals which crystallized at the same time (B. C a m b e l 1959, pages 190—199, tab. XVIII, fig. 1, 6). The homogenety and presence of Ni, Co, As, Sb minerals in corynite have to be checked.
6. Other Sb minerals. A qualitative and quantitative study of different minor elements in Sb minerals according to paragenetic relations and periodization of the process of mineralization is to be done. This problem is more completely studied in a separate paper which is prepared for the publishing.

All facts which were known about the minerals of the Malé Karpaty hydrothermal ore deposits (stibnite and polymetallic) until 1959 have been included in C a m b e l's work (1959). Pyrite and stibnite ores were later studied by J. K a n t o r (1974). He dealt with sulphur isotopes presented in different sulphidic deposits of the Malé Karpaty region. His papers complemented the existing knowledge and brought interesting details concerning the successive and paragenetic relations among different minerals especially some recently revealed ones in Sb ores that are worked up in the past few years the in Pezinok area. There is an interesting relation among Sb-Fe minerals from the Pezinok area. The formation of Sb-Fe minerals (gudmundite, bertierite, jamesonite) was influenced by an older pyrite mineralization. This fact (already ascertained by B. C a m b e l) results from the occurrence and mutual suppression of these minerals. Sb-Fe minerals can be often found in places where a younger Sb mineralization has penetrated a pyrite mineralization. This phenomenon also supports ideas about the formation of Sb-Fe minerals.

The relation between hexagonal and younger monoclinic pyrrhotite in pyrite deposits of the Malé Karpaty has been explained in mineralogical and geochemical works of J. K a n t o r (J. K a n t o r — J. Ď u r k o v i č o v á 1973). He found out that pyrrhotite in hydrothermal Sb mineralization was monoclinic. J. K a n t o r (1974) obtained interesting conclusions from an isotopic research of sulphur in the minerals of the Malé Karpaty area. The presence of light sulphur was mainly found out in iron minerals. The presence of senarmontite was proved also by X-ray diffraction analysis. Scheelite has not been found so far in primary Sb-ores and adjacent rocks. On the other hand, the presence of heavy minerals from river fluvial accumulations would suppose an opinion about increased content of scheelite in such areas where pyrite productive zones have occurred.

Polished blocks were qualitatively and quantitatively studied by X-ray microanalysis method.

Discussion of results

Abbreviations to the pictures of composition (backscattered electron image)

Sf	— sphalerite	Kv	— quartz
Py	— pyrite	Ulm	— ullmanite
Brn	— bournonite	Chalk	— chalcopyrite

Bert – bertierite
Gud – gudmundite
Jam – jamesonite
Co-gers – cobaltgersdorffite
Gers – gersdorffite
Sb_2S_3 – stibnite

X-ray microanalysis measurements were carried out by J. Krištín. Japanese microprobe JXA-5A was used under following conditions:

Accelerating voltage 25 kV, sample current 2. 10^{-8}A, analyzing crystals: Quartz PET, LIF, KAP, expositure time for taking pictures 40 sec.

The chemical composition of individual minerals was checked with two independent crystals. Total chemical composition was computed with CDC 3300 computer. Atomic number, absorption, fluorescence and dead time corrections were applied.

Results

1. Supposed minerals andorite – ($Pb(AgCu) Sb_6S_{12}$) on polished blocks BH_6, BH_7 This phase has been surrounded by sphalerite and pyrite. A considerable confirmed by X-ray microanalysis. We consider the main reason why both supposed minerals were not identified the method of sample preparations. Polished blocks BH_6 and BH_7 were obliged to be prepared again in accordance with the microprobe demands before measurements. So the electron microprobe searched different flatness compared to the previous study.

A phase with the high reflection of backscattered electrons has been found. and freislebenite ($Pb_3Ag_5Sb_5S_{12}$) on polished block BH_7 have not been content of Pb, Cu and Sb has extended the presence of andorite and freislebenite (Fig. 1–8). No isomorphous substitution between Ag and Cu was ascertained (X-ray spectrum study was done in the interval of wave lenghts near Ag Lα). The presence of bournonite was confirmed by quantitative X-ray point analysis (tab. 1). Bournonite had been surrounded by sphalerite, pyrite and quartz. Bournonite grain (Fig. 7) has been enriched by Zn along grain boundaries. This phenomenon confirms the diffusion of sphalerite into bournonite.

2. Supposed occurrence of bertierite, gudmundite and jamesonite has been fully confirmed by X-ray microanalyzer. Some examples can be given: suppression of pyrite by bertierite can be seen on Fig. 9–12. Such suppression can be often observed in ores of Kuchyňa Sb deposits. Sb minerals in paragenesis do not usually form stibnite but bertierite because pyrite is partially suppressed by bertierite. A similar process of gudmundite suppression by bertierite can be seen in Fig. 13–16.

Fissures in gudmundite can be cemented not only by bertierite but also by stibnite (see Figs. 17–20). This phenomenon occurs without transition of gudmundite into bertierite or without enrichment of stibnite by Fe near gudmundite. The formation of bertierite can therefore not be understood as stibnite transition into bertierite in situ near an iron mineral which had been treated with antimony containing solutions. Such Fe enrichment takes place in another place.

The described process of gudmundite suppression by stibnite is more frequent in Pezinok deposits than in Kuchyňa deposits where there is an overbalance of bertierite and gudmundite. Here Fe enrichment of ore-forming solutions is most typical.

