GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA, 36, 3, BRATISLAVA, JUNE 1985, Pp. 283—291

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CHEMICAL COMPOSITION AND MINERAL ASSOCIATIONS OF SULPHOSALTS IN THE PRECIOUS METAL DEPOSITS FROM DIFFERENT GEOLOGICAL ENVIRONMENTS

(Figs. 6)

Abstract: Chemical composition and assemblages of sulphosalts in ores of the gold and silver-gold deposits have been examined. Sulphosalts found in these deposits are fahl-ores, lead-copper and lead-silver sulphoantimonites and lead-silver-copper sulphobismuthites. Chemical composition of these minerals is correlated with the geochemical features of the deposits. Evolution in the mineral composition in time and space was observed.

Резюме: На примере золотых и золото-серебряных месторождений показаны особенности химизма и парагенезисов сульфосолей. Сульфосоли в них представлены минералами группы блеклых руд, сульфоантимонитами свинца и меди, свинца и серебра, сильфовисмутитами свинца, серебра и меди. Химический состав этих минералов коррелируется с геохимическими особенностями месторождений. В пределах месторождений установлена скрытая минералого-геохимическая зональность, причем эволюция химизма сульфосолей прослеживается в пространстве и во времени.

The precious metal deposits we have studied are located in different geological environments. The variation in mineral composition in the sulphide percentage, in the Ag/Au ratio of deposits, the differences in the structures of ores, the body morphology and the country rock alteration have been found. This lead to the assumption that they were formed in the wide range of the formation conditions.

The detail studies of the variations in chemical composition of minerals, the mineral assemblages and their depositional sequence and their distribution in the space are very important for an explanation of the precious metal deposit origin. The valuable information may provide the sulphosalt minerals, especially fahl-ore, sulphoantimonites and sulphobismuthites of Cu, Ag and Pb.

Although the sulphosalts rarely constitute significant ore masses these minerals deserve attention because, first, they have proved valuable sources of such elements as silver and bismuth; second, a complex crystal chemistry of sulphosalts may lead to an unusual range of composition (for example, fahl-ore) or an appearence of series of mineral species of the same constituents (for example, the aikinite-bismuthinite and lillianite homologous series), and these give a possibility to recognize the variation in the sulphosalt composition in space and time (the hidden mineral-geochemical zonality), and, third, the numerous experimental studies of the sulphide systems involving the sulphosalt minerals provide the basis for understanding of physical and chemical conditions of the mineral deposition during the late ore formation stage.

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The problem of using of the sulphosalt minerals as the indicators of the mineral formation has been considered by E. A. Radkevich, E. K. Lazarenko, M. S. Sakharova, N. N. Mozgova, P. Barton-Jr, B. J. Skinner, J. Craig. This investigation is a further development of the idea the above-mentioned authors on the typomorphic significance of sulphosalts.

We have studied in detail the sulphosalt in gold, silver-gold and silver-lead--zinc deposits, located at shallow and medium depths in various geological environments in different regions of the U.S.S.R. (Middle Asia, Transbaikalian, North-East Territory). The most detail information we have obtained on chemical composition and mineral assemblages of sulphosalts from the near surface deposits in Late Paleozoic volcanic-plutonogenic belt Tien Shan (Middle Asia) and Mesozoic—Kainozoic volcanogenic Okhotsk—Chukotsk belt (North-East Territory of the U.S.S.R.). Numerous data have been obtained on minerals from the near surface deposits of early Jurassic age located within continental terrigenous sediments in a tectonic depression in a basement of a volcanic structure (Transbaikalian). Same results of studies of sulphosalts from a medium depth gold deposit located within a large tectonic block of gabbro and hybridic rocks (Transbaikalian) have been discussed as well. Our conclusions are based on more than 600 microprobe analyses performed by Drs Troneva, Tsepin and Ing. Malov and more than 400 microprobe data published by Drs Mozgova, Tsepin, Bermann, Sandomirskaya and others.

