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SULPHUR ISOTOPES AT THE SMOLNIK AND MNIŠEK NAD HNILCOM SULPHIDE DEPOSITS OF THE CAMBRO-SILURIAN SERIES, SPIŠ-GEMER ORE Mts, CZECHOSLOVAKIA

(Figs. 1—42)

Abstract: The Cambro-Silurian series of the Spišsko-gemerské rudohorie Mts contains: a) hydrothermal quartz-siderit-sulphide veins, b) disseminated to massive pyrite and pyrite-polymetallic deposits.

Microscopic examinations of the later type were carried out and sulphur isotope distribution studied.

The mineralization is confined to a sedimentary- volcanogenic complex. Porphyroids mostly water-laid, metamorphosed tuffs, tuffites, lavas, prevail. They are associated with more basic types: up to diabase, their metamorphosed pyroclastics — chlorite schists. Intercalations of products of acide and basic volcanism occur.

Colloidal textures are abundant in the massive ores. Deformation, recrystallization and remobilization phenomena are common.

Disseminated pyrite ores occur mainly in chlorite schists. The range of sulphur isotope ratios is very narrow (21,86 to 21,95), indicative of well homogenized source.

Owing to considerable enrichment in the heavy sulphur isotope, digestion of sulphate-rich sediments by the granitization processes, by which the source was formed, is postulated.

The massive ores display slightly higher ratios (21,98 to 22,09), the range being sharp too. Bacterial activity might have in certain parts and to very limited extend only, modified the distribution of sulphur isotopes.

The principal distribution was governed by the magmatic (granitization) source and the evolution of sulphur isotopes within. Slight enrichment in S^{32} as well as in Cu-Pb-Zn contents with time seems to be characteristic. This enrichment reached its maximum during formation of polymetallic ores in Mnišek nad Hnilcom.

The disseminated and massive ores are of exhalative-sedimentary origin, derived from submarine springs of magmatic hydrothermal solutions.

Mobilization into thin veinlets during hercynian and alpine movements was common. The mobile Cu-Pb-Zn minerals were preferentially concentrated in young veinlets. The sulphur is lighter than in disseminated ores and displays wider ranges in isotope ratios. For recrystallization of syngenetic ores decrepitation-temperatures of 200—250 °C were measured. The thermality in veinlets ranges 80—200 °C.

With decreasing thermality of sulphide an increase in S^{32} contents was found.

Fractionation of sulphur isotopes between coexisting sulphides is always present.

Two tendencies seem to be indicated by the distribution of sulphur isotopes in metamorph-mobilized veinlets: 1. General increase in S^{32} with respect to the primary, exhalative-sedimentary mineralization. 2. Fractionation during precipitation which results in an increase in S^{32} in coexisting minerals according to mineral species, from pyrite, carrying the heaviest S, through chalcopyrite, sphalerite, tetrahedrite to galena, characterized by the lightest sulphur.

Deposits of similar geological setting, mineralogy and distribution of sulphur isotopes were described from the Bathurst-Newcastle area, Canada by E. Dechow and W. N. Tupper.

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Резюме: Кембрийско-силурийские серии Спишско-гемерского рудогорья содержат: а) гидротермальные кварц-сидеритово-сульфидные жилы б) вкрапленные до массивных пиритовые и пирит-полиметаллические месторождения.

После ний тип был микроскопически изучен и было исследовано распределение изотопов серы.

Минерализация приурочена к осадочно-вулканическим комплексам.

Коллоидные текстусы многочисленны в массивных рудах. Вкрапления пиритовая руда находится главным образом в хлоритовых сланцах.

Очень узкие пределы соотношений изотопов серы (21,86 до 21,95) свидетельствуют о хорошей гомогенизации серы.

Массивные руды имеют немного высшие пределы соотношений (21,98 до 22,00). Бактериальная активность могла в определенных частях и только в ограниченных пределах модифицировать распространение изотопов серы.

Слабое обогащение S^{32} как и содержание Cu-Pb-Zn является характерным в зависимости от времени. Обогащение достигает максимума во время образования полиметаллических руд в Мнишке над Гнилцом.

Вкрапленные и массивные руды являются рудами эксглационно-осадочного происхождения.

Образование тонких жилок во время герцинского и альпийского горообразования было обычным явлением. Cu-Pb-Zn минералы концентрировались главнымным образом в молодых жилках. Сера имеет здесь более широкие пределы соотношения изотопов. Докрипитационная темпоратура для рекристаллизации сингенетических руд была 200—250 °C. Термальность жилок была 80—200 °C.

При снижении термальности сульфидов было замечено повышенное содержание S^{32}.

При распределении изотопов серы в метаморфических жилах было замечено две тенденции: 1. Обшее повышенное содержание S^{32} в связи с первичной эксгаляционно-осадочной минерализацей; 2. Распределение во время осаждения выражается в результате повышенным содержанием S^{32} в минералогических комплексах согласно их видам, от пирита, несущего самую тяжелую серу, через халькопирит, сфалерит, тетраэдрит до галенита, характеризованного самой легкой серой. Месторождения с подобной геологией, минералогией и распределением изотопов серы были описаны в Канаде, район Батгурст-Ньюкастл Е. Дешовым и В. Н. Таппером.

Introduction

The sulphide deposits of Smolník (Schmöllnitz) and Mníšek nad Hnilcom are situated in the central part of the Spišsko-gemerské rudohorie Mts (Spiš-Gemer Ore Mts.), the most important metallogenetic zone of West Carpathian.

Mining at the Smolník field dates back at least to the 13th century. Copper with some silver were the main object of mining and in the 18—19th centuries, Smolník was one of the largest Europ's producer of Cu. Since 1870 pyrite is the main object of activity, copper being recovered as by-product.

The mines near Mníšek nad Hnilcom were operated on a much smaller scale. Recently they were reopened and the area explored by the Geologický prieskum (Geological exploration).

As for similar deposits in Spain, Germany, Norway, Sweden, a. s. o., many attempts have been made since the last century to explain the genetical conditions of this remarkable mineralization.

Modern isotopic investigations were applied only recently. A syngenetic origin was postulated as the only plausible with the isotopic constitution of common lead (J. Kantor 1962, J. Kantor, M. Rybár 1964).

The aim of the present paper is to discuss the genetic aspects of the mineralization. The conclusions reached are based mainly on sulphur isotopes and detailed mineralogical investigation.

OUTLINE OF GEOLOGY

The ore deposits of Smolník and Mníšek nad Hnilcom occur in an area built by the Gelnica series (Cambro-Silurian series of O. Fusán, M. Máška, V. Zoubek 1955).

It consists of mighty complexes of sediments, which contain in their central part large masses of prevailingly siliceous volcanogenic material. A flyschoid sedimentation is characteristic for the bulk of the series. which resulted in alternating deposition of shales and sandstones and a considerable thickness (3—5 km) of the series.

With the exception of the border zones (N, S), the Spiš-Gemer Ore Mts. consist almost exclusively of epimetamorphosed rocks of the Gelnica series. They are host rocks to various mineralizations of epigenetic, magmatogene-hydrothermal and to lesser extent of syngenetic origin.

The rough subdivision of the series into the basal, detritic. middle-volcanogenic. and upper-organogenic complexes as proposed by O. Fusán (O. Fusán, M. Máška. V. Zoubek 1955) is still valid.

The lowest part of the Gelnica series is a flyshoid complex consisting of arenaceous sericite-chlorite schists (phyllites), which rhytmically alternate with sandstones and quartzites. They are overlain by similar sediments containing lyddite beds and sparse quartz porphyry lavas and pyroclastics. All these rocks are typically exposed in the W part of the Spiš-Gemer Ore Mts (Vlachovo beds L. Snopko 1957).

The middle part of the Gelnica series is formed by a sedimentary-volcanogenic complex. The sediments are prevailingly sericite-chlorite schists, sandstones and quartzites. They alternate with volcanogenic, metamorphosed rocks which include subaqueous lavas of quartz porphyries. quartz felspar porphyries, locally keratophyre and diabases and their pyroclastics. Both, vertically and laterally. transitions between the volcanogenic and sedimentary rocks are observed.

In fine-grained tuffites, the presence of volcanic ash may be veiled by later metamorphism and the rock may acquire the appearence of quartz-sericite schists in the case of siliceous extrusives, or that of chlorite schists, when more basic material was present.

For the middle part of the Gelnica series the term Pača beds was proposed by O. Fusán.

The upper part of the Gelnica series is less detritical than the preceeding ones. Dark phyllites, graphite schists dominate. Subordinate sericite, chlorite schists (sometimes arenaceous) occur. Typical reprezentants are dark lyddites and lenses of light, crystalline limestones. Thick limestone lenses are developed in the W part of the Spiš-Gemer Ore Mts, whereas their dimensions diminuish eastwards-to the surroundings of Smolník and Mníšek.

During the sedimentation of the organogenic complex a basic, submarine volcanism was active (diabases, tuffs, tuffites). It's intensity was considerably lower than that of the porphyries.

This upper part of the Cambro-Silurian (Gelnica) series termed Betliar beds (L. Snopko 1957) attains thicknesses of 200—500 m.

As no fossils were known, the Cambro-Silurian age of the Gelnica series was supposed from analogy with the Eastern Alps. In 1962 P. Snopková has determined the Cambrian age of the lowest part of the Gelnica series (Vlachovo beds) by spores. The lowest and the middle part of the Gelnica series therefore probably correspond to the Cambrian-Ordovician and the Betliar beds to the Silurian.

The Gelnica series is discordantly overlain by a complex of phyllites and diabases (Phyllite-Diabase, or Rakovec-series) of Devonian age.

Smolník Area

Geological Setting

The pyrite-bearing complex of Smolník has as it's northern boundary the volcanogenic rocks (quartz porphyries, quartz felspar porphyries, their pyroclastics) of the Pača-beds. In the South it is discordantly overlain by phyllites and diabases of Devonian age (Fig. 1, page XX).

The geology and the ore deposits were recently studied mainly by J. Ilavský (1956, 1960, 1964), J. Ilavský, J. Mrozek (1960) et all.

According to J. Ilavský the oldest rocks of the area are porphyroids which by gradual transitions developed into a flyshoid complex consisting of sericite-chlorite phyllites alternating with sandstones and quartzites. Tuffites of quartz porphyries are intercalated, too.

The productive zone is an E—W trending complex of predominantely dark schists (graphite, graphite-sericite phyllites), which gradually developed from the underlying flyshoid beds and are intercalated by lyddites. In it's upper part chlorite schists appear as metamorphic products of a basic volcanism. They alternate with dark phyllites, lyddites and sparse carbonates and are host rocks of the economic pyrite mineralization.

Smaller gabbrodiorite bodies were from the deposit for the first time described by

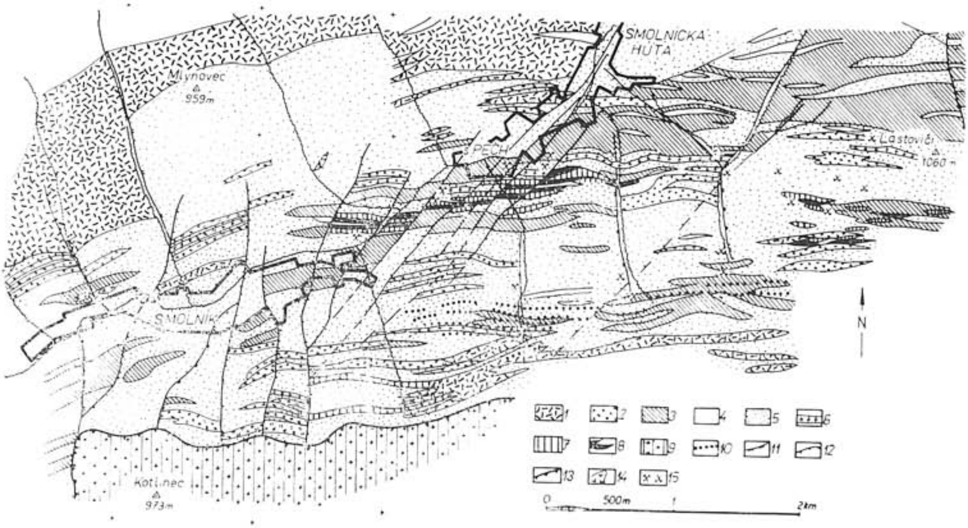


Fig. 1. Geology of Smolník, J. Ilavský 1964. 1 — Porphyries (porphyroids), their tuffs and tuffites. 2 — Tuffites of porphyries. 3 — Sericite-graphite phyllites. 4 — Lyddites. 5 — Sericite and quartz phyllites. 6 — Gabbrodiorites. 7 — Chlorite phyllites (metamorphosed tuffites of basic rocks). 8 — Bodies of pyrite-chalcopyrite ores. 9 — Phyllite-diabase series (Devonian). 10 — Siderite veins. 11 — Older dislocations. 12 — Younger faults. 13 — Transgressive boundary. 14 — Granites. 15 — Mines (open; unaccessible).

H. Schneiderhöhn in 1931 and regarded as genetically related to the pyrite mineralization. Similar rocks, found in the surroundings of Švedlár (W of Smolník) by O. Fusán, J. Kantor, were regarded as hypoabyssal channels for the extrusive volcanism of the Devonian Phyllite-Diabase series (Rakovec-series). Diabases and metamorphosed manganese deposits were from the Gelnica series described in 1954 by one of the authors (J. K.). The Smolník gabbro-diorites were also considered as deep seated equivalents of the carboniferous diabase volcanism (J. Ilavský 1956). In a recent paper (J. Ilavský 1964) their submarine extrusive nature is postulated.

The flyshoid and black shale complexes are highly folded, forming a monoclinal, steeply S-deepind structure (J. Ilavský 1964).

Pyrite Deposits

The main mass of the pyrite mineralization is confined to the chlorite phyllites (altered diabase tuffs and tuffites). Only to an insignificant extent, certain parts of the graphite phyllites are mineralized, too. Pyrite may exceptionally impregnate sedimentary carbonate rocks of the productive sequence. Various ore types may be distinguished according to mineralogy, textures, grade etc.

1. *Disseminated pyrite ores.* The term „glim" is used by the miners to designate this type. Probably derived from „Glimmer" (mica) of german miners, as the ore is always micaceous, rich in chlorite. These low-grade ores contain up to 20 % S.

The pyrite is generally well crystallized, showing cubic or pyritohedral outlines. The dimensions varying mostly in the range 0.1—5 mm. A grouping of the pyrite crystals into bands (mm to cm thickness) is often observed. Their size in one and the same band is approximatively constant, within narrow limits, while between different „bands"

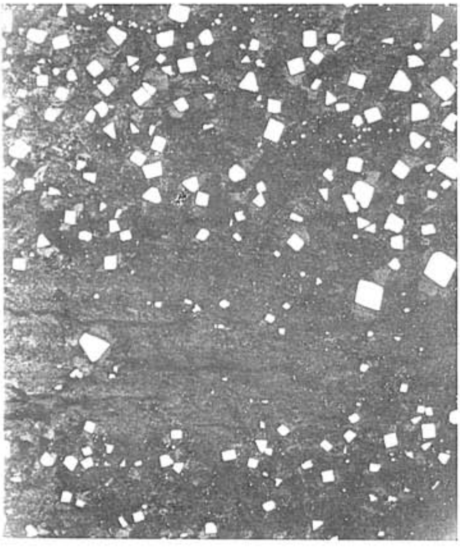


Fig. 2. Disseminated pyrite ore of the „glim"-type in chlorite schist. Mníšek nad Hnilcom, Jalovičí vrch. Polished section, 10 ×.