The group of Fig. 21—26 (specimen K7) shows the suppression of bertierite by jamesonite in Kuchyňa deposit. Sphalerite is also present. It can be similarly seen (Figs. 27—31) jamesonite and bertierite in association with stibnite. Results of quantitative point analysis are in Tab. 2, 3, 4.

3. Two specimens, one from Pezinok Sb deposit (Ca 37 from the chimney between pyrite and stibnite gallery), the other from Kuchyňa deposit, were

Table 1
Bournonite

	1	2	3
Pb	41,7	43,2	42,3
Cu	12,8	12,1	12,5
Sb	25,1	24,5	24,4
S	19,8	19,1	19,5
Sum	99,4	98,9	98,7

Table 2
Bertierite

	1	2	3
Fe	12,6	13,4	15,1
Sb	56,9	55,3	54,1
S	29,3	29,4	29,1
Sum	98,8	98,1	98,3

Table 3
Gudmundite

	1	2	3
Fe	26,8	28,1	25,1
Sb	57,2	55,1	57,8
S	15,1	15,9	16,1
Sum	99,1	99,1	99,0

Table 4
Jamesonite

	1	2	3
Pb	40,8	39,6	39,4
Fe	2,8	2,1	2,9
Sb	34,6	32,6	32,8
Cu	0,2	2,1	1,9
S	21,4	22,1	21,6
Sum	99,8	98,5	98,6

Table 5
Ullmanite

	1	2	3
Ni	25,8	26,1	24,8
Sb	54,7	53,1	55,6
Fe	2,1	2,8	3,2
As		1,2	1,4
S	15,2	14,8	14,4
Sum	98,6	98,0	99,4

Table 6
Gersdorffite

	1	2	3	4	5	6
Ni	32,40	33,4	34,4	20,9	18,5	17,9
As	40,4	38,1	40,2	48,4	46,1	45,9
Fe	4,6	3,5	2,5	2,4	2,6	2,1
Co	2,2	2,6	2,1	10,6	12,8	11,6
S	16,4	17,5	15,8	14,1	13,6	13,8
Sum	96,0	95,1	95,0	96,4	93,6	91,3

1—3 Gersdorffite
4—6 Co — gersdorffite
Owing to the inhomogeneity of measured gersdorffite and Co-gersdorffite grains the results of microanalysis in Tab. 6 are under the limit of accuracy.

analysed in order to determine the chemical composition of pure antimony. Microprobe analysis ascertained the mineral in question to be really pure antimonite and not allemontite (or Sb As allov) as it was referred by A. Koch (1925). Figs. 32—35 (specimen Ca 37) confirm the previous facts.

Besides pure antimonite, also gudmundite, Fe oxides and Fe carbonates are present. In Figs. 36—39 stibnite together with pure antimonite (bright phase) can be seen. Fe oxides are present on the bottom part of the Figure 37. Pure antimonite has so far always been found only with stibnite and not with antimony sulphur salts (enriched by Fe). Fe oxides could penetrate as a consequence of charge compensation. Such compensation took place during antimony and stibnite formation under reduction conditions.

4. Owing to the slight penetration of Ni minerals into Ni-Co sulphides, the ones from Častá polymetallic deposit could not be exactly identified by X-ray microanalysis method. The specimen which was studied with X-ray microanalyzer had been chalcographically studied and spectrochemically analysed by B. Cambel. The results were published in B. Cambel's work (1959, pages 190, 199).

The group of Ni minerals can be classified owing to the results of spectrochemical analysis (B. Cambel 1959, page 192):

100,0 — 1,0 %	1,0 — 0,01 %	0,01 — 0,001 %
Sb, As, Ni	Pb, Bi, Mn	Sn, Hg, V, Ti
Co, Cu, Fe	Ag, Zn	Ba, Sr, Au

The content of individual elements reflects local occupation of a mineral in an analysed mixture. The mixture of these basics is very well characterized by figures 40—47.

X-ray identification and determination of individual Ni minerals by E. Šamajová (B. Cambel 1959, pp. 194—196) is also not unique.

Diffraction values of corynite are very close to table values of gersdorffite, vilianite, kallinite and ullmanite. According to X-ray spectrochemical data, Ni minerals from Častá are members of the cobaltite group together with gersdorffite corynite, ullmanite, viliamite and kallinite.

Chemical analysis of crystal mixture which is formed by minerals containing Ni, Co, As and Sb was obtained with X-ray microanalyzer.

Discussion of figures 40—47.

Backscattered electron image (composition) of polished block No. 47 from Častá is in Fig. 40. Ullmanite, chalcopyrite, gersdorffite, can be seen on specimen surface.