The Tien-Shan gold-silver and silver-lead-zinc deposits related to the Upper Paleozoic volcanic structures are within different structural-lithological unit of the Hercynian structural story, which is the inside continental area of the postorogenic activity. The gold deposits are located in the lower structural-lithological unit (the basement of volcanic structure), which is made up of the metamorphic schists of the Ordovician—Silurian age, the intrusive and subvolcanis bodies of granodiorite-porphyries, diorite-porphyrites. The quartz-gold--sulphide fracture-filled veins occur in granodiorite-porphyry massive. The gold with silver and gold-silver mineralization is found to associate with the volcanic rocks of andesite-dacite series of the Medium—Upper Carbonic age which compose the medium structural-lithological unit. The silver-polymetallic mineralization is in upper structural-lithological unit which consists of the acid volcanic rocks of C_3-P_1.

Although there are the obvious differences in the geological position of the studied deposits, all occurrences possess some common features showing genetical relation of these ores. It should be stressed that the deposits studied have the nearly same age of a formation (260—285 m.y.) and percentage of sulphides (5—25 %) in the quartz veins, the similar wall rock alteration is typical of these deposits. The resemblance in mineral composition of ores and their depositional sequence were found as well. The principal ore minerals are pyrite and fahl-ores, the minor constituents are chalcopyrite, galena, sphalerite, tellurides and selenides, the copper-tin sulphide and sulphobismuthites and sulphoantimonites of copper, lead and silver. However, some differences in mineralogy of the deposits have been observed. The typical minerals in the gold ores from lower unit are enargite and luzonite and bismuth sulphosalts — micharaite and aikinite. The silver-bearing gold mineralization from the medium unit contains native bismuth, the bismuth sulphoselenides, the selenium-bearing copper-bismuth sulphosalts, tellurides, sulphobismuthites and sulphoantimonites of copper, silver and lead are more common in the gold-silver ores. Native silver, sulphides and sulphoantimonites of silver, silver and copper are widespread in the silver-polymetallic in the upper lithological unit. In general, the main ore elements in the deposits are gold, silver, copper, antimony, bismuth, tellur, selenium, tin.