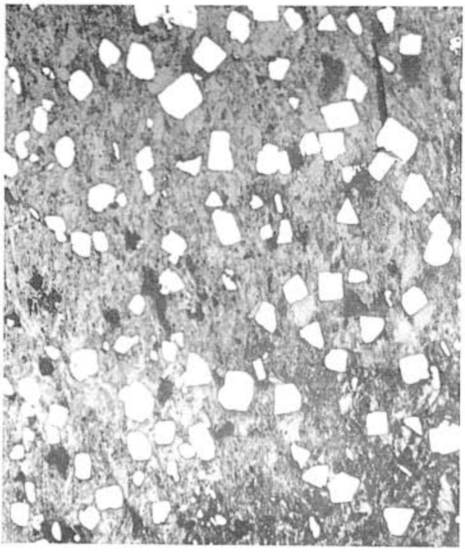


Fig. 3. Disseminated pyrite ore in carbonate country rock. Smolník. Polished section.10 ×.

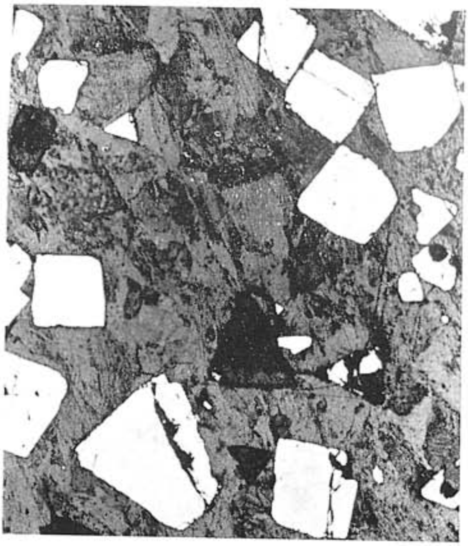


Fig. 4. Disseminated pyrite ore in chlorite schist. Fractured pyrite. Smolník, Glim-adit. Polished section, 10 ×.

considerable changes may occur. The intensity of mineralization may vary too from band to band and rich pyrite dissemination alternate with barren chlorite schists.

The mineralogy of the poorer disseminated ores is extremely simple, pyrite being almost the only suphide. Small, irregular inclusions of chalcopyrite occur sometimes in the porphyroblastic pyrite. They may be dispersed in the chlorite phyllites too, but their content is generally very low.

The euhedral pyrite crystals may be well preserved at one place, more or les corroded at the other, where later mobilization, took place or they may be highly fractured by tectonic movements (Fig. 2, 3, 4).

The disseminated pyrite ores occur around massive pyrite bodies or independently. Their thickness may be considerable (several 10 m). (See Fig. 5, page 9).

2. *Massive pyrite ores.* In the upper parts of the deposit large, lense-shaped bodies of massive ores were mined. They reached up to 50 m in thickness. With depth, there is an increase of disseminated ores at the expense of massive ones.

The highest grade ore is very compact, dense and hard. The term „*cast pyrite*" is used by the miners for this type. For the unaided eye, in the uniform pyritic mass, only small to hardly visible crystals arranged in bands or discontinuous patches are visible. A banding may also be macroscopically indicated by irregular lenses of darker gangue minerals (Fig. 6) rarely exceeding few millimeters in dimensions. It may be relic of primary deposition, which has been accentuated by metamorphic recrystallization.

The fine grained pyrite of „cast pyrites" ranges 0.01—0.03 (generally 0.0X mm). By etching a mosaic structure is revealed (Fig. 7). A part of the pyrite crystals is elongated and by their preferred orientation a recrystallization under pressure indicated.

The interstices of the fine-grained pyrite may be filled by chalcopyrite, which is relatively abundant in this oretype. Porphyroblasts and poikilobasts of arsenopyrite occur sporadically as well as tetrahedrite and galena.

Sphalerite is common. It contains exsolution-type blebs of chalcopyrite, which are more concentrated near the grain boumdaries, leaving the central parts without inclusions. Large chalcopyrite grains in sphalerite are surrounded by a halo of chalcopyrite blebs with gradually diminuishing density. Trace amounts of sulphosalts occur in association with chalcopyrite.

With the exception of pyrite, all the sulphides display owing to their higher mobility a tendency to be concentrated with coarser carbonates and quartz in the lense-shaped patches.

Another type of massive ores is the somewhat porous, so called „*farinaceous*" *pyrite.* The porous aggregates are relatievly soft and can be easily reduced to powder-hence their designation. Owing to this property, good polished sections are difficult to obtain.

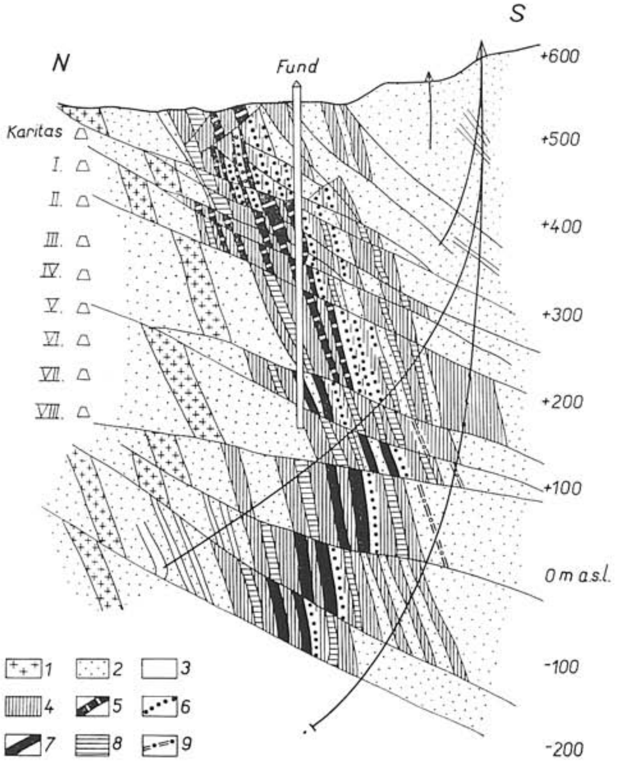


Fig. 5. Vertical section of the Smolník deposit. After J. Ilavský 1964. 1 — Gabbrodiorites. 2 — Sericite-quartz phyllites. 3 — Lyddites. 4 — Chlorite phyllites (Tuffites of basic volcanics). 5 — Massive pyrite ores. 6 — Copper ores (vein and „layers"). 7 — Supposed massive pyrite ores. 8 — Dispersed pyrite ores („glim" and „grocyn"-types). 9 — Quartz veins with copper minerals.

The grain size is very low-down to fractions of a micron. Greater dimensions are found in idioblastic, recrystallized pyrites.

The finest crystallites are dispersed, or arranged in clusters, spherical aggregates and concretions up to 0,3 mm. Colloidal deposition is well preserved. Other sulphides occur in quite subordinate amounts. The ores may display a more or less pronounced banding (Fig. 8).

The „farinaceous" is the dominating type in massive ores, which grades 30—45 % S.

A transition between the massive and dispersed ores form the so called „*grocyny*", a term of unknown origin, designating ores of 20—30 % S. They have certain specific textural features, too. In contrast to the disseminated ores, the pyrite euhedra are not so well preserved. They are irregular, often corroded and fractured. Great differences in grain size exist in one and the same band. Globular and concretionary forms are common.

Quartz is generally more abundant than in disseminated ores and so are various sulphides: chalcopyrite, sphalerite, less galena, tetrahedrite, arsenopyrite, marcasite, sulphominerals a. s. o. The sulphides may be restricted to pyrite only.

Fig. 6. Compact pyrite ore with coarser recrystallized pyrite lining quartz-carbonate lenses containing chalcopyrite, sphalerite etc. Smolník. Polished section, 4 ×.

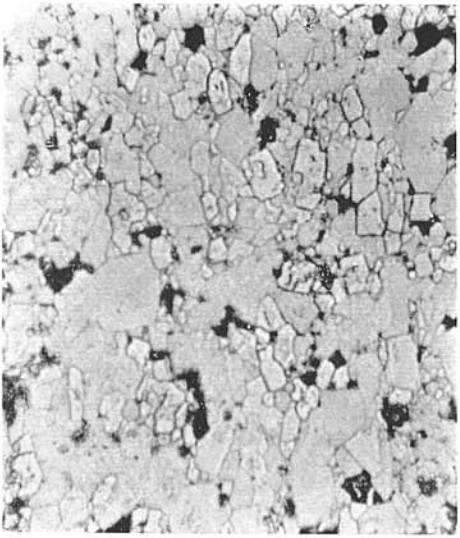


Fig. 7. Compact pyrite ore. Prefered orientation resulting from recrystallization under pressure. Smolník, Ignác-adit. Polished section, 220 ×.

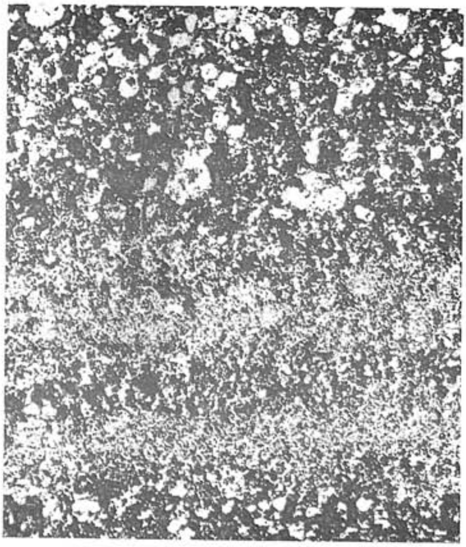


Fig. 8. Fine grained pyrite ore of the „mučniak" (farinaceous)-type. Bands of finegrained pyrite surrounded by coarser pyrite. Smolník, Ignác-adit. Polished section, 10 ×.

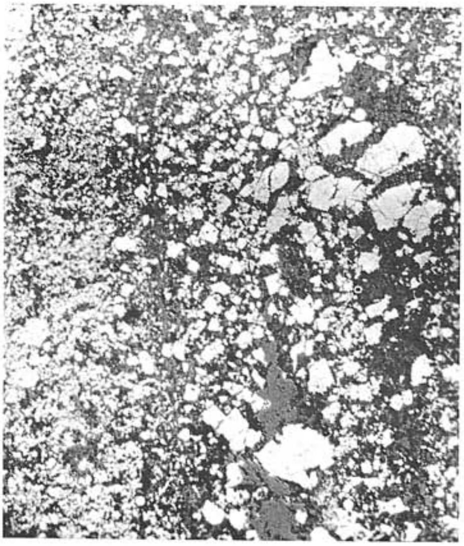


Fig. 9. Rich pyrite ore („grocyn"-type). Coarse grained in the central part with transition into glim-tpye dispersions Smolník, second level. Polihsed section, 10 ×.

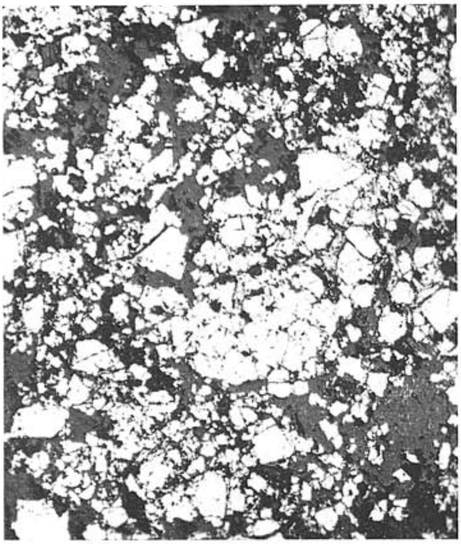


Fig. 10. Pyrite ore „grocyn"-type. Intense fracturing. Smolník. Polished section, 10 ×.

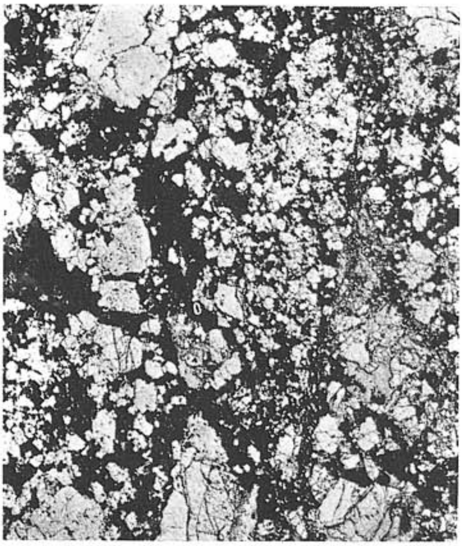


Fig. 11. Rich pyrite ore („grocyn"-type), fractured, containing chalcopyrite, sphalerite, galena. Smolník, Glim-adit. Polished section, 10 ×.

Fig. 12. Banded pyrite ore, fine-grained. Smolník, Ignác-adit. Polished section, 4 ×.

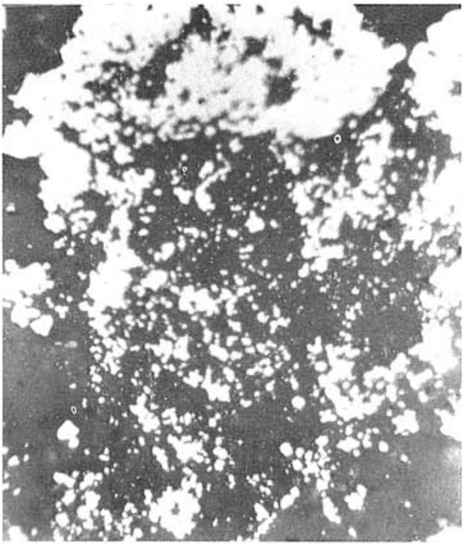


Fig. 13. Clusters of finest pyrite crystals, concretionary to garland-like. Transitions into dispersed crystallites. So called „sulphur bacteria" at upper side. Smolník, banded ore. Polished section, 320 ×.

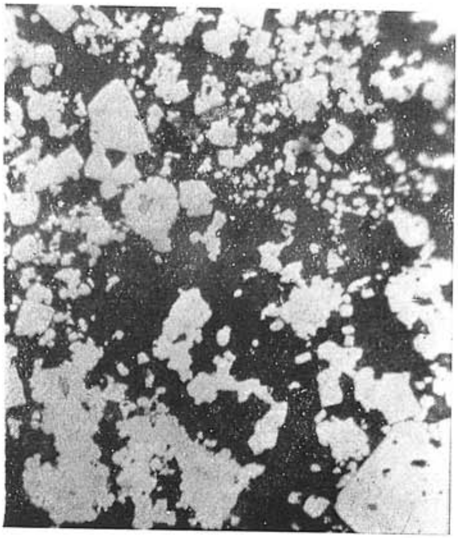


Fig. 14. Irregular dispersions, loosely packed clusters and tight spheres of the type „mineralized sulphur bacteria" formed by minute pyrite crystals. Smolník, banded ore. Polished section, 480 ×.