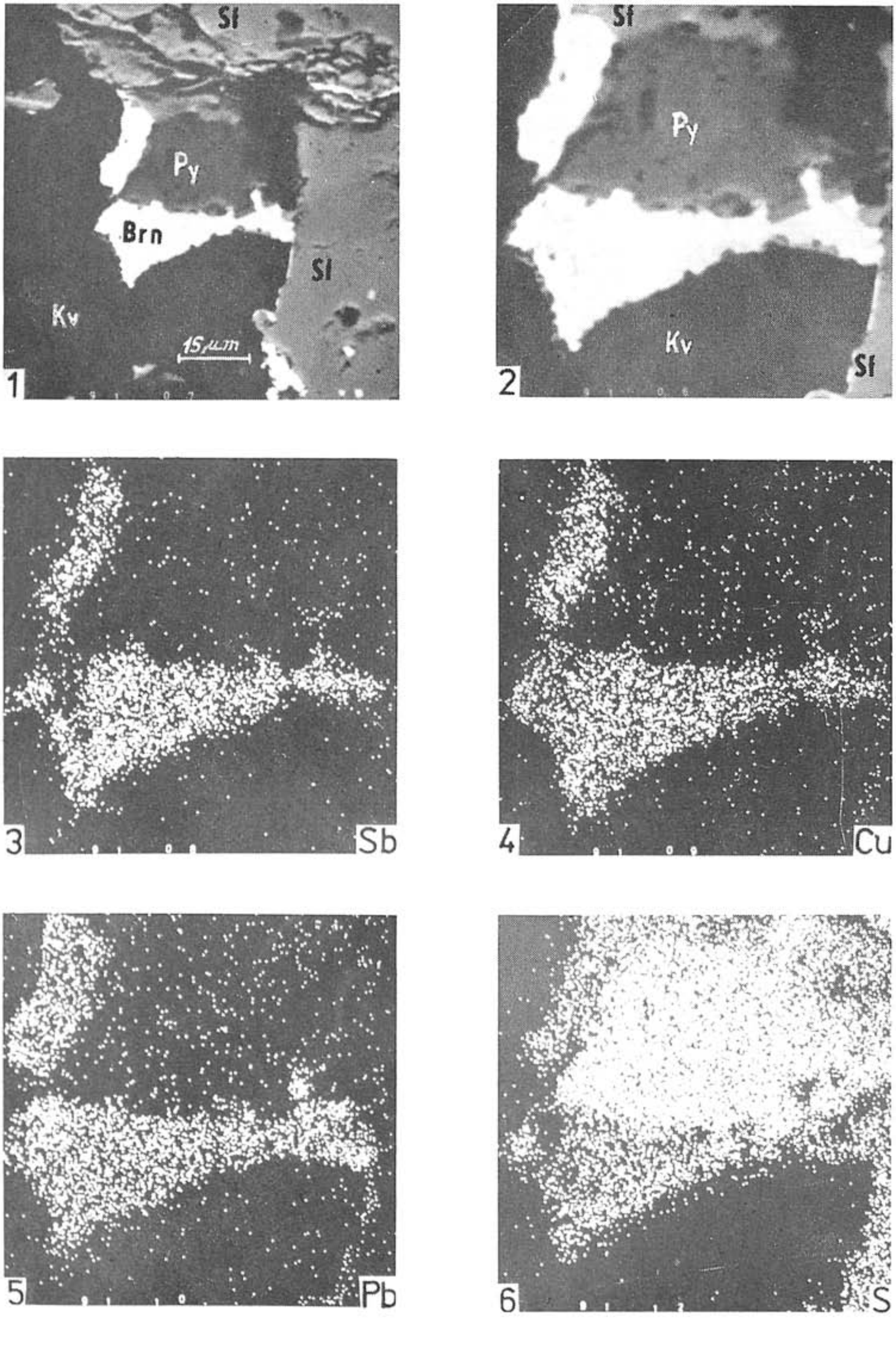
Ullmanite (NiSbS — bright phase, ulm) contains besides Sb also As (a small amount). The presence of ullmanite is confirmed also by quantitative analysis (tab. 5) and by Sb X-ray image in fig. 41. Chalcopyrite (dark grey phase chalk) is geometrically determined by Cu X-ray image (Fig. 46). Gersdorffite (a mineral from the crystal chemical group of cobaltite) can be found by means of As, Ni and Co X-ray image (Figs. 42, 45, 46). Gersdorffite contains also high concentrations of Ni and Co and lower concentration of Fe (Fig. 47). Co is present in the central part of Fig. 47 and absent in the right upper corner of the figure. In gersdorffite (dark grey-gers) isomorphous substitution between Sb and As can be observed (therefore higher content of Sb). The remaining part of the picture has been identified as Co-gersdorffite with variable content of Ni, Co and Fe. A zone structure can be observed on the piece where Co is inhomogeneously distributed. As it can be seen, the minerals are relatively homogeneous. Ullmanite-gersdorffite and ullmanite-cobaltite intergrowing can be deduced from the result of quantitative analysis of the upper grain (Fig. 40, tab. 6). Also the formation of Co-gersdorffite with variable content of Ni, Co, Fe and corynite with variable content of Sb, As, S can be explained by similar means.

The so called corynite structure as the consequence of ullmanite-gersdorffite intergrowing has not been observed (H. Gies 1971).

According to the results of spectrochemical analysis of Ni minerals from Častá it can be concluded that antimony originates from ullmanite (NiSbS), whereas As originates from gersdorffite. Corynite plays an outside role among Ni-Co minerals and it is not probably main source of Ni, Co, As and Sb elements in the association of Ni Co mineralization in Častá.

At the end we point out that a few bertierite specimens were analysed with X-ray microanalyzer. It was ascertained that stibnite can contain Fe up to 0.02 % as an isomorphous addition. Hg was analysed by atomic absorption in concentration range up to 10 ppm. Hg originates from the heterogeneous submicroinclusions of cinnabarite and metacinnabarite. Conclusions and discussions of minor elements (Fe, Hg etc.) in stibnite were already published in the paper by B. Cambel — J. Jarkovský — H. Gerthofferová, J. Krištín, — V. Streško (1976).

Translated by S. KOŠINA — J. KRIŠTÍN.