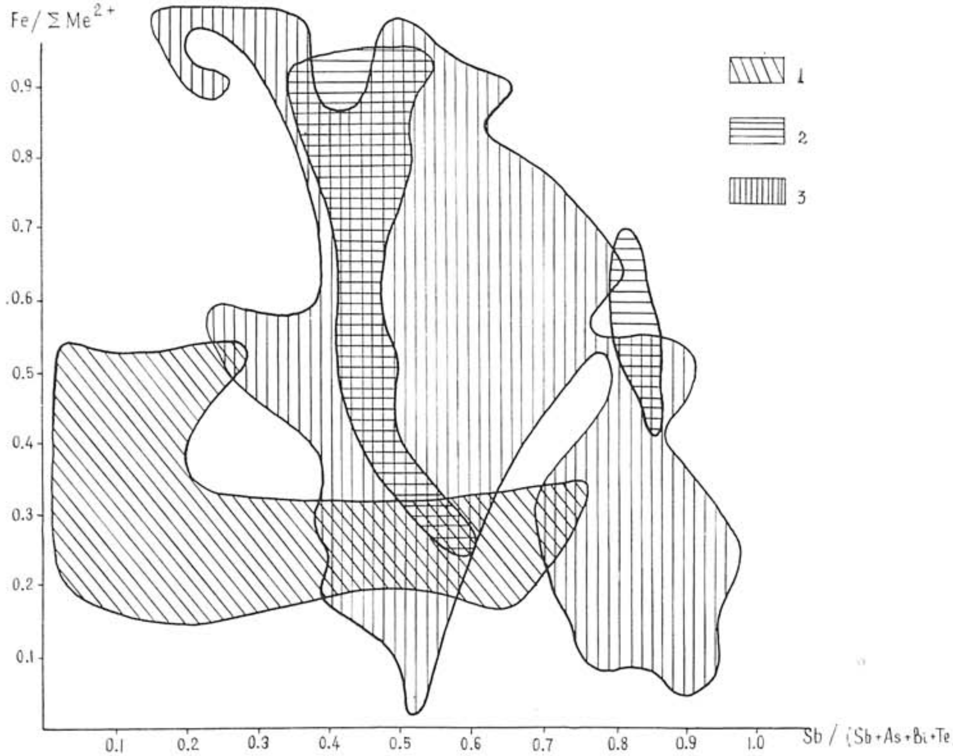

Fig. 1. The variation of the $Fe/\Sigma Me^{2+}$ ratio and $Sb/\Sigma\, Sb + As + Bi + Te$ ratio in fahl-ore in the gold deposits from Middle Asia.
Explanations: 1 — a gold mineralization in the bottom structural-lithological unit; 2 — silver-bearing gold mineralization from the medium structural-lithological unit; 3 — silver-gold mineralization from upper structural-lithological unit.

There are some differences between the gold mineralization described above and the Mesozoic—Kainozoic gold-silver ores from North-East Territory and Transbaikalian. The latter are more poor in the sulphide contents (< 1—3 %). The silver minerals (sulphides, selenides, sulphoantimonites) are widespread in the deposits from these regions, but the bismuth-bearing minerals were not found. The geochemical features are the prevalence of selenium over tellurium and the high concentration of selenium and silver.

An examination of the fahl-ore chemical composition revealed the differences in these minerals from the different deposits. The principal variations in the composition are the change of the $Fe/\sum Me^{2+}$ ratio and $Sb/\sum Sb+As+Bi+Te$ ratio.

Fig. 1 shows that arsenic prevails over antimony and zinc prevails over iron in fahl-ore from the gold deposits in the lower structural-lithological

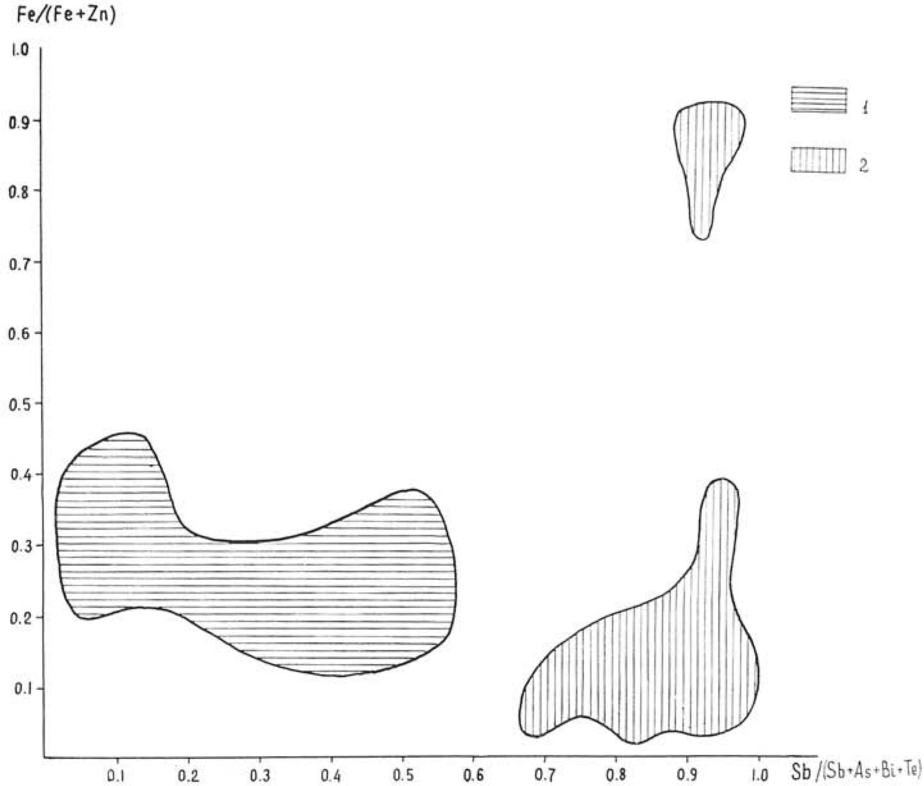

Fig. 2. The variation of the Fe/(Fe + Zn) ratio and Sb/(Sb + As + Bi + Te) ratio in fahl-ore from the silver-polymetallic deposits (Middle Asia).
Explanations: 1 — earlier generations; 2 — young generations.

unit within the Hercynian volcanogenic belt (Middle Asia). Fahl-ores in the deposits in the middle structural unit from Middle Asia exhibit the wide iron and zinc content variation (from pure iron to pure zinc member). The antimony-arsenic ratio shows that there are two narrow compositional fields: earlier fahl-ore contains 40—60 tetrahedrite component and later generation is tetrahedrite with the low arsenic content and Fe/Me^{2+} ratio equals to 0.4—0.7. Fahl-ore from the gold-silver deposits in this structural unit is tetrahedrite.