Fig. 15. Part of a large cluster consisting of idiomorphic pyrite (white) and interstitial chalcopyrite (light gray). Recrystallization of mixed gels. Smolník, Ignác-adit. Banded ore. Polished section, 1000 ×.

A more complicated origin than in disseminated ores is evident. Examples are reproduced in Fig. 9, 10, 11.

3. *Banded pyrite ore.* It does not belong to typical representants of the Smolník deposit and was available from the Ignác adit only, where it occurs in smaller amounts. In grain size they are comparable to the „cast pyrites", though grains of few microns are quite common.

The characteristic banding is produced by alternating bands and lenses of pyrite with gangue minerals, predominantely carbonates, quartz (Fig. 12).

The minute pyrite crystals are irregularly dispersed or display a tendency to form clots, concretionary bodies or spheres of the type „mineralized sulphur bacteria" (Figs. 13, 14).

Recrystallization fenomena of mixed chalcopyrite-pyrite gels are common. Fig. 15 shows a part of a large gel cluster, in which pyrite recrystallized into well developed euhedra and chalcopyrite occurs as infillings of interstices.

In Fig. 16 two tightly-packed pyrite spheres of the same origin are reproduced. The simultaneous and colloidal precipitation of pyrite and chalcopyrite is evident.

Sphalerite, galena and tetrahedrite occur in minor to trace ammounts. Owing to high mobility, they are preferably concentrated in coarser recrystallized parts of the ore. Pyrite and the sparser arsenopyrite are found in large poikiloblasts enclosing other minerals, too (Fig. 30).

In the banded ores abundant textures indicating colloform precipitation and later recrystallization have been well preserved.

4. *Non economic mineralizations in sediments.* The sedimentary rocks contain insignificant amounts of pyrite which has typical signs of sedimentary origin. Scattered

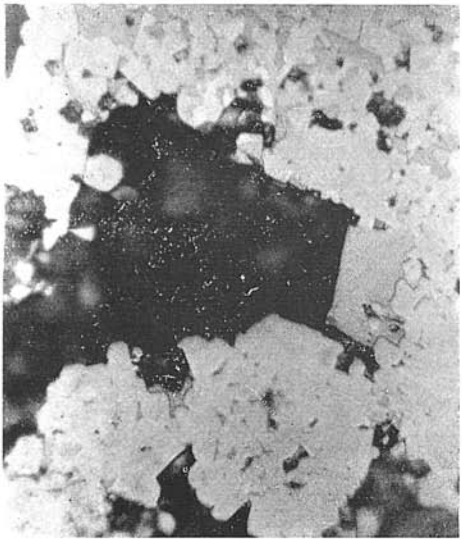


Fig. 16. Relatively compact pyrite spheres (interstitially some chalcopyrite). Richer chalcopyrite surrounding well-developed pyrite crystals at the upper side of the photograph. Colloidal deposition. Quartz — black. Banded ore. Smolník, Ignác-adit. Polished section, 1000 ×.

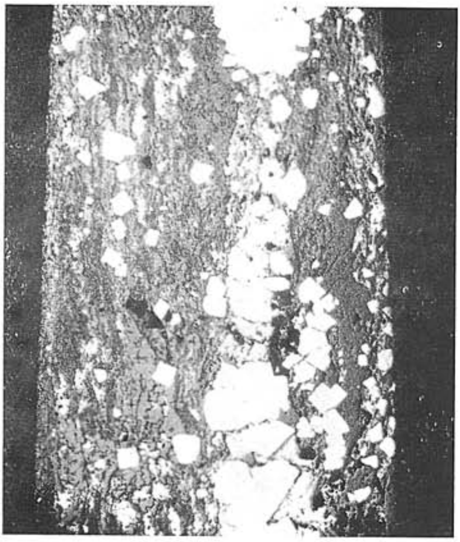


Fig. 17. Chalcopyrite-pyrite band (coarse grained) in disseminated ore. Smolník. Sample 173. Polished section, 4 ×.

euhedra, not accompanied by other sulphides are common. In graphite phyllites they are often associated by minute crystallites and spherical aggregates of the type „mineralized sulphur bacteria".

In feebly mineralized tuffites of the deposit, microscopic examination revealed remarkable textures. The rocks are greyish, to brownish-green, rich in chlorite. Macroscopically white to brown, spheroid bodies scattered in the rock may be observed. They consist of iron bearing carbonates inbedded in a matrix of chlorite, lighter carbonate and quartz. The diameter ranges 1—3 mm. Some indicate concentric-colloform deposition, which has been preserved after recrystallization and tectonization (Fig. 18). In others the concentric textures may be completely lacking, or just indicated (Fig. 19).

The pyrite occurs, as idioblastic euhedra, scattered in the rock, in bands or as clots of minute crystals. Younger veinlets may be found, too. In some samples clusters of very fine grained pyrite formed the nuclei on which deposition of the colloidal carbonates took place (Fig. 19).

Interesting pyrite-chalcopyrite aggregates are commonly observed in this rock. They consist of an outer, dense pyrite rim around nuclei of fine grained chalcopyrite, pyrite and minute micaceous clay minerals. In some the center is formed by a larger pyrite porphyroblast and the space between it and the pyrite-rim filled by a pyrite-chalcopyrite mixture (Fig. 20).

Spheroidic bodies of pyrite only were also observed. In some the outer boundary is sharp. The crystallites tightely packed at the circumference, become loosely bound towards the inner part, leaving an unmineralized core of sedimentary gangue minerals only. In rarer cases the reverse is found. The tight core is surrounded by gradually

Fig. 18. Concentric colloform deposited brown carbonate, recrystallized and surrounded by light carbonate, chlorite, quartz. Fractured. Two bands of pyrite (black). Smolník, thin section, 10 ×.

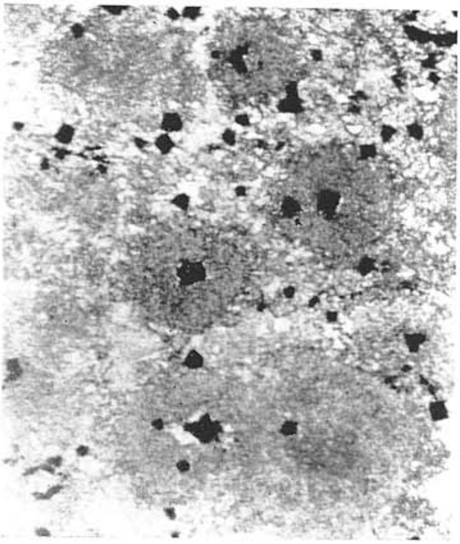


Fig. 19. Recrystallized colloform deposited spheres of carbonates. Some with clumps of minute pyrite crystals in the center. Interstitially between spheres: quartz, chlorite, carbonates. Smolník, thin section, 10 ×.

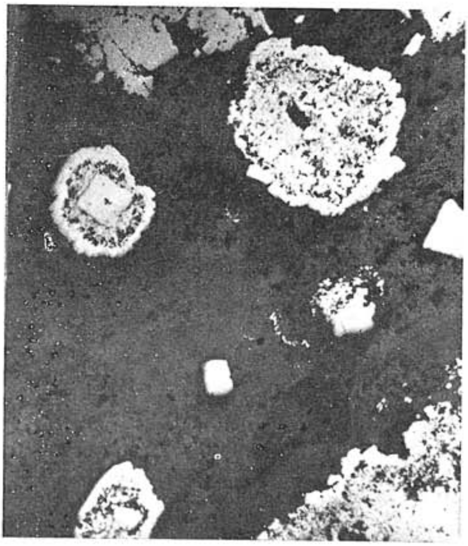


Fig. 20. Concretionary, zoned pyrite-chalcopyrite bodies. Outer rim of dense pyrite, inner of chalcopyrite, pyrite and micaceous gangue minerals. From same sample as Fig. 19. Polished section, 60 ×.

Fig. 21. Pressure shadows of chlorite around pyrite porphyroblast (bottom and pyrite aggregate (top) in carbonate country rock. Smolník. Thin section, 120 ×.

Fig. 22. Pyrite aggregates with quartz in pressure shadows. Smolník. Thin section, Nicols X, 32 ×.

Fig. 23. Fractured pyrite surrounded and veined by chalcopyrite (light grey), sphalerite (medium grey). Quartz and chlorite (dark grey). Copper rich pyrite ore. Smolník. Polished section, 109 ×.

sparser and sparser dispersions. Pyrite euhedra of the „glim"-type are dispersed in the rock, too.

A certain similarity between these carbonate and sulphide textures and parts of the so called „kniest" in the Rammelsberg deposit, Germany (E. Kraume 1955) may be found.

It is interesting to note, that even in the carbonates of this soft rock pressure shadows have been preserved. They consist of chlorite and were found around pyrite porphyroblasts (Fig. 21, top), as well as around clusters of finest pyrite crystallites, or so called „mineralized sulphur bacteria" (Fig. 21, bottom). The common type with feathery quartz in a matrix of carbonates, quartz, chlorite and pyrite is represented in Fig. 22.

A simultaneous, syngenetic and pre-tectonic origin of the pyrite, chalcopyrite and carbonate is evident.

5. *Chalcopyrite ore.* Chalocpyrite, after pyrite the most important sulphide of the Smolník deposit, is generally in small amounts associated with the higher grade pyrite ores.

Rich copper ores (up to 10 % Cu) are concentrated in the so called „layered veins", which — 3 to 8 in number — were intensely mined in the past. They strike parallel to the pyrite lenses and attain thicknesses up to 1 m.

The ores contain subordinate pyrite in euhedral cubic crystals, fractured and veined by chalcopyrite and other sulphides (Fig. 23).

Sphere-like aggregates of pyrite are sparse. The less abundant sphalerite contains emulsion-like blebs of chalcopyrite (Fig. 24).

Galena, tetrahedrite, arsenopyrite, bournonite, native bismuth, sulph minerals are noted less frequently

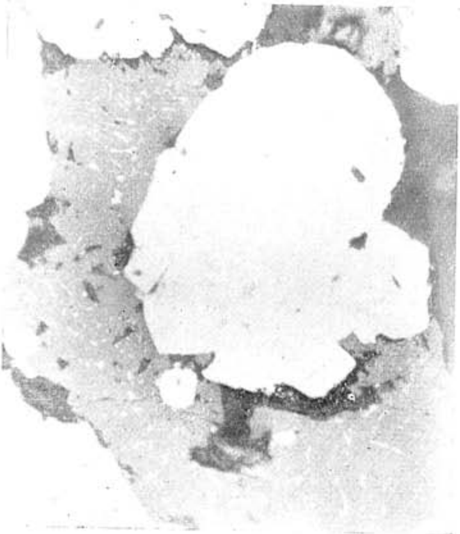


Fig. 24. Pyrite sphere overgrown by idioblastic pyrite. Sphalerite containing numerous chalcopyrite blebs. Compact chalcopyrite-pyrite ore. Smolník. Polished section, 320 ×.

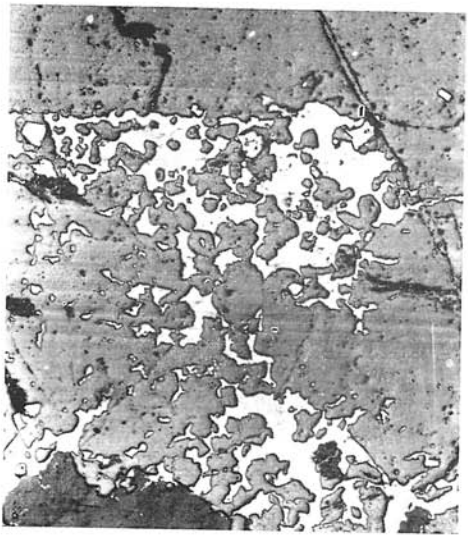


Fig. 25. Sphalerite replaced by galena in a thin quartzcarbonate-sulphide veinlet. Quartz — black. Smolník, Charitas-adit. Polished section, 10 ×.

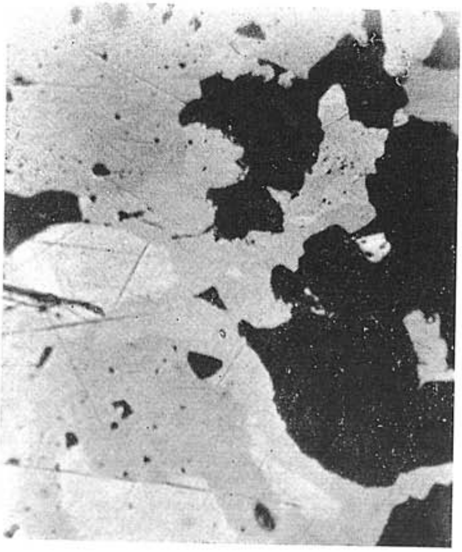


Fig. 26. Bournonite rim between tetrahedrite and gangue (black). Chalcopyrite (centre) and galena (bottom) included in tetrahedrite. Younger mineralization. Smolník, Ignác-adit. Polished section, 480 ×.

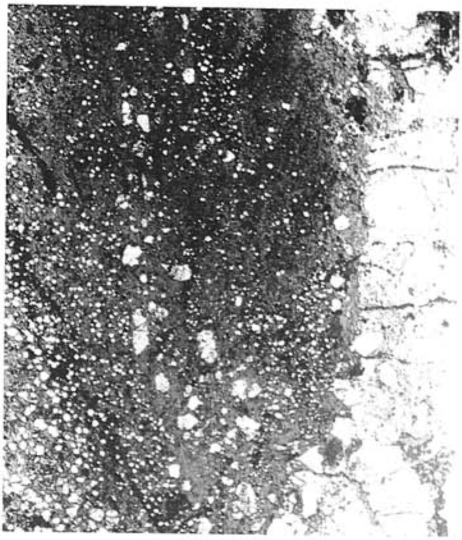


Fig. 27. Band of massive, coarse grained, pyrite-chalcopyrite in disseminated pyrite ore. Chlorite schist — dark grey. Smolník, Ist level. Polished section, 4 ×.

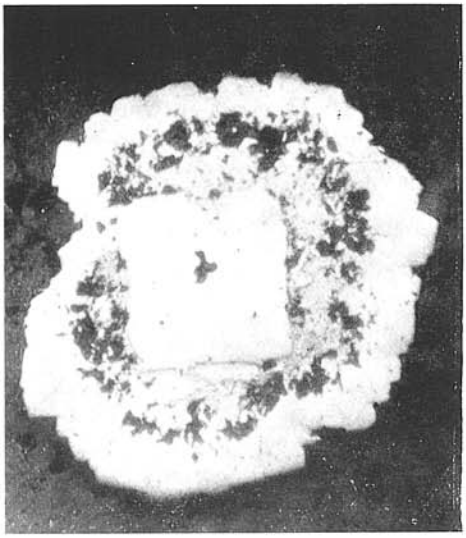


Fig. 28. Colloidal textures. Mixed chalcopyrite-pyrite gels. Idioblastic pyrite in center. Carbonate-chlorite rock, feebly mineralized. Smolník. Polished section, 240 ×.