Sf
Py
Brn
Sf
Kv
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1
Sf
Py
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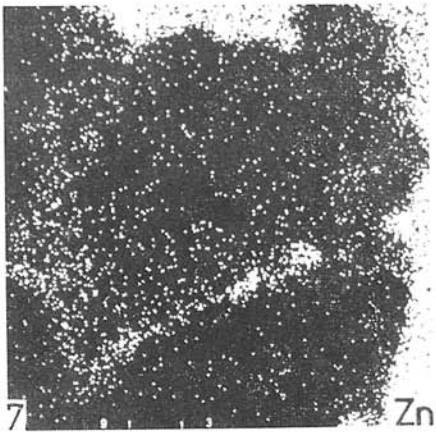
Pb
6
S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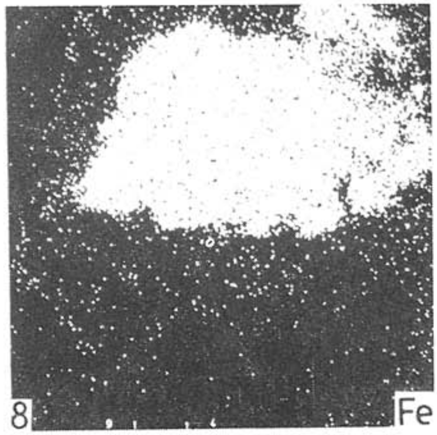
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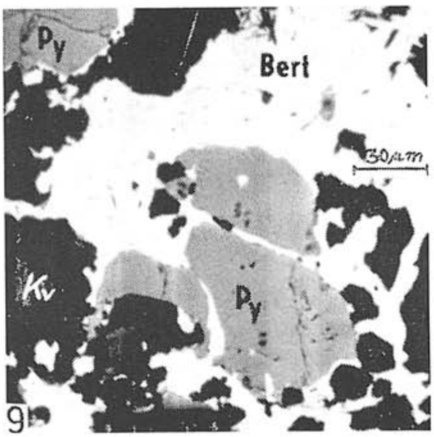
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Bert
30 µm
Kv
Py
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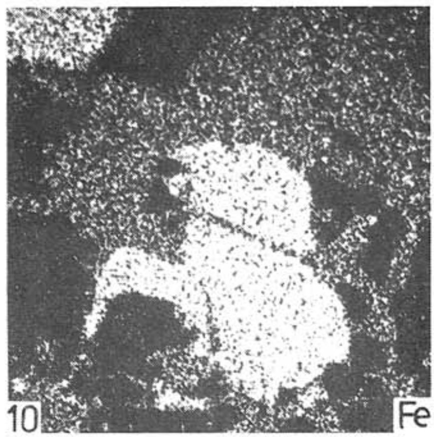
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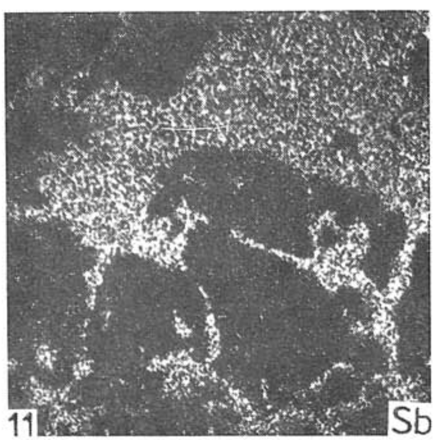
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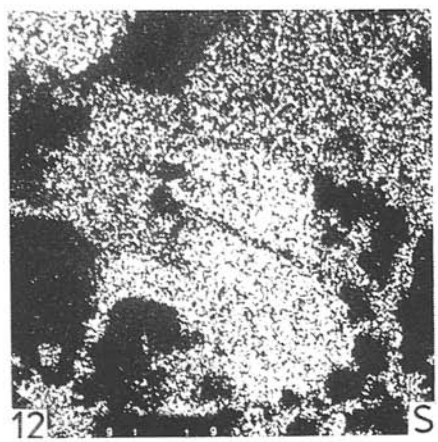
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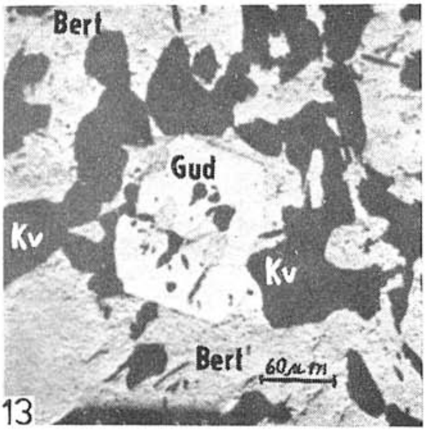