Iron and zinc contents vary considerably in this mineral. The antimony and zinc concentrations increase from an earlier to a later generation. Fig. 2 shows that the antimony content in fahl-ore in the silver deposits also increases from earlier to the later generation, but iron and zinc exhibit a different behaviour: the silver-poor generation is richer in zinc, whereas the silver-rich one is richer in iron.

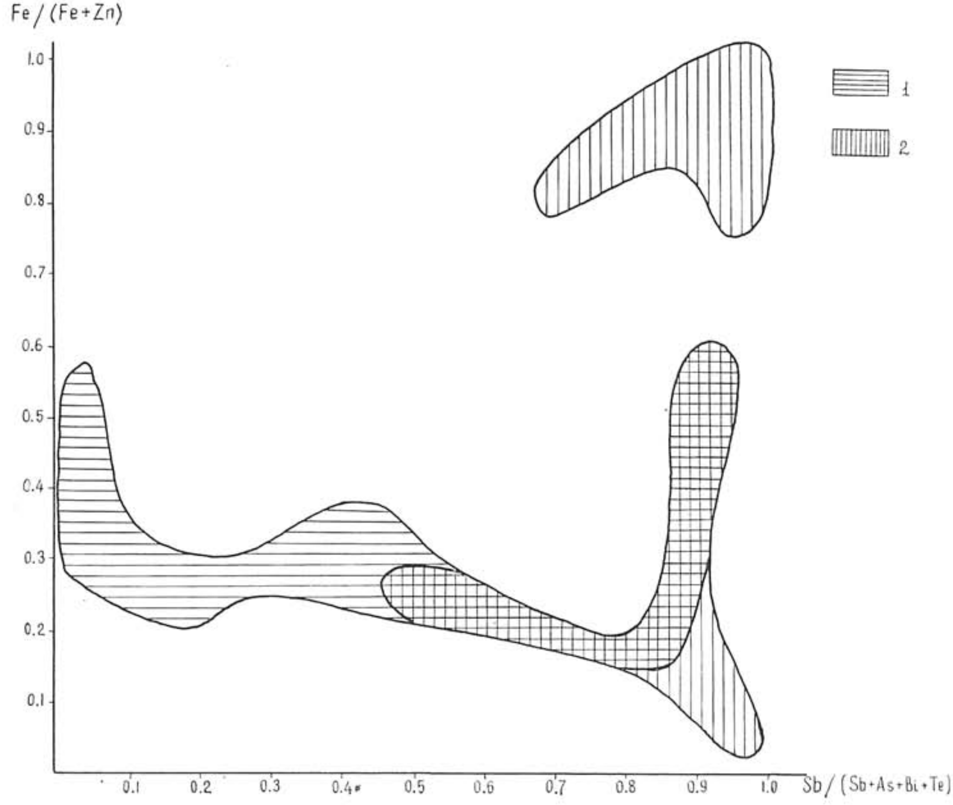

Fig. 3. The variation of the Fe/(Fe + Zn) ratio and Sb/(Sb + As + Bi + Te) ratio in fahl-ore from the deposits in the North-East territory of the USSR.
Explanations: 1 — silver-bearing gold mineralization; 2 — silver-gold mineralization.

Fahl-ore from the gold-silver deposits in the North-East of the USSR has the same features. Fig. 3 shows that the antimony content increases from the earlier generation to later one: zinc prevails over iron in silver-poor fahl-ore and iron predominates over zinc in silver-rich varieties. The same features are typical of fahl-ore from the Transbaikal deposits (Fig. 4). However, their composition is in the tetrahedrite range (65—95 per cent of tetrahedrite component). This resembles the As/Sb ratio in fahl-ore from the gold-silver deposits of Middle Asia.