Fig. 29. Native bismuth (white) with bismuthinite in chalcopyrite. Arsenopyrite lining a fracture. Compact Cu-ore. Smolník. Polished section, 1000 ×.

6. *Epigenetic veinlets.* Varied types occur in the Smolník deposit. Quartz and carbonates are the usual gangue, sulphides being present in variable amounts and mutual proportions. Chalcopyrite, sphalerite, tetrahedrite, pyrite, arsenopyrite, marcasite, galena, bournonite, boulangerite, Cu- and Bi- sulphominerals, native gold, native bismuth were noted (Figs. 25, 26).

Many of the veinlets exhibit signs of intense tectonization and are pre-tectonic. Others consist of massive sulphides, almost without gangue minerals, reminding layered bands of sedimentary sluphides (Figs. 27, 17).

7. *Hydrothermal veins* The Smolník area is rich in hydrothermal vein deposits. Quartz-stibnite veins, siderite veins, siderite-quartz--sulphide veins with variable proportions of the valuable minerals are innumerable.

For comparison with the Smolník deposit, results of sulphur isotopes analyses from the Rákoci und Kríž adits will be given.

The veins are rich in sulphides and have a quartz-siderite gangue. Pyrite, present in more generations, dominates. The subordinate arsenopyrite is younger; chalcopyrite, pyrrhotite, sphalerite, marcasite a. o. occur in minor amounts.

Chemical Composition of the Smolník Ores

The tenors of the ores mined in Smolník ranged: S: 8—47 % Fe: 7—45 %; As up to 0.55 %; Sb up to 0.06 %; Cu 0.2—4 % (exceptionaly 10 %); Pb up to 0,33 %; Zn up to 0,37 %; Bi up to 0.03 %; Ag up to 8 g/t (J. Hlavský 1967).

The trace elements in pyrites were studied in detail by B. Cambel, J. Jarkov-

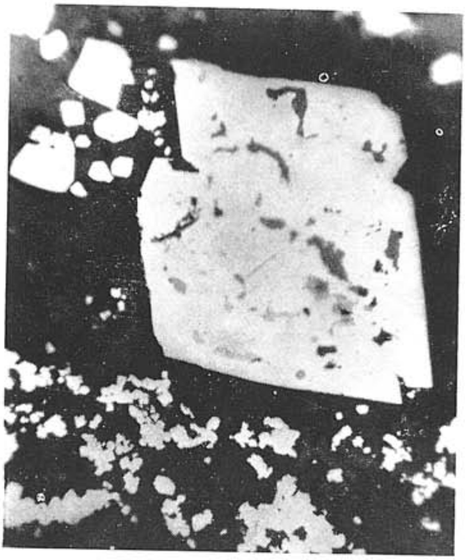


Fig. 30. Idioblastic arsenopyrite with inclusions of chalcopyrite, galena and gangue. Banded ore. Smolník, Ignác-adit. 320 ×.

ský (1967). Their result are reproduced in Fig. 31, 32, page 19.

The Se content of pyrite was found to vary between 5—60 g/t (average 20) and that of chalcopyrite between 8—360 g/t (J. Babačan, J. Forberger, J. Ilavský 1962).

Mníšek nad Hnilcom area

Geological Setting

The deposit is situated about 8 km NNE of Smolník. Published data regarding geology and ore deposits are scarce and almost limited to a paper by P. Grecul'a (1963). They are based on detail mapping and material from explorations made by the Geologický prieskum (Geological exploration).

A flyshoid complex was recognized by P. Grecul'a (1963) as oldest member in the area (Fig. 33, page 20). It consists of alternating chlorite-sericite phyllites, dark arenaceous phyllites, quartzites and sandstones. Subordinate quartz-felspar porphyry tuffs (quartz and felspar phenocrysts reaching (3—4 cm), tuffites and lavas occur.

The flyshoid complex is overlain by graphite-sericite phyllites, intercalated by thin beds of lyddites.

The flyshoid complex, dark phyllites included, is supposed to be an equivalent of the Vlachovo beds (P. Grecul'a 1963).

In the basal parts of the younger Pača-beds, products of a more basic volcanism up to typical diabase tuffites, tuffs and subordinate lavas, were deposited.

They are followed by 70—100 m mighty pelitic sediments (chlorite-sericite phyllites, locally siliceous, subordinate quartzites).

Higher in the sequence, typical representants of the Pača beds, i. e. quartz porphyries, quartz-felspar porphyries, their pyroclastics are abundant.

From local intercalations of the porphyry pyroclastics by diabases a close association of the siliceous with the basic volcanism may be deduced.

The top of the volcanogenic sequence is represented by products of the siliceous volcanism only.

A horizon of graphite-sericite and chlorite phyllites forms the top of the Pača beds in the area.

Lense shaped bodies of gabbro-diorites occur locally and are supposed to be younger than the Pača-beds (P. Grecul'a 1963).

Ore Deposits

Besides siderite sulphides and quartz sulphides, hydrothermal, typical vein deposits, the most important mineralization of the area is of the disseminated type.

The disseminated mineralization (P. Grecuľa 1963) is confined to the upper part of the pelitic sediments of the Pača beds, respectively to the base of the volcanogenic complex (Fig. 33, page 20).

Two types are distinguished:

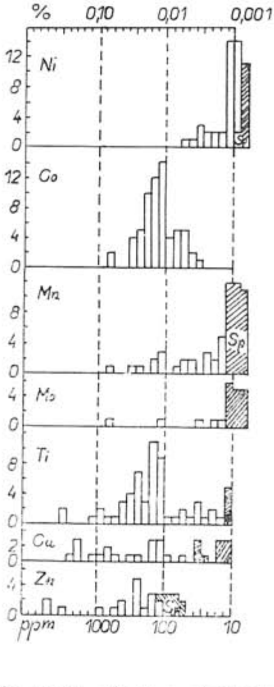
1. Disseminated pyrite mineralization in chlorite schists, very similar to that of Smolník (Fig. 2).

2. Disseminated lead-zinc-copper mineralization, more or less closely associated with the first type. Pyrite, galena, sphalerite, chalcopyrite, arsenopyrite, tetrahedrite, quartz and carbonates are common. They occur in thin veinlets too, and tend to be especially enriched in the vicinity of tectonic lines, where compact ores are found. Silicification of the country rocks, at places accompanied by chalcopyrite impregnations, is often observed.

GENETICAL VIEWS REGARDING THE SMOLNÍK AND MNÍŠEK DEPOSITS

The Smolník deposit has been regarded as a typical example of a hydrothermal, deep seated deposit of the Rio Tinto type.

According to H. Böckh (1905) and H. Schneiderhöhn (1931), diorites were the source of the pyritebearing hydrotherms. A metasomatic replacement of Silurian (?) limestones by hydrothermal solutions related to gemeride granites (of Hercynian or Cretaceous age) was proposed by J. Ilavský (1956).



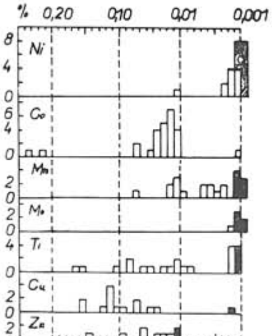


Fig. 31. Histogram of trace elements distribution in pyrites of the Smolník deposit. After B. Cambel, J. Jarkovský 1967.

Fig. 32. Histogram of trace elements distribution in pyrites of the Mníšek nad Hnilcom deposits. B. Cambel, J. Jarkovský 1967.

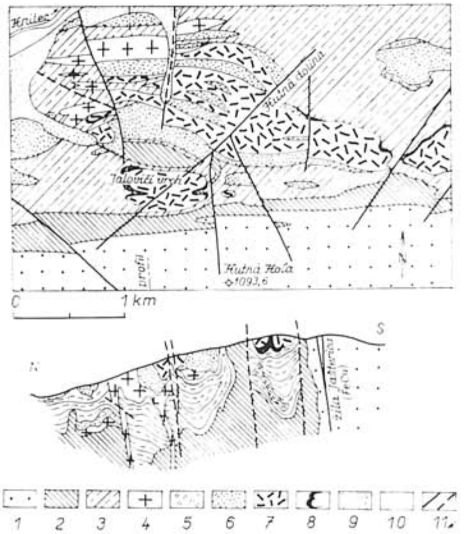


Fig. 33. Geological map and vertical section of the Mníšek nad Hnilcom (Jalovičí vrch) deposit. After P. Grecula 1965. 1 — Flyshoid complex (quartzites-phyllites). 2 — Graphite-sericite phyllites. 3 — Chlorite sericite phyllites. 4 — Basic rocks. 5 — Tuffites of acide volcanics. 6 — Tuffs of acide volcanics. 7 — Quartz porphyries. 8 — Sulphide ore bodies. 9 — Loam. 10 — Alluvial deposits. 11 — Tectonic lines.

B. Cambel (1957) indicated by analogy with the pyrite deposits of the Malé Karpaty Mts, he had studied in detail, a possibility of sedimentary-exhalative origin for the Smolník deposit.

Masspetrometric investigations of common lead revealed in the Smolník deposit the oldest isotopic pattern in the Spišsko-gemerské rudohorie Mts, according to which an exhalative-sedimentary origin of probably Cambrian age was-postulaed (J. Kantor 1962).

New, important data, supporting the exhalative-sedimentary origin were published by J. Ilavský in 1964 and certain geochemical evidences in favour of it by B. Cambel, J. Jarkovský (1967).

Similar views were expressed regarding the Mníšek-deposit.

For the disseminated pyrite mineralization a syngenetic origin and derivation from basic members of the volcanic complex was postulated. The Cu-Pb-Zn mineralization was supposed to have used the same, revived tectonic zone as channelways for the hydrothermal solutions. The same origin and age was admitted as have the other hydrothermal Cu-Pb-Zn deposits of the Spiš-Gemer-Ore Mts. (P. Grecuľa 1963).

This view regarding the dispersed Cu-Pb-Zn mineralization is in contrast with lead isotope data. The lead of galena was found to have considerably lower contents of radiogenic isotopes than lead from the younger, hydrothermal vein deposits. The isotope ratios are very similar to those of the Smolník deposit (J. Kantor 1962).

Similar relation between both these deposits was found by B. Cambel, J. Jarkovský (1967) in the distribution of trace elements in pyrites. (Compare Figs. 31, 32, page 19.)

The genetical schemes proposed for the Smolník and Mníšek nad Hnilcom deposits will be discussed in the light of sulphur isotopes investigations.

SULPHUR ISOTOPES

The four stable sulphur isotopes occuring in nature have approximative abundances: S^{32} 95 $^{0}/_{0}$; S^{33} 0,7 $^{0}/_{0}$; S^{34} 4,2 $^{0}/_{0}$; S^{36} 0,017 $^{0}/_{0}$. In sulphure bearing minerals con-

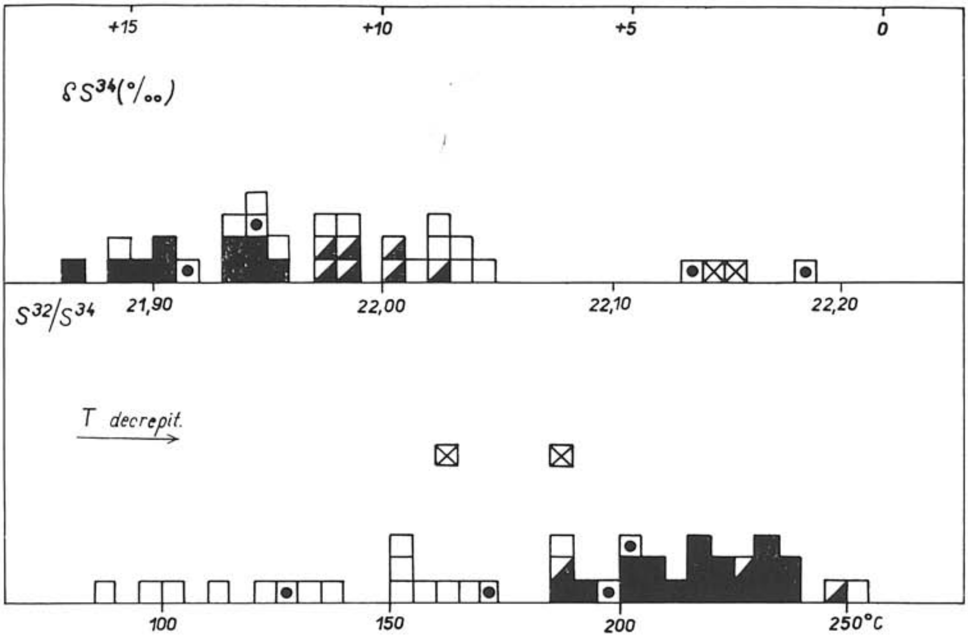


Fig. 34. Upper part: Sulphur isotope ratios in sulphides of the Smolník-Mníšek nad Hnilcom deposits. Dispersed pyrite ore — black squares. „Groeyn"-type ores: squares with circles. Compact and polymetallic ores — diagonaly black and white. Veinlets and bands — white squares. Hydrothermal veins — crossed.
Lower part: Decripitation temperatures of sulphides in various ores of the Smolník-Mníšek nad Hnilcom deposits. Explanations as above.

siderable differences against these mean values may be encountered. They are due to the geochemical history of the minerals. The most effective process of separation of sulphur isotopes in nature is the kinetic effect, especially during the bacterial reduction of sulphates.

As sulphur compounde have a universal distribution in all rock types, and tend to be highly concentrated in mineral deposits, the study of sulphur isotopes may provide important data for the understanding and tracing of various geological processes.

From the four isotopes, the ratio S^{32}/S^{34} of the most abundant ones, is generally used for characterization. The ratio S^{32}/S^{33} giving half the value of S^{32}/S^{34} may be used, too. High precision in the absolute measurement of the ratio of two isotopes in a sample is difficult to obtain. But high accuracy determinations are possible, if the sample S^{32}/S^{34} ratio is measured against the ratio of the same isotopes in a standard.

Troilitic sulphur known to have a strikingly uniform S^{32}/S^{34} ratio is used as a primary standard. The isotopic compositions of the samples are expressed as permil deviations ($\delta\ S^{34}\ ‰$) from the standard according the relation:

$$\delta S^{34}\ ‰ = \frac{(S^{34}/S^{32})\ \text{sample} - (S^{34}/S^{32})\ \text{standard}}{(S^{34}/S^{32})\ \text{standard}} \times 1000$$

For the Smolník and Mníšek nad Hnilcom samples, the permil deviations as well as the S^{32}/S^{34} are given in relation to the meteoritic standard ratio of 22,22 (Table 1 page 22, Fig. 34 page 21).