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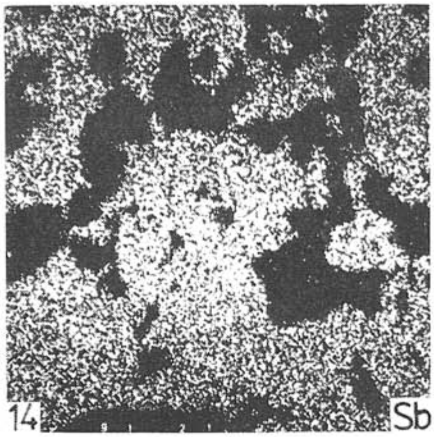
Gud
Kv
Kv
Bert'
60 μm
13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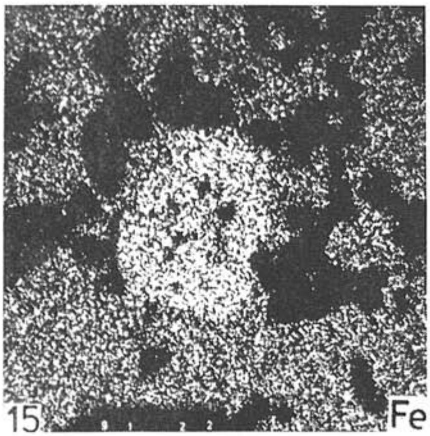
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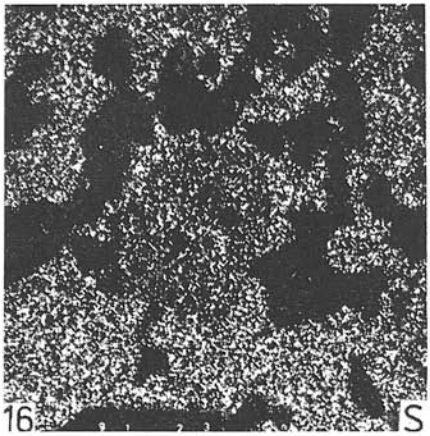
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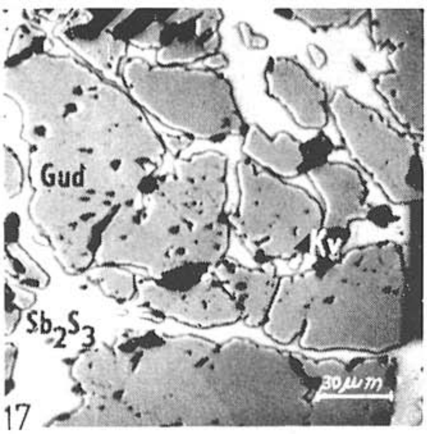
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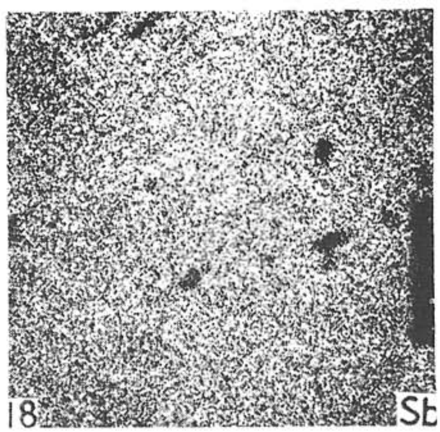
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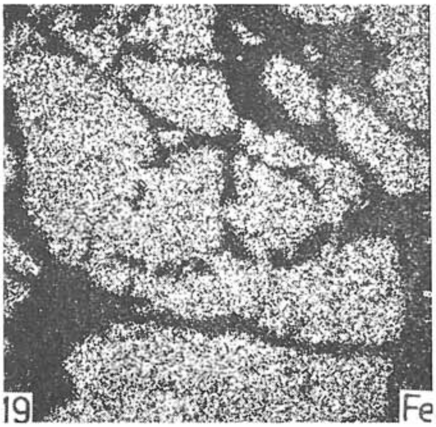
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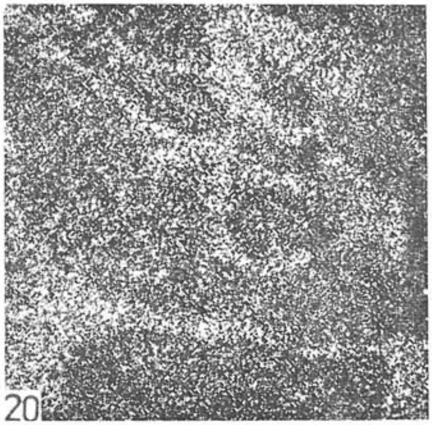
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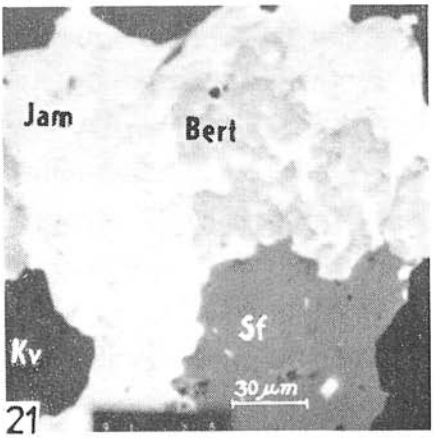