Thus, fahl-ores in the gold-silver deposits, occurring in volcanogenic belts of different ages, exhibit common features: 1) they display wide variation in the iron and zinc, antimony and arsenic contents, and 2) as a rule, the tetrahedrite component and zinc content in the mineral increase from the earlier generation to the later one. Iron prevails over zinc only in the silver-rich varieties. It should be noted that tennantite is more common in the gold deposits, whereas tetrahedrite predominates in the silver-gold deposits.

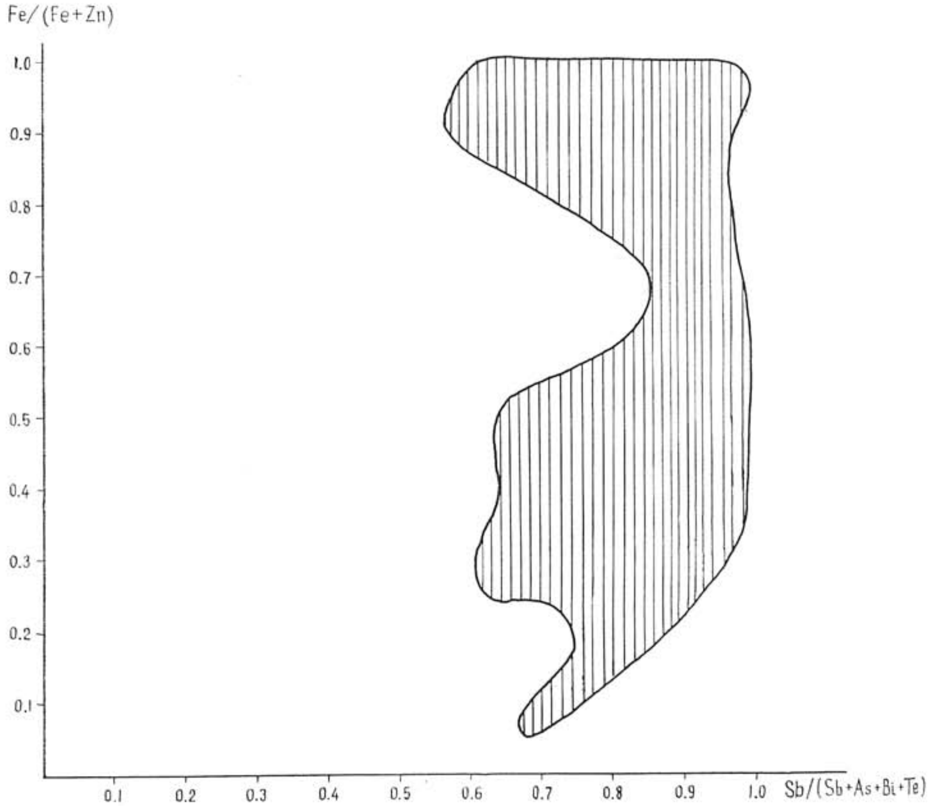

Fig. 4. The variation of the Fe/(Fe + Zn) ratio in fahl-ore in a gold-silver deposit from Transbaikalian.

Now we would like to consider the behaviour of silver in fahl-ore from the above-mentioned ore deposits. Fig. 5 presents the results of the statistical treatment of the microprobe data for fahl-ore in the studied deposits. The left-asymmetrical one-mode distribution curves of silver were revealed for fahl-ore in deposits from Middle Asia: the maximum of a silver content in this mineral in the gold deposits occurs in the range of 0—0.2 wt. percent; this value for the mineral in the silver-gold deposits lies in the 0.2—5 wt. percent. On the contrary, a bimodal silver distribution with two distinct peaks in the 1—5 wt.

percent and 20—25 wt. percent silver range, corresponding, respectively, to earlier arsenic-rich and late antimony-rich generations was found. Multi-modal silver distribution curves for silver-rich fahl-ores in the young deposits of the North-East and Transbaikal provinces were recognized. In this case, there is a correlation between the silver content in tetrahedrite and in ores. Fahl-ore in the gold- and silver-bearing deposits of the Upper Paleozoic—Mesozoic terrigenous formation (Yakutia) are closely similar in their chemical features. The