The separated samples were checked for purity under a binocular microscope and combusted with CuO in a vacumm system. The Soviet made MI-1305 model mass-spectrometer, modified, was used for the isotopic analyses.

The results are discussed in connection with an outline of characteristic features of sulphur isotopes in sulphides of various origins that were proposed for the Smolník and Mníšek deposits.

Sedimentary Origin of Sulphides

In the cycle of sulphur and the sulphur isotopes balance of the crust, the oceans though averaging only 0.09 % S, play by their masses an important role.

The homogenous distribution of sulphur isotopes in the dissolved ocean-water sulphates was early recognized (A. Trofimov 1949, A. Szabo, A. Tudge, A. Mac Namara, H. G. Thode 1950, H. Sakai 1957, H. W. Feely, L. Kulp 1957, A. Vinogradov, M. S. Chupakhin, V. A. Grinenko 1956). The

Table 1

Sample No	δS^{34} (‰)	S^{32}/S^{34}	Sample No	δS^{34} (‰)	S^{32}/S^{34}
167a	16,3	21,86	164	10,9	21,98
28	15,5	21,88	180a	10,9	21,98
174b	15,1	21,89	11	10,6	21,99
57	15,1	21,89	13	10,1	22,00
51	14,5	21,90	168	10,1	22,00
56	14,2	21,91	*105	9,7	22,01
29	13,8	21,92	179a	9,6	22,01
174a	13,0	21,93	*178a	9,6	22,01
53	12,9	21,94	172a	9,1	22,02
*106	12,8	21,94	173a	9,0	22,02
5	12,7	21,94	171b	8,9	22,02
167b	12,6	21,94	*166	8,6	22,03
*14	12,5	21,95	173b	8,6	22,03
*107	11,9	21,96	172b	8,0	22,04
180	11,9	21,96	30	4,0	22,13
171a	11,8	21,96	17	3,5	22,14
3	11,4	21,97	20	3,1	22,15
167c	11,2	21,97	2	1,6	22,18

* Samples from the Mníšek nad Hnilcom mineralizations.

Short description of the analyzed samples:

a) Disseminated ores („glim"-type):

167a, b, c — Pyrite euhedra (0,1—0,4 mm) from fine grained, „glim"-type ore in chlorite schist. Subordinate chalcopyrite, Fig. 27, upper right corner. Permil deviation and S^{32}/S^{34} ratio-Pyrite I : 16,3 21,86. In the disseminated ore about 1 cm thick band of compact pyrite-chalcopyrite. Coarse grained up to 4 mm (Fig. 27 left). Pyrite II (Sample No 167b) from band: 12,6 21,94. Chalcopyrite (167c) 11,2 21,97. Smolník, 1st Level.

28 — Fine grained disseminations of pyrite hexaedra (up to 0,5 mm) in chlorite schist. Other culphides absent. Pyrite: 15,5 21,88. Decrepitation graph Fig. 37 page 30. Smolník, Červená Voda.

57 — Disseminations in chlorite schits. Pyritohedra (0,1—0,4 mm) not associated with other sulphides. Pyrite: 15,1 21,89. Smolník, Ist Level.

51 — Disseminations in chlorite-carbonate rock, veined by thin carbonate veinlets. Pyrite hexaedra up to 1 mm, locally cataclastic. Traces of chalcopyrite and galena. Rutile present. Pyrite: 14,46 21,90. (Fig. 3.) Smolník, Ignác adit.

56 — Typical disseminated ore in chlorite schist. Sulphides represented by pyrite only. Pyrithedra up to 2 mm, fractured. Pyrite: 14,2 21,91. (Fig. 4.) Smolník, Glim adit.

53 — As No 56. Pyritohedra up to 0,8 mm. Pyrite: 12,9 21,94. Smolník, Karol adit.

106 — Rich pyrite disseminations in chlorite schists. Pyrite: 12,8 21,94. Subordinate chlacopyrite. Ore intersected by thin quartz veinlets. Mníšek nad Hnilcom, Hutný potok.

14 — Pyrite disseminations in chlorite schists. Hexaedra up to 0,4 mm. Traces of chalcopyrite. Pyrite: 12,5 21,95. Fig. 2. Mníšek nad Hnilcom, Jaloviči vrch.

107 — Pyrite dissemination in chlorite schist. Subordinate chalcopyrite bands. Pyrite: 11,9 21,96. Mníšek nad Hnilcom, Hutný potok.

3 — Very fine grained disseminations of euhedral pyrite and colloform deposited pyrite-chalcopyrite aggregates in chlorite-carbonate rock. Figs. 19, 20. Decrepigram Fig. 37, page 30. Pyrite: 11,4 21,97. Smolník, IInd Level.

b) Compact and polymetallic ores:

164 — Very fine-grained, porous pyrite ore („farinaceous"-type) with preserved sedimentary textures. Fig. 8. Pyrite: 10,9 21,98. Smolník, Ignác adit.

11 — Compact ore (so called „cast" pyrite type). Fig. 6, 7. Decrepigram Fig. 37, page 39. Pyrite: 10,6 21,99. Smolník.

13 — Pyrite from galena-pyrite-pyrrhotite ore. Walchen near Öblarn, Austria. Metamorphosed deposit of similar geological setting as the Smolník-Mníšek deposits. Pyrite: 10,1 22,00.

168 — Banded ore. Alternating bands of fine-grained sulphides and gangues. Figs. 12, 13, 15. Decrepigram Fig. 37, page 30. Pyrite: 10,1 22,00.

105 — Pyrite from irregular disseminations in chlorite schists. Sampled by B. Cambel, J. Jarkovský. Pyrite: 9,7 22,01. Mníšek nad Hnilcom, Jaloviči vrch.

178a — Disseminated polymetallic ore, fine-grained. Pyrite with Pb-Zn-Cu-minerals in quartz-sericite schist. Pyrite: 9,6 22,01. Mníšek nad Hnilcom, Jaloviči vrch.

166 — Same type of ore as No 178a. Pyrite: 8,8 22,03. Mníšek nad Hnilcom, Jaloviči vrch.

c) Disseminated to compact ores („grocyn"-type):

29 — Typical „grocyn"-type ore in chlorite schists. Large differences in grain size. Pyrite, fractured and corroded: 13,8 21,92. Traces of chalcopyrite and sphalerite. Poor in quartz. Fig. 10. Smolník, IInd Level, Zbornák- adit.

5 — As sample No 29. In the fine-grained pyrite (Fig. 9) sparse marcasite and concretionary pyrite occur. Pyrite: 12,7 21,94. Decrepigram Fig. 37, page 30. Smolník, IInd Level.

2 — Pyrite ore („grocyn"-type). Pyrite fractured, irregular shapes, up to 2 mm in size. Rich in quartz and veined by thin quartz-pyrite-chalcopyrite veinlets. Poor in chlorite. Smolník, Charitas adit. Pyrite: 1,6 22,18.

30 — As sample 2. More cataclastic and richer in chalcopyrite and sphalerite. Fig. 11. Pyrite: 4,03 22, 13. Smolník Glim adit.

d) Veinlets, bands and hydrothermal veins:

174a, b — Quartz veinlet intersecting feebly mineralized chlorite schists in the immediate hanging of the deposit. In the quartz irregularly distributed chalcopyrite, pyrite and galena. 174a — galena: 13,0 21,93. 174b — chalcopyrite: 15,1 21,89. Decrepigram Fig. 38 page 32. Smolník.

180a — Irregular, epigenetic sulphide mineralization in carbonate-quartz gangue. Tetrahedrite, galena, chalcopyrite, sphalerite, pyrite, arsenopyrite, native gold. 180 — tetrahedrite: 11,9 21,96. 180a — galena: 10,9 21,98. Tetrahedrite earlier in succession than galena. Decrepigram Fig. 38, page 32. Smolník, Ignác adit.

171a, b — Quartz veinlet with chalcopyrite, pyrite. 171a — pyrite: 11,8 21,96. 171b — chalcopyrite: 8,9 22,02. Decrepigram Fig. 38, page 32. Smolník, Charitas adit.

179a — Quartz veinlet with chalcopyrite and galena intersecting chlorite schists. Galena: 9,6 22,01. Mníšek nad Hnilcom, Jaloviči vrch.

172a, b — Carbonate-quartz veinlet, sulphide bearing. Sphalerite, galena, tetrahedrite, bournonite, pyrite etc. Fig. 25. 172a — sphalerite: 9,1 22,01. 172b — galena: 8,0 22,04. Decrepigram Fig. 38, page 32. Smolník, Charitas adit.

173a, b — Thin band of compact chalcopyrite-pyrite in dispersed ores of „glim"-type. Fig. 17. Decrepigram Fig. 38, page 32. 173a — octohedral pyrite: 9,0 22,02. 173b — chalcopyrite: 8,6 22,03. Smolník.

167b, c — See disseminated ores.

17 — Sulphide rich quartz, siderite ore from hydrothermal vein. Prevailing pyrite (2 generations), subordinate arsenopyrite, chalcopyrite, marcasite, pyrrhotite in quartz gangue with small amounts of siderite. Pyrite: 3,5 22,14. Smolník, Rákoci adit.

20 — Same type of hydrothermal mineralization, but other vein. Pyrite: 3,1 22,15. Smolník, Kríž adit.

S^{32}/S^{34} ratio was found by A. MacNamara and H. G. Thode (1951) as averaging 21.80 ± 0.5.

Subsequent investigations, based on refined techniques and high precision instruments resulted in more raliable values, W. V. Ault, J. L. Kulp (1959) report for geographically and vertically careful selected samples of ocean bodies an average ratio S^{32}/S^{34} of 21,76 ± 0.01 ($\delta S^{34} = 20.3$), whereas H. G. Thode, J. Monster, H. B. Dunford (1961) have for the presentday sea water found an average permil value δS^{34} of 20,1 ± 0,3.

J. R. Kaplan, K. O. Emery, S. C. Rittenberg (1963) have obtained similar results. In 8 analyses of dissolved sulphate from the Santa Barbara, Santa Monica and Santa Catalina sills of California the spread of permil values was 20.2 to 20.6 with the average value of + 20.4 permil with regard to the meteoritic standard.

A good homogenization of the sulphur isotopes in sea water has thus been proved. It is comparable only to the very narrow spread in sulphur isotope ratios of meteorites.

Another remarkable feature is the concentration of the heavier isotope S^{34} in ocean water. A similar enrichment in S^{34} is generally observed in evaporites, anhydrite and gypsum.

H. G. Thode, J. Monster, H. B. Dunford (1961) give for present day deposited gypsum on the bottom of the Boca de Virila, Peru $\delta S^{34} = 22.5$ and W. V. Ault, J. L. Kulp (1959) for similar deposits of the Laguna Madre, Texas, $\delta S^{34} = 20.7$ i. e. practically identical values with present-day ocean water sulphates.

The indetity between the isotope ratios of evaporites and those of the ocean water may be preserved, when the evaporation of the water bodies in the more or less restricted lagoons proceeds rapidly, almost completely and is not disturbed by other processes.

With negligible influx of river waters carying lighter sulphur and contact of the depositional basin with the inexhaustible sulphate revervoir of the ocean, the deposited evaporites may have the same, or, due to bacterial activity, a somewhat heavier sulphur than the ocean (J. Monster, H. G. Thode 1964).

Changes in the influx of river waters, ocean water, intense bacterial activity, precipitation of sulphides a. s. o. may produce a complex pattern in the distribution of sulphur isotopes.

The broadest range in isotope ratios exhibit sulphides of sedimentary origin, as found by H. G. Thode, A. MacNamara, A. Collins (1949) and many investigators afterwards (W. V. Ault, J. L. Kulp 1959, H. G. Thode et al. 1953, A. P. Vinogradov, M. S. Chupakhin et al. 1956, M. L. Jensen 1958, J. R. Kaplan, K. O. Emery, S. C. Rittenberg 1963 a. s. o.).

H. G. Thode. H. Kleerkoper. D. Elcheran discovered in 1951 isotope fractionation in the bacterial reduction of sulphates. This. mostly non-equilibrium. kinetic. process. governs the distribution of sulphur isotopes in sedimentary basins and is of dominant importance in the geochemistry of sulphur isotopes.

During the reduction $S^{32}O_4''$ reacts faster than $S^{34}O_4''$. the lighter isotope being enriched in H_2S and consequently in the precipitated sulphides.

The value of the kinetic effect depends on various factors. At very low sulphate concentrations or at very rapid metabolic rates it may drop to zero, whereas at slow metabolic rates it may reach 25 $^0/_0$ (A. G. Harrison. H. O. Thode 1958).

Extreme dispersion of sulphide isotope ratios may take place, where a limited body of sulphates is almost completely reduced. The early formed sulphides are characterized by the lightest sulphur. With successive deposition. they become richer and richer in S^{34}. On the other hand. bacterial reduction produces a gradual enrichment of the sulphate in the heavier isotope.

Sulphides of sedimentary origin display wide ranges of S^{32}/S^{34} ratios. With an average about 22,49 the sulphur is considerably lighter than in meteorites (W. V. Ault. J. L. Kulp 1959).

Pyrite in the dispersed ores („glim" type) of the Smolník and Mníšek nad Hnilcom deposits is characterized by a narrow spread of S^{32}/S^{34} ratios (21,86 to 21,95) (Fig. 34. page 21).

Very fine grained and massive pyrite ores are depleted in S^{34}. the ratios varying within relatively narrow limits. too.

The total spread of the combined (dispersed and massive) ores is low. and does not fit the conditions expected for a sedimentary. origin of the ores with prevailingly bacterial activity.

Another feature. not quite compatible with such an assumption is the heavy sulphur in pyrite as will be discussed in connection with the origin of the sulphur.

Hydrothermal Origin of Sulphides

The largest quantity of published sulphur isotope data pertains to samples from hydrothermal deposits „sensu lato". Their isotope ratios cover almost the whole range observed in sulphur of various rock types.

W. V. Ault and J. L. Kulp (1959) have summarized the availabble analyses and found an average of 22.13 for the S^{32}/S^{34} ratio (span 21,53 to 22,52). With the inclusion of ground water deposits" of M. L. Jensen (1960). the range-would be extended to much higher. negative permil values.

In spite of the broad overall range. certain hydrothermal deposits display a strikingly uniform isotopic composition. This uniformity is characteristic for a well homogenized source.

In the Yellowknife gold district. Canada. the averages for various vein systems range + 1.7 to + 3.8 permil deviation (A. Wanless. A. Boyle. D. London 1960). W. V. Ault and J. L. Kulp (1960) report uniform sulphur ratios in deposits hundreds of kms apart. along the Southamerican Andes. A. Ryznar. A. Campbel. A. Krouse (1962) for the Quemont ore body. Canada (+ 0.096 to + 1.73 permil deviation). a. s. o. In cases mentioned above. the permil values are slightly positive. the sulphur being heavier than the troilitic one.

The narrow spread. and ratios approaching those of meteoritic and terrestrial values. indicate besides a well homogenized source a possible derivation from the mantle or deeper parts of the crust, where the melted blocks were large enough to produce sulphur of the representative average value. Hydrotherms of other origin, may of course, deposit sulphur of quite similar composition.