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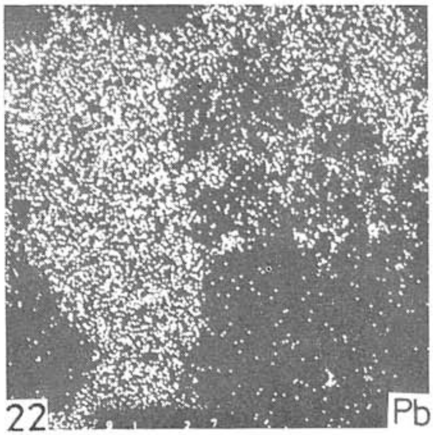
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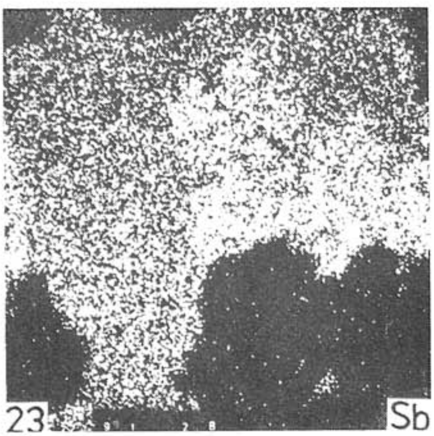
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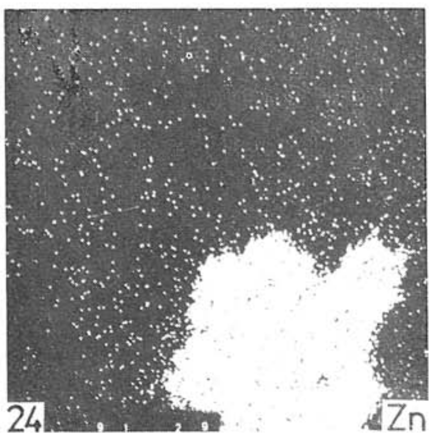
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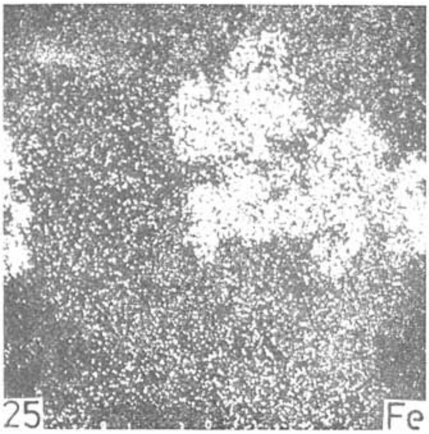
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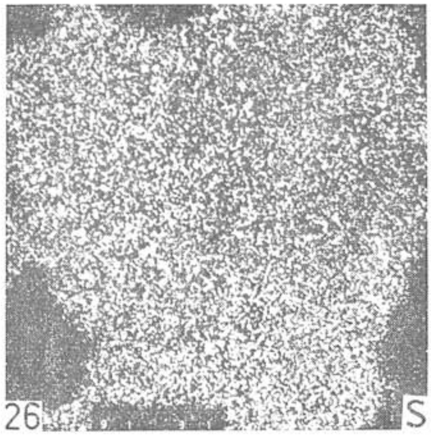
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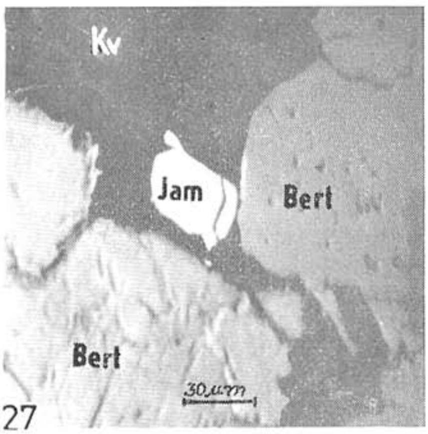
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Bert
Bert
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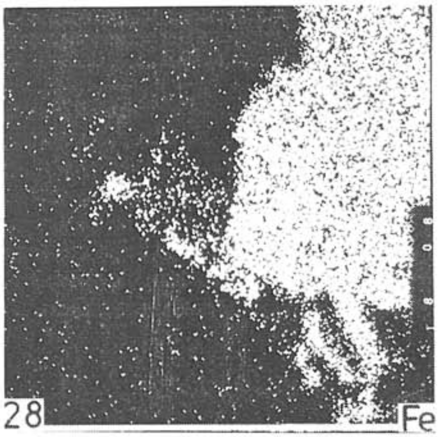
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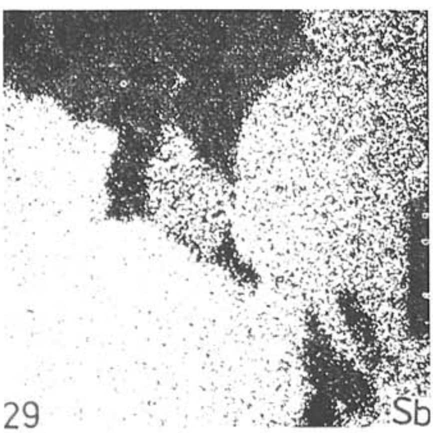