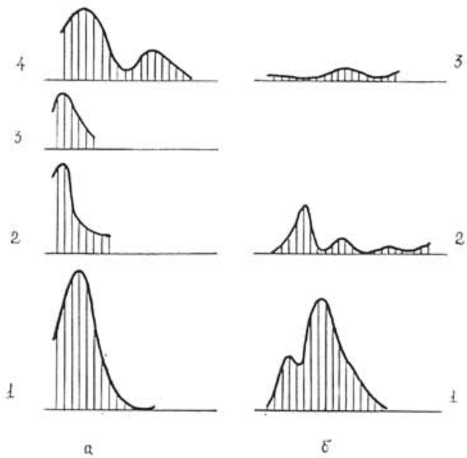

Fig. 5. Histograms of the silver-bearing fahl-ores.
Explanations: a) the deposits of Middle Asia (1 — gold mineralization; 2 — silver--bearing gold ores; 3 — gold-silver mineralization, 4 — silver-polymetallic mineralizaton); b) the Transbaikalian deposits (1) and the North-East territory of the USSR.

earlier generations of fahl-ore are the silver-poor intermediate tennantite-tetrahedrite, whereas the later generation is enriched in silver and tetrahedrite molecules. These data allow to make following conclusions: 1) the mean (statistical) silver content in fahl-ore increases in the sequence gold ores — silver--gold — silver deposits, and from deposits of ancient volcanogenic regions to younger deposits; 2) within each type of deposits the silver content in fahl-ore increases from earlier to the later generations, this enrichment in silver is correlated with the increase in tetrahedrite component in mineral.

A remarkable fact was recognized for the Late Paleozoic deposits of Middle Asia. Fahl-ore in the gold and silver-gold deposits contains considerable amounts of tellurium and bismuth, whereas those in the silver-lead-zinc deposits are enriched in bismuth and lead.

Fig. 6 shows the chemical composition of fahl-ore in these deposits. The tennantite-anyvite series was found in the gold deposits; the member of tennantite-tetrahedrite-goldfieldite-anyvite series were discovered in the gold-silver deposits of the middle structural unit; minerals of the tetrahedrite-goldfieldite series are present in the silver-gold deposits of the same structural unit. The total silver content in the deposits increases in the same sequence. Thus, the typical element of the gold deposits are arsenic and bismuth, and those of the gold-silver deposits are antimony and tellurium. This is in good agreement with the bulk chemical composition of the ore deposits, where a stable correlation has been observed between bismuth and arsenic, bismuth-tellurium-arsenic-antimony, and tellurium and antimony. It is of interest that admixture of selenium (up to 0.8 wt. percent) in fahl-ore in deposits containing sulphoselenides and selenide-sulphosalts has been recognized; the widespread minerals in deposits containing minerals of the goldfieldite series are tellurides. In those deposits of this region where tin-bearing minerals are present, the tin admixture (up to 2 wt. percent) in fahl-ore was found. These data clearly indicate that the chemical composition of fahl-ore may reflect the chemical features of the ore deposits, and may serve as an ore evaluation criterion in metallic mineral deposits.