The granitized sedimentary complexes might have been of limited size and might have contained large accumulations of sulphate evaporates and small quantities of sedimentary sulphides. The deposits derived should cary heavy sulphides with a probably narrow spread in isotope ratios.

If in the granitization processes blocks with considerable accumulations of sedimentary sulphides are incorporated, lighter sulphides are produced by the related hydrothermal solutions.

Hydrothermal deposits displaying sharp, but from one deposit to the other different sulphur isotope ranges indicate derivation from a well homogenized source.

Broader variations in sulphur isotope ratios may, on the other hand, indicate inhomogenous, incomplete extraction, which is characteristic for shallow parts of the crust.

Mixing of sulphur in hydrothermal solutions derived from different sources, may also result in similar broad spread in isotope ratios at one and the same deposit.

Sandstone uranium deposits, lead zinc mineralizations of the Mississip, Missouri, Joplin types, copper mineralizations of the Kennecott type are typical represants with broad ranges in isotopic composition of sulphur (M. L. Jensen 1959).

The Smolník and Mníšek nad Hnilcom deposits exhibit a uniform distribution of sulphur isotopes, especially in the dispersed ore types. The remarkable constancy does not contradict the assumption of a magmatic hydrothermal origin.

Similar narrow ranges were found in the massive ores, where the sulphur is generally somewhat lighter.

Sulphides from bands and veinlets intersecting the dispersed and massive ores display on the other hand a relative wide spread, covering almost the whole range of both ore types. A gradual depletion in the heavier isotope is evident.

Source of Sulphur

The troilitic sulphur of meteorites is known to be extremely uniform in isotopic composition. The overall variation of the $S^{32} S^{34}$ ratios does not exceed 0.5 ‰ or $\delta\ S^{34} \pm 0.5$ ‰ (W. V. Ault, J. L. Kulp 1959) or ± 0.2 ‰ (H. G. Thode, J. Monster, H. B. Dunford 1961). A not insignificant spread of the reported values is of instrumental origin.

A. P. Vinogradov, M. S. Chupakhin, V. A. Grinenko (1957) found, using high-precision techniques, identical values of $S^{32} S^{34} = 22.20$ for nine stony meteorites and one achondrite.

No significant difference — grand mean of permil value equal to $+ 0.2 \pm 0.1$ ‰ — was found in troilitic sulphur from meteorites, studied by A. Smitheringale, M. L. Jensen (1963).

Meteoritic sulphur is a generally adopted standard and provides a base level in relation to which the extent of sulphur isotope fractionation in natural processes may be measured.

The meteoritic sulphur is supposed to represent primordial sulphur in a similar way as lead in iron meteorites.

The constancy of S isotope ratios in meteorites suggests that similar results may be expected in basic to ultrabasic rocks from the mantle, where a high degree of homogenization and small deviations from the meteoritic standard are highly probable.

A limited number of experimental results supporting such ideas was published by A. P. Vinogradov et al. (1957), A. Mac Namara, H. G. Thode (1950), W. V. Ault, J. L. Kulp (1950) a. o.

Decisive data, based on detailed investigations of large ultrabasic to basic intrusive sills, are reported by M. Shima, W. H. Gross, H. G. Thode (1963). The follownig mean values of permil deviations were obtained: Leitch sill, Ontario, Canada (+ 0.1); Cobalt sill, Ontario, Canada (0.70); Palisades sill, New Jersey, USA (0.95); Insizwa sill, East Criqualand, S. Africa (1.00), (Fig. 35 page?)

In norites of the Sudbury district, Canada, and in the associated Ni-Co ores, slightly positive permil values were found by H. G. Thode, H. B. Dunford, M. Shima 1962). Micropegmatites and the probably genetically related Cu-Pb-Zn ores display on the other hand higher positive values.

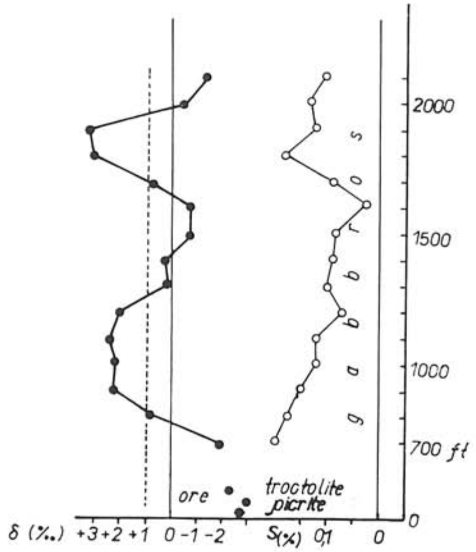


Fig. 35. Distribution of sulphur isotopes in the Insizwa sill. After M. Shima, W. H. Gross, H. G. Thode 1963.

The Triassic igneous rocks of the Newark group, Eastern USA, are supported to be of mantle origin. A. Smitheringale and M. L. Jensen (1963) report for the sulphur of the intrusive diabases only small premil deviations (+ 0.1 ± 0.4) from troilitic sulphur.

Table 2. Sulphur Isotope Ratios in Coexisting Minerals

Sample No	Mineral	S^{32}/S^{34}	δS^{34}	Mineral	$\triangle\delta S^{32}/S^{34}$	δS^{34}	$\triangle\delta S^{34}$	N
167	Cp	21.97	11.2	Py	21.94	12,6	1,0014	1,4
171	Cp	22.02	8.9	Py*	21.96	11.8	1,0027	2.9
173	Cp	22.03	8.6	Py	22.02	9.0	1,0005	0,4
180	Gn	21.96	11.9	T	21.98	10.9	1,0009	1.0
172	Gn	22.04	8.0	Sp	22.02	9.1	1,0009	1.1
174	Gn	21.93	13.0	Cp	21.89	15.1	1,0018	2.1

* Probably slightly contaminated by pyrite with heavier sulphur from country rock.
Py — pyrite, Cp — chalcopyrite, Sp — sphalerite, Gn — galena, T — tetrahedrite.

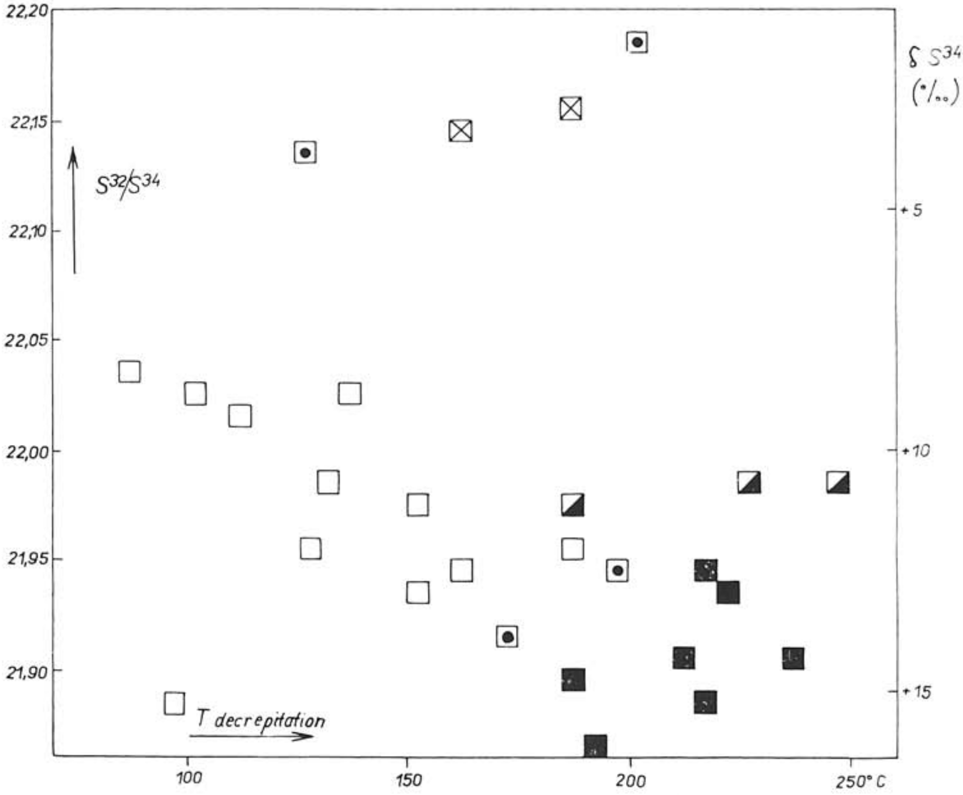


Fig. 36. Relation between sulphur isotope ratios and decrepitation temperatures of sulphides at the Smolník and Mníšek nad Hnilcom deposits. Explanation: Fig. 34, page 21.

These data seem to be a reasonable support of views, that uncontaminated sulphur of mantle origin is characterized by an isotopic constitution, which is close to that of meteoritic sulphur, but is slightly enriched in S^{34}.

Contamination by sulphur of crustal rocks as well as fractionation may considerably increase the differences against the meteoritic standard and the spread of the S^{32}/S^{34} ratios.

A mantle origin of sulphur in the Smolník and Mníšek nad Hnilcom deposits would thus require sharp limits in the isotopic composition and ratios closely approaching meteoritic sulphur. The first condition only is satisfied. The sulphur is too enriched in the heavy isotop to be regarded as uncontaminated, primordial sulphur.

Sulphur with narrow isotopic range and composition close to the meteoritic one may be produced by processes of granitization. Lower parts of the crust, where large blocks of sedimentary rocks containing both, the heavy sulphur of the evaporites as well as the light one of sedimentary sulphides, are incorporated in the granitization process, represent such sites of homogenization.

If only small blocks are melted and digested, homogenization may proceed far enough to yield sulphur of sharp isotopic range, but the resulting isotope ratios depend on the prevailing type of sulphur compounds in the blocks:

a) It may be heavier than the troilitic sulphur when the sedimentary material was rich in sulphates (gypsum, anhydrite).

b) In magmatic hydrothermal deposits related to granitization of strata containing appreciable quantities of sedimentary sulphides, the sulphur may be lighter than the meteoritic one, and may have sharp limits of ratios too.

c) When apropriate amounts of sulphates and sulphides are digested, sulphur closely approximating the isotopic composition of meteorites may be produced even by granitization of smaller blocks.

Sulphur isotope ratios found in the Smolník and Mníšek nad Hnilcom deposits, especially in the dispersed ores, do fit the conditions expected in magmatic hydrothermal deposits related to granitization of sulphate-rich sedimentary complexes.

Interpretation of Sulphur Isotope Data from Smolník-Mníšek Deposits

The prevailing mass of ores at the Smolník and Mníšek nad Hnilcom deposits consists of two types:

1. dispersed pyrite ores („glim"-type),
2. massive pyrite ores and polymetallic ores.

The dispersed pyrite ores occuring almost exclusively in chlorite schists show a very narrow spread in isotope ratios and an enrichment in the heavy isotope (21.86 to 21.95). See Table 1, page 22, Fig. 34, page 24, Fig. 2, 3, 4.

From the foregoing discussion follows that the sulphur was derived from a well homogenized source. Hydrothermal solutions associated with granitization of sedimentary piles, rich in sulphates, would yield sulphur of these characteristics.

Fractionation of sulphur during crystallization of basic to ultrabasic rocks may produce heavy sulphur, too. Recent investigations of M. Shima, W. H. Gross, H. G. Thode (1963) revealed the tendency of sulphides to be enriched in S^{34} during the process of magmatic differentation. In the Insizwa sill, South Africa, of presumably mantle origin, there is a pronounced gravity differentiation, with picrite at the base, followed by troctolite and gabbros. In the coppernickel mineralization of the basal zone the sulphur is lighter than the meteoritic one, permil values ranging — 2.50 to — 3.05. For the systematically sampled gabbro an average permil value of + 1.0 was found. (Fig. 35, page 27).

For the large sills in the Eastern USA isotopic fractionation was negligible during the early stages of crystallization. It became important in the later ones, the sulphides formed being successively enriched in S^{34}. Enrichments of 3 to 8 permil were commonly observed (A. Smitheringale, M. L. Jensen 1963).

In nature the inorganic reduction of sulphates to sulphides during granitization is the main source of heavy sulphides, more important than fractionation during differentiation. It is supposed to have yielded the heavy sulphur of the Smolník and Mníšek nad Hnilcom deposits too. Other evidences indicate exhalative sedimentary deposition of the dispersed pyrite ores.

In the massive and banded ores of Smolník an increase of Cu-Pb-Zn contents relative to the dispersed ones of the „glim"-type is observed. The sulphur is depleted is S^{34} [S^{32}/S^{34} ratios range 21.98 to 22.00].

Considerably higher base metal tenors are present in the dispersed to massive Cu-Pb-Zn ores in Mníšek nad Hnilcom where the S^{32}/S^{34} ratios range 21.96 to 22.03.

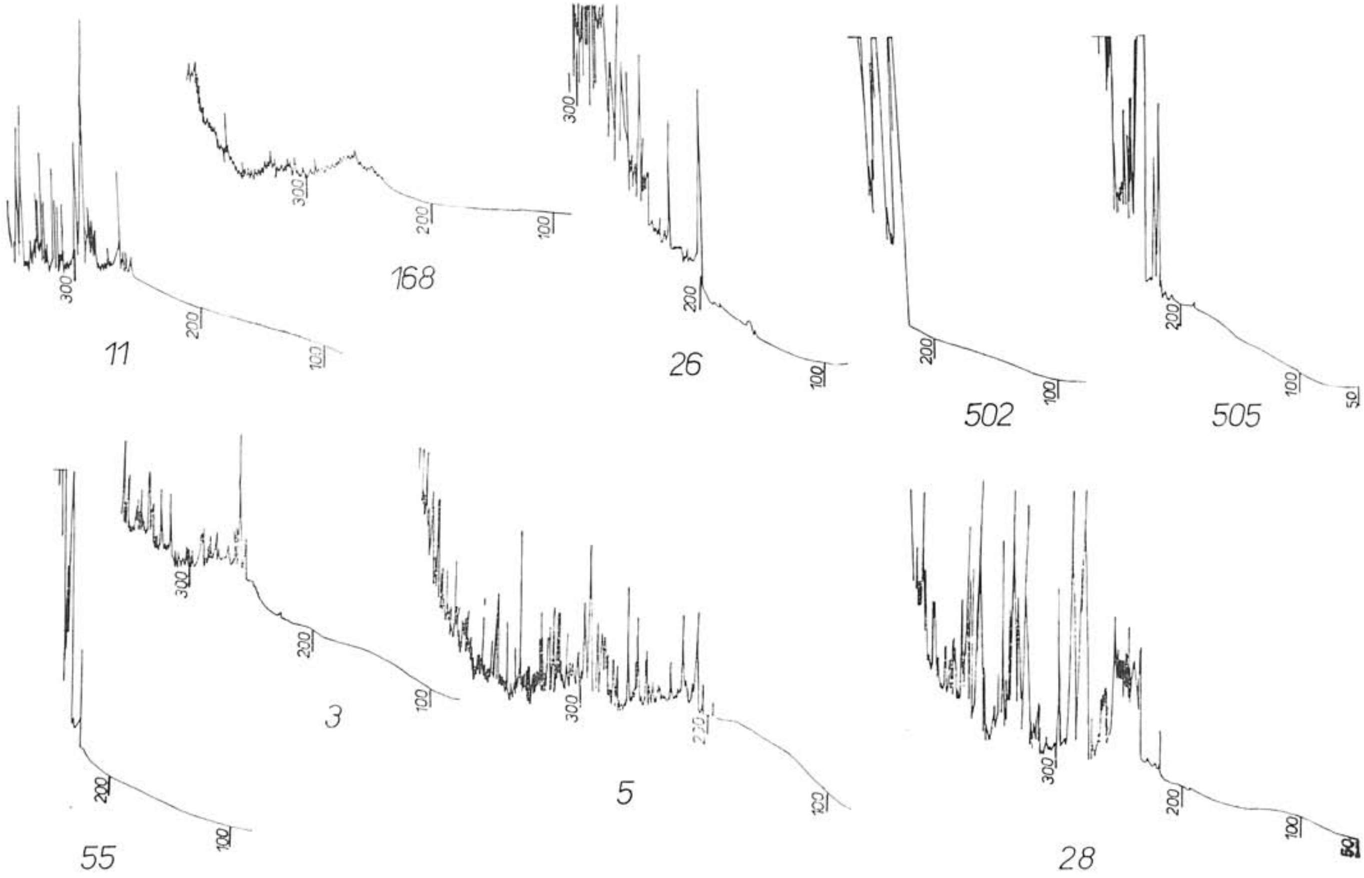


Fig. 37. Decrepigrams of pyrites from compact (11), banded (168), „grocyn"-type (5) and dispersed (26, 505, 502, 55, 3, 28) ores.