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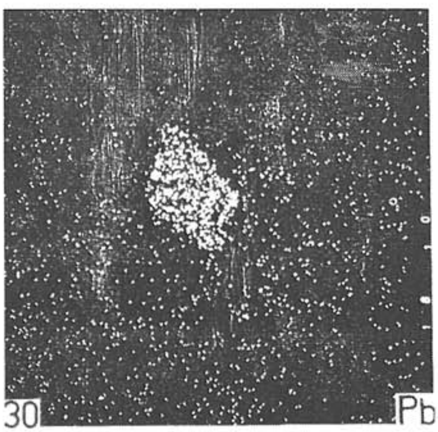
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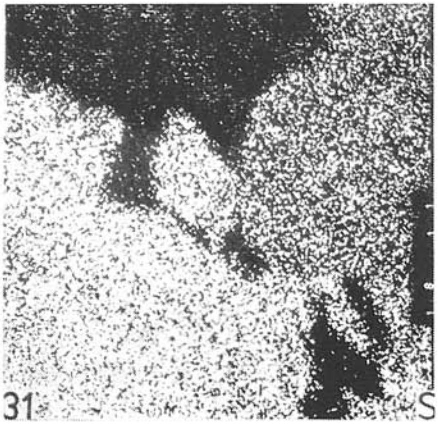
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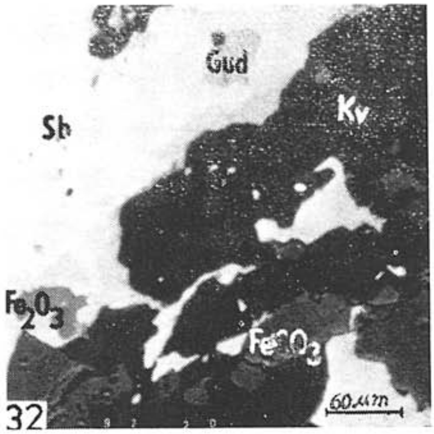
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Kv
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Fe2O3
60 µm
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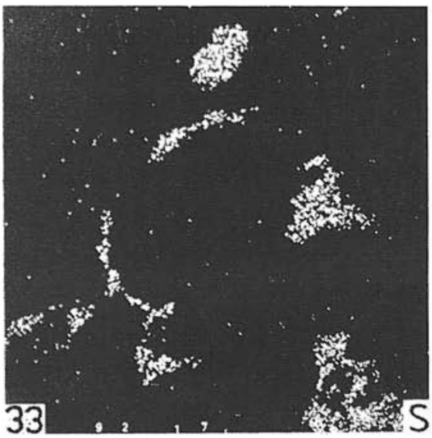
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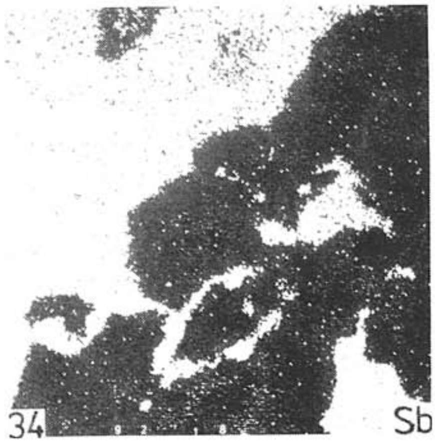
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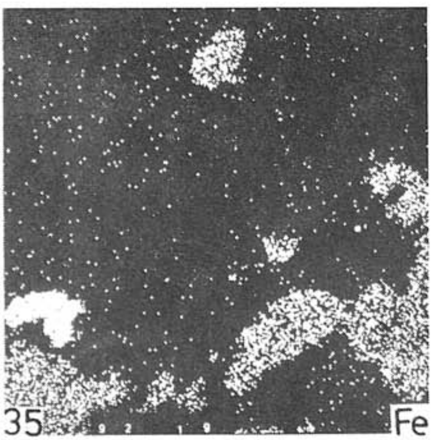
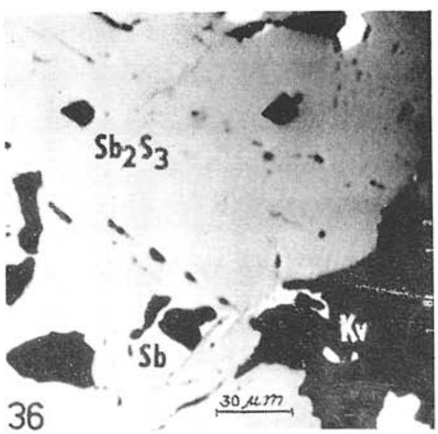
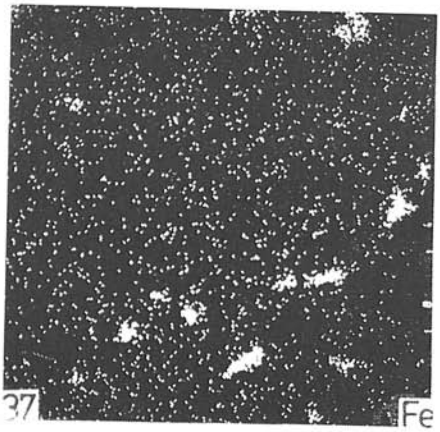
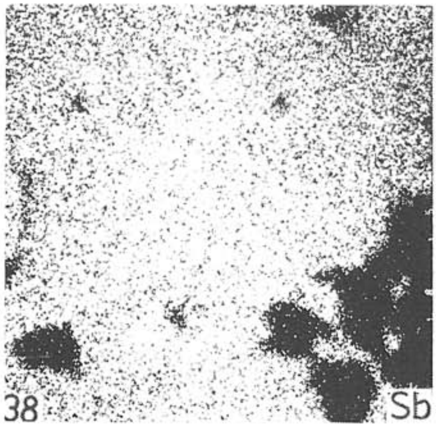
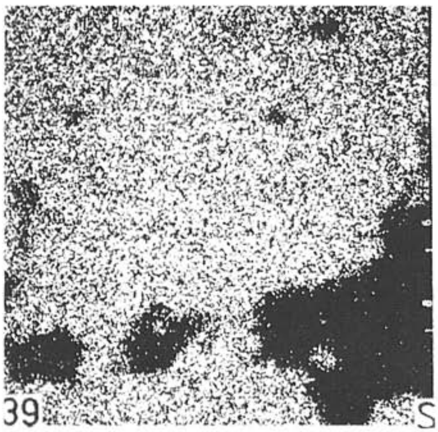
Sb