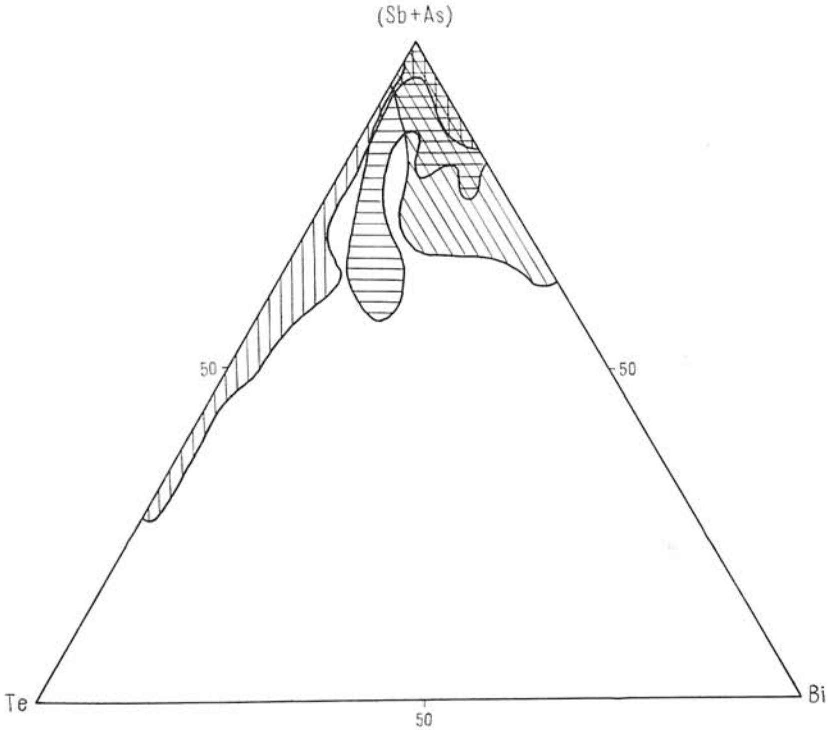

Fig. 6. The variation of the semimetal contents in fahl-ore in the deposits of Middle Asia.
Explanations are those that in Fig. 1.

It is of interest to give several examples concerning the zonal distribution of sulphosalts. The sulphosalt assembleges in the gold deposits of the middle structural unit include selenium-bearing bismuthinite, emplectite, hodrushite and cuprobismuthite.

The same mineral assemblages occur in the upper horizons of the gold-silver deposits of the middle structural level. However, in the deeper horizons the Pb-Cu-Bi-sulphosalts appear, they are replaced at deeper depth by berryite and minerals of the lillianite series. The most widespread sulphoantimonite in the upper horizons is chalcostibite, in lower horizons it is replaced by bournonite in association with less common plagionite and heteromorphite.

Thus, these data indicate that the role of copper, silver, lead and iron increases in the sulphobismuthites from the upper horizons downward in the section. A somewhat different zonality in the distribution of the antimony sulphosalts has been observed: the silver sulphoantimonites are abundant in the upper horizons, whereas the copper and lead sulphoantimonites occur in the deeper horizons.

In the volcanogenic deposits of the North-East and Transbaikal region selenium bearing sulphoantimonites are more common. They were found in association with the silver selenides. The sulphosalts found in the quartz-sulphide veins in the gold deposits in the metamorphosed gabbro and granite rock massive are bournonite, boulangerite, jamesonite, zinckenite and less common semseyite and plagionite. The sulphobismuthites in these deposits are lillianite, cosalite and galenobismuthite and kobellite is widespread here. The characteristic feature of the sulphobismuthites in the Transbaikal deposits is the high content of antimony, the sulphoantimonites contain the admixture of bismuth. Unfortunately, it is impossible to explain the differences in the sulphosalt associations found in the deposits from different geological environments. However, we believe that the sulphosalt ores were deposited under different physical and chemical conditions: at various temperatures and the sulphur activity. We think that the antimony-bismuth sulphosalts were formed at the highest temperature of 270—425 °C. The Cu-Pb-Bi sulphosalts in the Middle Asia deposits were deposited below 250 °C. The formation temperatures of the sulphosalt association in gold and silver-lead-zinc deposits in terrigenous formations are 180—300 °C.

We understand that the data we have presented here are not as yet sufficiently precise to clarify the factors responsible for differences in sulphosalt assemblages and the variation in their chemical composition. However, we believe that our study has demonstrated the importance of the information on sulphosalt chemistry for understanding the evolution of certain physical and chemical parameters of the hydrothermal solution with respect time and space. We hope these data can serve as a guide in prospecting and exploring of precious metal deposits.

Acknowledgements: The authors would like to thank Dr. A. D. Genkin and Prof. T. N. Shadlun for their valuable remarks and advice.

Manuscript received November 26, 1984

The authors are responsible for language correctness and content.