The highest ratio of the dispersed ores is equal to the lowest one of the massive and polymetallic ores. The ranges being relatively narrow in both cases.

Two possibillities for the explanation of the observed differences in isotopic composition are to be considered:

A. They may be due to changes in isotopic composition of sulphur in the source of hydrothermal solutions. The relatively narrow spread and higher Cu-Pb-Zn contents would be in accord with this assumption.

B. The isotope ratios in the source were during the ore forming process almost constant, equal to those of the dispersed ores. The lighter sulphur of the massive ores of the Smolník deposit consists of a mixture of this hydrothermal sulphur with biogenic sulphur formed during the deposition in the sea. Microscopic investigation revealed colloform deposition which is often associated with bacterial activity.

With large scale bacterial reduction of the sea water sulphate, great variability in isotopic composition of the sulphides and considerably lighter sulphur would be expected. This was not confirmed by masspectrometric analyses.

Owing to the very fine-grained nature of the massive ores the greater variability in isotopic composition may be to a certain extent veiled by the fact that mean values for a very large number of sulphide grains are measured.

In coarser ores of the „groeyn"-type consisting of pyrite without other sulphides (Fig. 9, 10) isotope ratios (21.94—21.92) in the range of disseminated pyrite ores were found. In others, intensely fractured, rich in chacopyrite, sphalerite, galena and quartz (Fig. 11) considerable enrichment in S^{32} (ratios 22.13—22.18) took place. Genetic relations of these samples to hydrothermal veins (ratio 22.14—22.15) can not be excluded. Processes of mobilization might have modified the textures, mineralogy as well as introduced lighter sulphur.

A derivation of the massive ores in Smolník and of the polymetallic ones in Mníšek from the same source as the dispersed pyrite ores is thus plausible. The differences in isotope ratios are mostly due to the evolution of the hydrothermal solutions during the granitization and ore forming processess. Light sulphur may result from isotope exchange reaction: $H_2S^{34} + S^{32}O_2 = H_2S^{32} + S^{34}O_2$ which under magmatic conditions favours it's entrance into hydrogene sulphide. This might have been accumulated in certain parts of the magmatic chamber and by tectonic movements channeled into the Cambro-Silurian sea. The prevailingly anorganic, exhalative sedimentary deposition of the massive sulphides was to a limited extend only accompanied by bacterial production of hydrogene sulphide.

An evolution of the isotopic composition of sulphur in the source is indicated not only by the observed differences in isotope ratios between the dispersed and massive deposit. The dispersed pyrite ores are there, on the contrary, devoid of Cu-Pb-Zn ores bat also by higher concentration of Cu-Pb-Zn in the later type. It rearches a maximum in the dispersed to massive polymetallic ores of the Mníšek nad Hnilcom minerals.

Sulphur Isotopes in Coexisting Sulphide Minerals

Most of the sulphide bearing veinlets and bands of the Smolník-Mníšek deposits rarely exceed few centimeters in thickness. From this and textural evidences a contemporaneous formation or at least a relative short time interval between the precipitation of the minerals may be deduced.

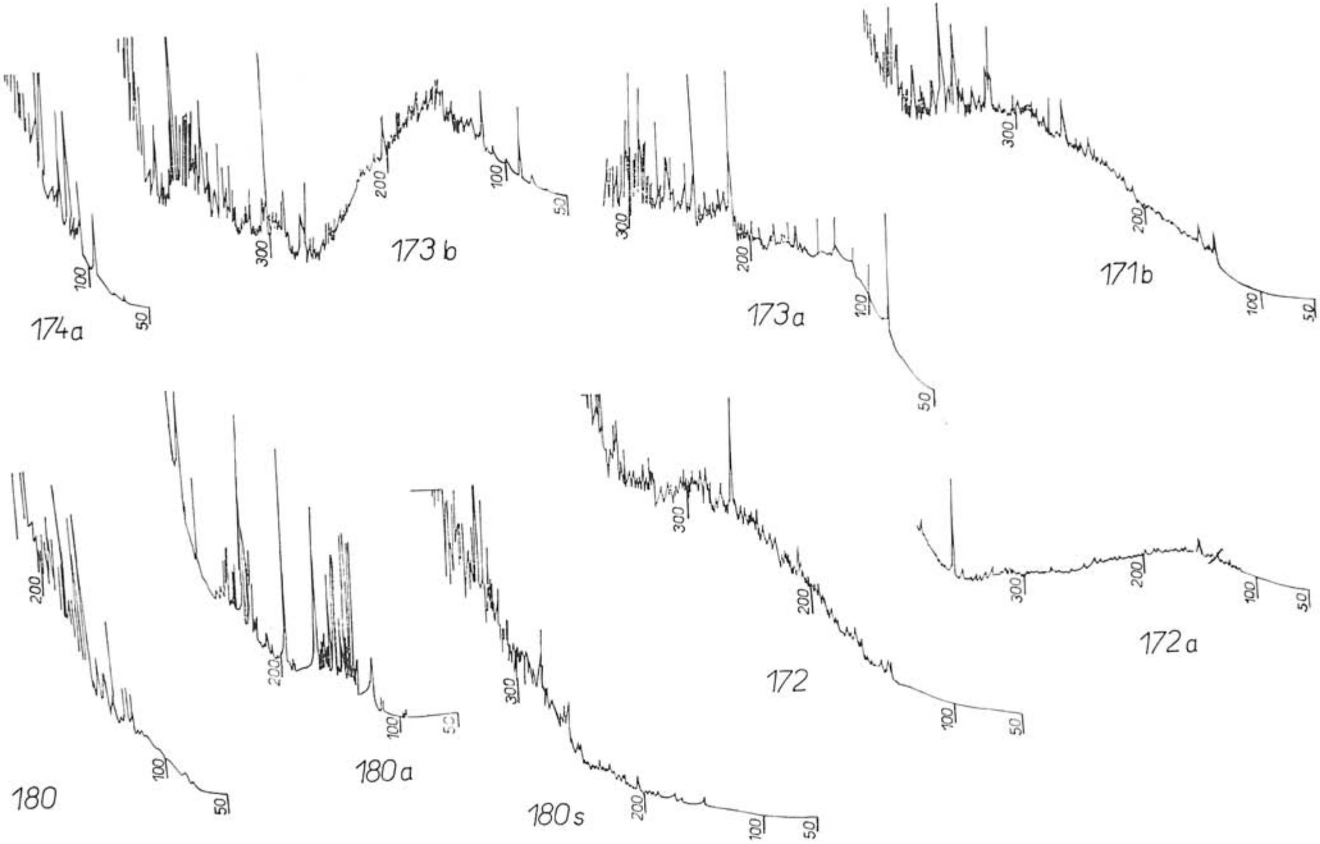


Fig. 38. Decrepigrams of minerals from veinlets and bands. Pyrite (173a), chalcopyrite (171b, 173b), galena (174a, 180a), tetrahedrite (180), sphalerite (172a), carbonate (172), quartz (180s).

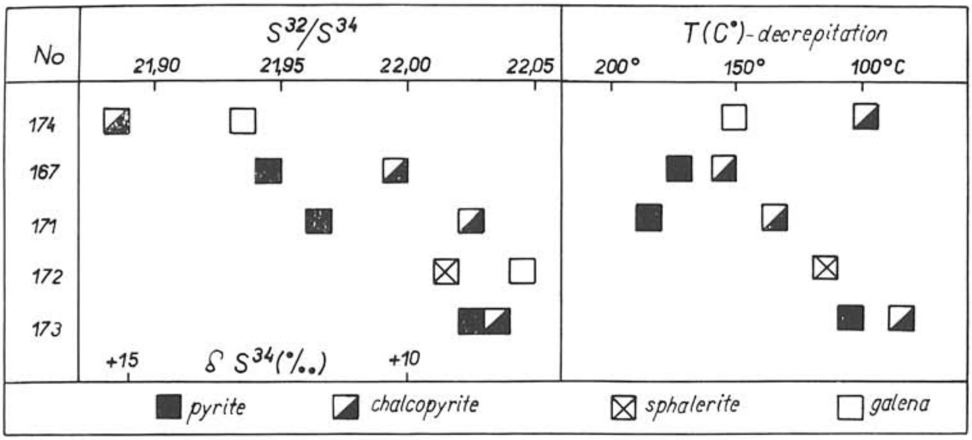


Fig. 39. Sulphur isotope ratios in coexisting mineral pairs (left side of graph), with corresponding decrepitation temperatures (right side). Smolník deposit.

Under these conditions identical sulphur isotope ratios in different coexisting sulphides would be expected. In Table 2, page 27 results are presented for samples from different veinlets and bands. All supposedly contemporaneous mineral pairs display slight, but distinct differences in isotopic composition.

Sulphur in pyrite is in all cases heavier than in chalcopyrite. Galena was found to carry lighter sulphur than coexisting chalcopyrite, sphalerite and tetrahedrite.

Although the data are meager still, they indicate that increasing amounts of the light sulphur isotope S^{32} are built into the lattices of contemporaneous minerals from pyrite-carrying the heaviest-, through chalcopyrite, sphalerite, tetrahedrite, to galena-displaying the lightest sulphur.

Instructive is the relation between sulphur isotope ratios (permil values) and the thermality of minerals presented in Fig. 36, page 28. The thermality was measured by a highly sensitive thermo-vaccummetric device, constructed at the D. Štúr Institute of geology by one of the authors (J. K.) with K. Eliáš and J. Lux. Decrepitation graphs are presented in Fig. 37, 38, page 30, 32.

In the graph Fig. page 28 the disseminated ores occupy a distinct field, which is characterized by low 32 to 34 ratios and high decrepitation temperatures. The massive and banded ores display similar decrepitation ranges but have slightly lighter sulphur. In both, the dispersed and massive ores, the decrepitations correspond with the lowest, uncorrected, recrystallization temperatures.

The S^{32}/S^{34} ratio against decrepitation temperature plots for minerals of veinlets which carry heavier sulphur and were formed at higher temperature, issue from the field of the disseminated ores. With decreasing thermality a marked increase in the S^{32}/S^{34} ratios is observed.

In the present work no marked difference in crystallization temperature between hexaedral and pyritohedral pyrite was found, both belonging to the 190—250 °C range. The rare octohedral pyrite formed below 100 °C.

In the first part of the graph Fig. 39, page 33 coexisting sulphides are arranged by their increasing S^{32}/S^{34} ratios, whereas the second shows the distribution of the respective decrepitation temperatures. Certain correlation is evident even from these few examples. Detailed investigations on richer material may clarify better he temperature dependance of the fractionation factor for coexisting sulphide pairs.

The papers by E. Dechow (1960), W. M. Tupper (1960), A. Smitheringale, M. L. Jensen (1963), F. Buschendorf et al. (1963) a. o. contain data concerning differences in isotopic composition of coexisting sulphides. It was only Tatsuo Tatsumi (1965) who paid attention to the fractionation of sulphur between sulphides.

His observations are based — with the exception of the metamorphosed Hitashi deposit — on samples from Late Tertiary deposits of Japan.

The following fractionation factors were found for sulphide pairs from Japanese deposits (Tatsuo Tatsumi) and for the veinlets of the Smolník deposit:

Mineral pair	Fractionation factor	
	Japan	Smolník
chalcopyrite-pyrite	1,0005—1,0016	1.0005—1,0014—(1.0027?)
galena-tetrahedrite	1.0028	1,0009
galena-sphalerite	1.0009—1.0034	1.0009
galena-chalcopyrite	1.0024	1.0018

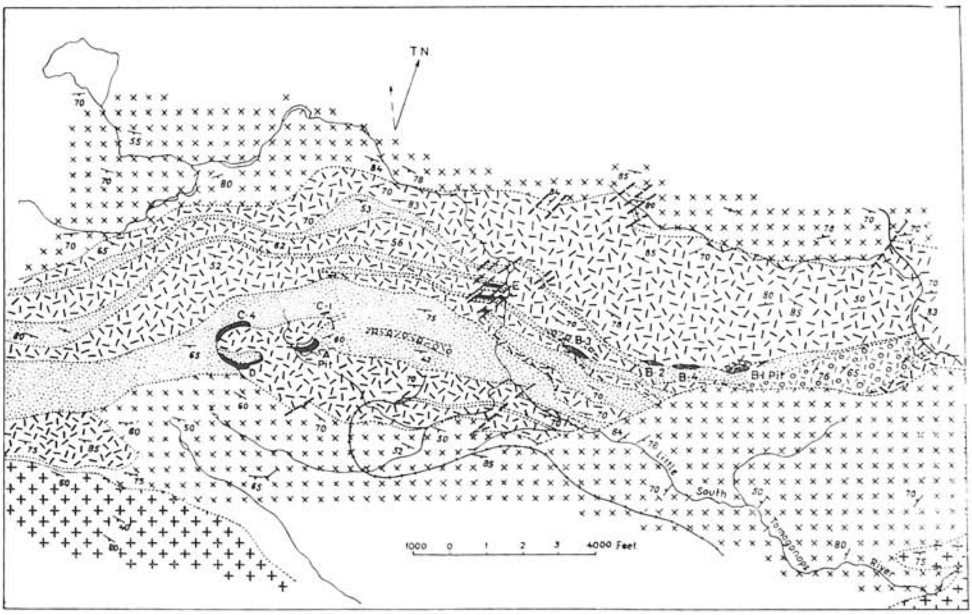


Fig. 40. Geological map of Heath Steele mine area, Canada. After E. Dechow 1960. 1 — Basic volcanic rocks, 2 — Siliceous volcanic rocks, 3 — Sulphide bodies, 4 — Quartz and quartz feldspar porphyries, 5 — Quartz eye rocks, 6 — Quartz sericite schists, 7 — Geologic contacts, 8 — Inferred faults, 9 — Folliation, 10 — Schistosity, 11 — Fracture cleavage.