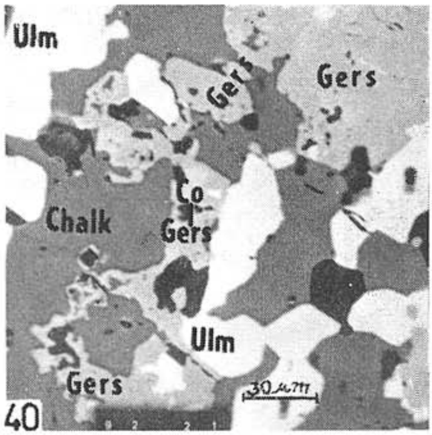

35
Fe

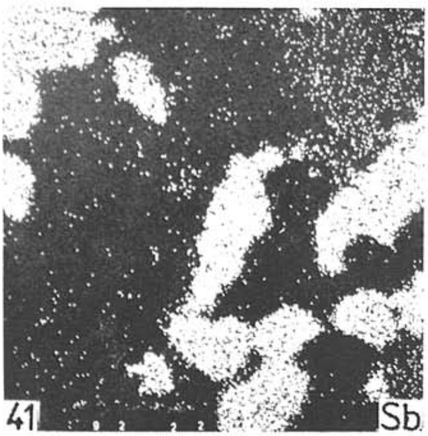

Sb2S3
Kv
Sb
30 µm
36

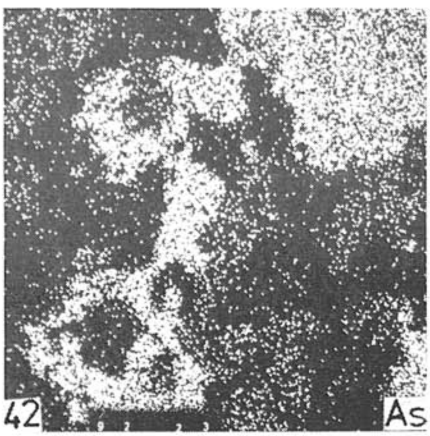

37
Fe

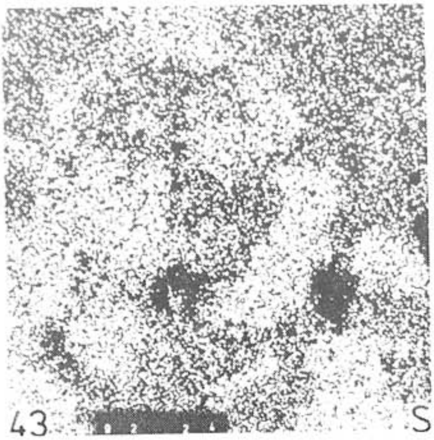

38
Sb

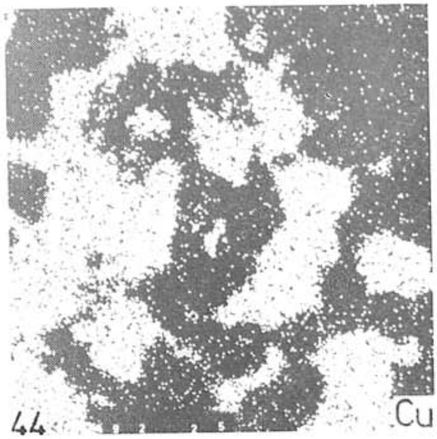

39
S

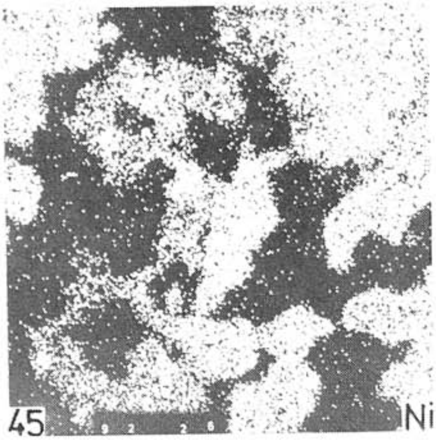

40
Ulm
Gers
Gers
Chalk
Co
Gers
Ulm
Gers
30 μm

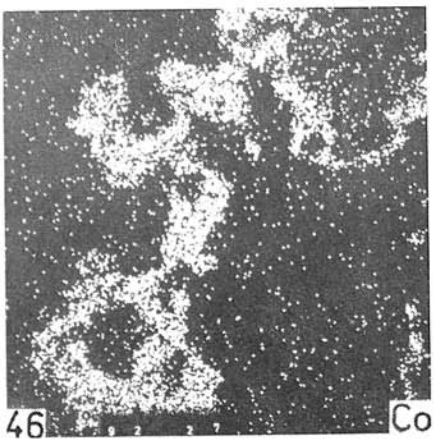

41
Sb

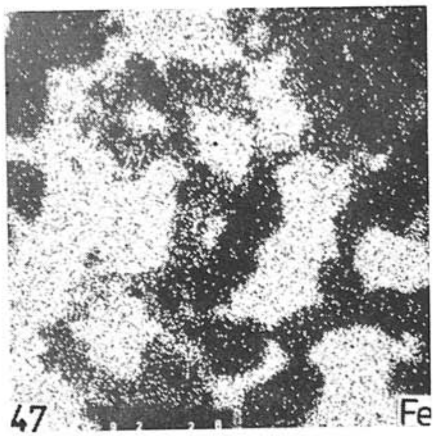

42
As


43
S


44
Cu


45
Ni


46
Co


47
Fe

On the Fig. 27 instead of Bert near of Jam have to be Sb_2S_3.

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