Low thermality of the Japanese samples was supposed by Tatsuo Tatsumi and was measured for the Smolník deposit by the authors. Practically identical ranges of fractionation factors were found.

The fractionation of sulphides is explained by the following isotope exchange reactions (Tatsuo Tatsumi):

$$S^{32''} + PbS^{34} = S^{34''} + PbS^{32}$$
$$S^{32''} + FeS_2^{34} = S^{34''} + FeS_2^{32}$$
$$PbS^{34} + FeS_2^{32} = PbS^{32} = eFS_2^{34}$$

In contrast to the hydrothermal sulphides of Japan, the veinlets of the Smolník deposit were formed by mobilization from older exhalative sedimentary mineralizations. The isotopic constitution might have been therefore — with respect to the primary mineralization — modified two times.

During the process of resolution the more mobile S^{32} isotop might have been preferentially removed from the sulphides, producing solutions enriched in S^{32} and sulphides depleted in S^{32}.

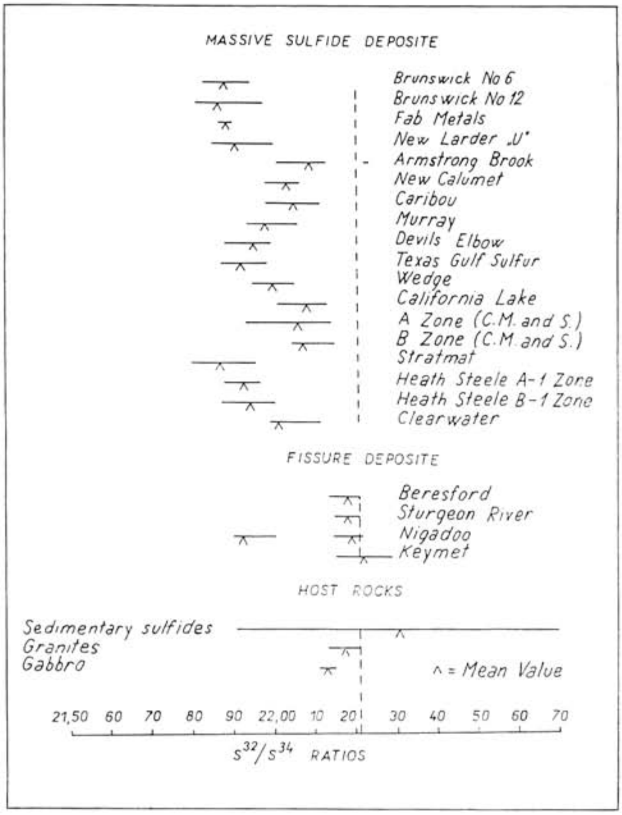


Fig. 41. Sulphur isotope variations in the Bathurst-Newcastle area, Canada. After W. M. Tupper 1960.

The final modification was connected with the precipitation of the sulphides in the veinlets. The fractionation of sulphur isotopes between various sulphides was governed by the P-T conditions and the lattice energy of the minerals formed.

The sulphur of the veinlets thus seems to exhibit an enrichment in S^{32} with respect to the primary mineralization as well as an enrichment in the same isotope according to mineral species in coexisting minerals which increases from pyrite to galena.

Comparison with Other Sulphide Deposits

Similar types as the Smolník-Mníšek mineralizations seem to be present among the metamorphosed pyrite and pyrite-polymetallic deposits of Eastern Alps in Austria. The geological setting is analogous and so are the ores. Isotopic evidence is still lacking. Sulphur isotope ratios in pyrite-pyrrhotite-galena ore of the Walchen near Oblaren deposit (Table 1, No 13) are in the range of polymetallic ores from Smolník-Mníšek. Earlier the authors (J. Kantor, M. Rybár 1962) have found similar isotope ratios in galenas. Though these single analyses are not in contrast with such assumption, a large quantity of sulphur isotope ratios based on detail investigations is needed, owing to the variations of sulphur isotopes in metamorphosed deposits of this type.

Regarding the sulphide deposits of the Bathurst-Newcastle area, Canada, sufficient data are available to reveal similar features as the Smolník-Mníšek nad Hnilcom deposits. The similarities cover geology, stratigraphic position, ore deposits, mineralogy and sulphur isotopes.

A review of the geology of the area was published by H. C. Smith and P. Skinner (1958). Futher details regarding geology and ore deposits contain papers by E. R. Lea, C. Rancourt (1958), E. Dechow (1960), W. M. Tupper (1960), the last two with rich isotope data.

The large sulphide bodies of the area are confined to the Ordovician folded belt which is in the east unconformably overlain by the flat lying Pennsylvanian and to the north deeps under the Silurian belt.

The Ordovician belt consists of siliceous volcanic rocks, porphyries, basic volcanic rocks, siliceous and argillaceous sediments. Their relations are not always clear. The siliceous metasedimentary rocks are generally older than the siliceous volcanic rocks, whereas the argillaceous are generally younger. The age of the later was confirmed by graptolite finds as Middle Ordovician.

The siliceous metasedimentary rocks are quartzose, with varying amounts of sericite, chlorite, whereas the argillaceous include vari-coloured slates, locally graphitic or ferrugineous. Both types are at places interbeded.

The siliceous volcanics with corroded and fractured felspar ± quartz phenocrysts contain breccias and agglomerates, and are therefore regarded mostly as of tuffaceous origin.

The porphyries include-owing to various origin and grade of metamorphosis-rocks displaying great variability. Characteristic are large phenocrysts of quartz and/or feispar in a shistose groundmass of quartz, felspar, sericite and chlorite.

In the Spiš-Gemer Ore Mts. the term porphyroid is used to designate practically identical rocks with the porphyries of the Bathurst-Newcastle area.

Basic rocks include diabase dykes and sills, rare gabbros and diabase effusives, metamorphosed to greenstones. The later are commonly interlayred with sediments, though tuffaceous varieties occur within the siliceous volcanic rocks, too.

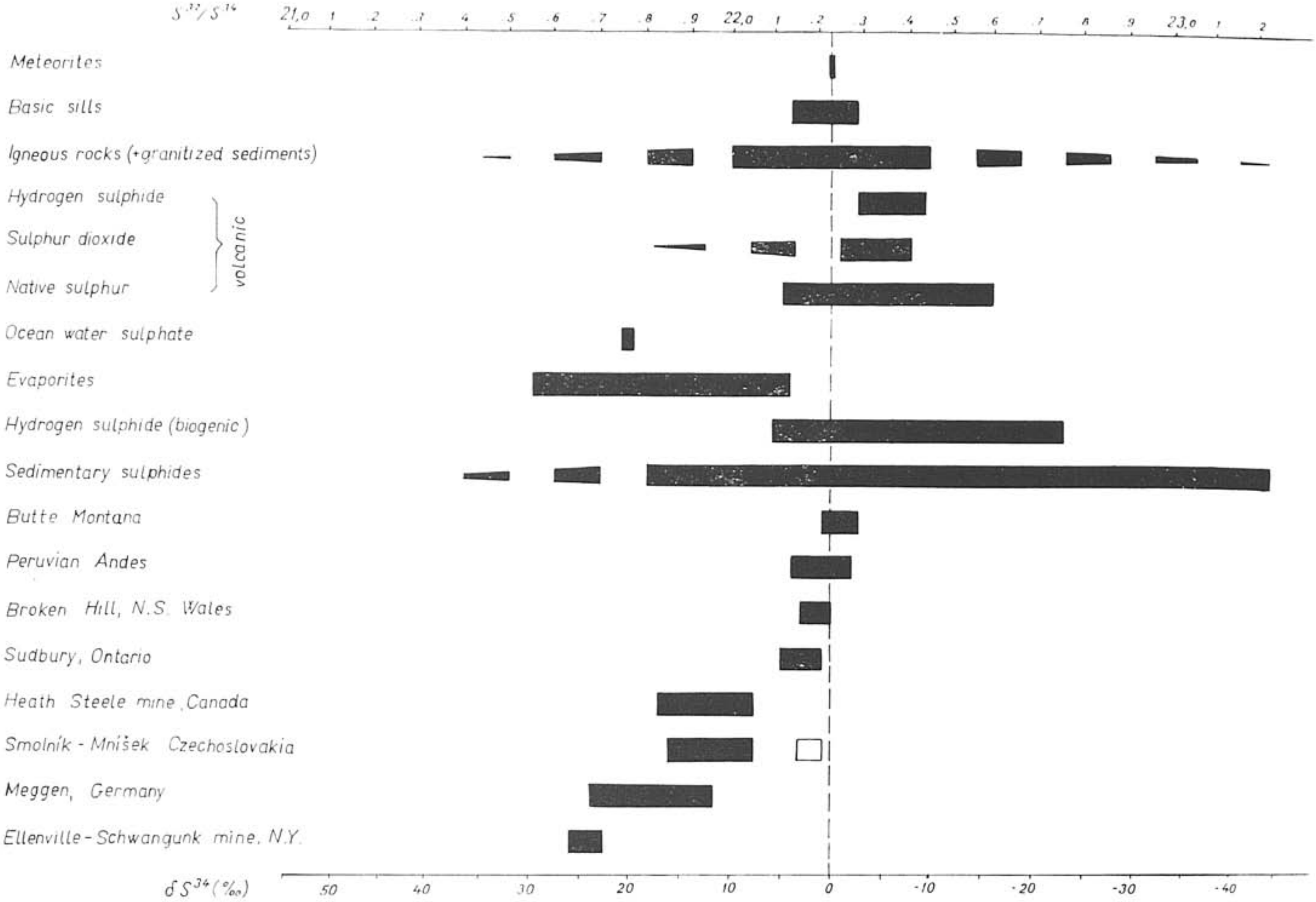


Fig. 42. Sulphur isotopes of various origin and in selected ore deposits, compaired with the Smolník-Mníšek nad Hnilcom deposits. W. U. Ault, J. L. Kulp 1959, H. G. Thode 1963, M. L. Jensen 1957, 1959, E. Dechow 1960, F. Buschendorf et al 1963, present paper.

The ordovician is penetrated by granites of post middle Silurian and pre-Pensylvanian age.

Sulphide deposits are of two types:

1. Massive sulphide bodies. Generally very fine grained pyrite with pyrrhotite, sphalerite, chalcopyrite, galena, arsenopyrite, marcasite, tetrahedrite-tannantite a. o.

2. Small, coarse grained fissure deposits.

Most of the massive sulphide deposits occur within the interlayered sedimentary-„porphyry" complex. The majority being spatially related to the porphyry-sedimentary contacts. Volcanic rocks are barren. Sulphide bodies are common in chlorite schists, ferruginous slates, or iron formation.

E. Dechow (1960) reports for the Heath Stelle mine (Fig. 40, page 34, compare with Fig. 33, page 20) isotope ratios within the range 21. 82 to 22. 03. A magmatic hydrothermal origin and genetic relations to granites are admitted.

The distribution of sulphur isotopes in most of the sulphide deposits of the area was studiet by W. M. Tupper (1960). The summary is reproduced in Fig. 41, page 35. S^{32}/S^{34} ratios for the massive sulphide bodies range 21.88 to 22.05. For the hydrothermal vein deposists the very narrow spread of 22.18 to 22.21 was found. (Compare with Fig. 42, page 37 and Fig. 34, page 21.) W. M. Tupper too postulates an epigenetic origin for the massive ores and emphasizes genetic relations to granites.

Sulphide deposits of this type seem to be confined to Cambro-Silurian volcanogenic-sedimentary sequences with dominating porphyry volcanism which is closely associated with basic rocks.

The exhalative sedimentary deposits of Meggen (F. Buschendorf et al. 1963) and Rammelsberg (G. Anger et al. 1966) in Germany show less agreement with the Smolník-Mníšek nad Hnilcom mineralizations in sulphur isotopes distribution (Fig. 42).

Conclusions

In the Cambro-Silurian series of the Spiš-Gemer Ore Mts.

a) hydrothermal quartz-siderite-sulphide veins and

b) disseminated to massive pyrite and pyrite-polymetallic ore deposits occur.

Microscopic examinations of the later type were carried out and sulphur isotope distribution studied.

The mineralization is confined to a sedimentary-volcanogenic complex. Porphyroids — mostly water-laid, metamorphosed, tuffs, tuffites, and lavas — prevail. They are associated with more basic types, up to diabases and their metamorphosed pyroclastic-chlorite schists. Intercalations of products of the acide and basic volcanism occur.

Colloidal textures are abundant in the massive ores. Deformation, recrystallization and remobilization phenomena are common.

The disseminated pyrite ores occur prevailingly in chlorite schists. The range of sulphur isotope ratios is very nerrow (21.86 to 21.95), indicative of derivation from a well homogenized source.

Owing to the considerable enrichment of sulphur in the heavy isotope, digestion of sulphate-rich sediments by the granitization processes by which the cource was formed, is postulated.

The massive ores display slightly higher ratios (21.98 to 22.0), the range being sharp, too. Bacterial activity might have in certain parts, and to a very limited extend only, modified the distribution of sulphur isotopes.

The principal distribution was governed by the magmatic (granitization) source and the evalution of the sulphur isotopes within. Slight enrichment in S^{32} as well as in Cu-Pb-Zn contents with time seems to be characteristic. This enrichment reached it's maximum during the formation of the polymetallic ores in Mníšek nad Hnilcom.

The disseminated and massive ores are of exhalative sedimentary origin, derived from submarine springs of magmatic hydrothermal solutions.

Mobilization into thin veinlets during hercynian and alpine movements was common. The more mobile Cu-Pb-Zn minerals were preferentially concentrated in the young veinlets with quartz-carbonate gangue. The sulphur is generally lighter than in disseminated ores and displays wider ranges in isotope ratios.

For the recrystallization of the syngenetic ores decrepitation temperatures of 200—250 °C were measured. The thermality in veinlets ranges 80 to 200 °C.

An increase in S^{32} content with decreasing thermality of sulphides was found.

Fractionation of sulphur isotopes between coexisting sulphides is always present.

Two tendencies seem to be indicated by the distribution of sulphur isotopes in metamorph-mobilized veinlets:

1. General incerase in S^{32} with respect to the primary, exhalative sedimentary mineralization.

2. Fractionation during precipitation which results in an increase of S^{32} in coexisting cinerals according to mineral species, from pyrite, carrying the heaviest sulphur, through chalcopyrite, sphalerite, tetrahedrite to galena characterized by the lightest sulphur.

Deposits with similar characteristics and sulphur isotope distribution were describedfrom the Bathurst-Newcastle area, Canada, by E. Dechow (1960) and W. M. Tupper (1960).

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