Mobilization of Ore and Gangue Minerals in Some Slovenian Mineral Deposits

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With 11 Figures

Summary

During the Alpidic orogeny the ore and gangue minerals in Permian and probably also in Triassic deposits were mobilized. Illustrative examples of mobilization have been found in the copper deposit Škofje and in the uranium deposit Žirovski vrh, where Middle Permian clastic rocks contain numerous quartz and quartz-carbonate veins. In those places where the ore beds are cut by the veins these contain also ore minerals. Proofs for mobilization have been found furthermore in the mercury deposit Idrija; syngenetic ore beds include epigenetic cinnabar and cinnabar-quartz veinlets.

An attempt has also been made to interpret the origin of the discordant orebodies in the lead-zinc deposit Mežica by mobilization of ore and gangue minerals from mineralized Wetterstein carbonate rocks containing concordant orebodies. In favour of such an interpretation especially the different characteristics of galena in concordant and discordant orebodies can be considered; mobilization should include geochemical differentiation and homogenization of sulfur isotopes.

Introduction

The most important Slovenian mineral deposits are situated in the Permian and Triassic beds. During the Alpidic orogenic cycle they were brought into deeper parts of the litosphere, to be later on, following the paroxysm of the orogeny, brought to higher levels. Under such circumstances in some deposits ore and gangue minerals were mobilized. In certain cases the evidence for mobilization is very convincing, although all physico-chemical conditions of process are not known. In other cases

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many data speak in favour of the mobilization of ore and gangue minerals, but indisputable proofs are still missing.

Changes and developments in concept of genesis of our mineral deposits in the last 20—25 years resulted also in the recognition of mobilization. Thus, for instance, for many years the opinion prevailed, that copper deposits in the Middle Permian Val Gardena sandstones are in close relationship with magmatic activity. Now we are convinced that copper sulfides originated during the diagenesis of clastic sediments. Veins and veinlets cutting the mineralized sandstones have been used in the past to demonstrate the magmatic-hydrothermal origin of these deposits. Today they are regarded a product of epigenetic mobilization of ore and gangue minerals. In a similar way originated also veins and veinlets in the uranium deposit Žirovski vrh as well as in a part of the mercury deposit Idrija. In all these cases the distances of migration of material are small, generally measurable in centimeters, decimeters and meters.

On the contrary, in the lead-zinc deposit Mežica several important orebodies probably originated by mobilization of material from more distant sources.

Let us look now at mentioned examples!

Copper Deposit Škofje

We made acquaintance with the mobilization of copper sulfides and gangue minerals during exploration of the Škofje deposit which is situated in the western part of the Sava folds. Orebodies occur in the upper part of the Val Gardena sandstones where red coloured clastic rocks prevail, but the mineralization always took place in the gray and green varieties. In the past the copper mineralization was considered to be associated with the Tertiary (I. GANTAR, 1952) or with the Triassic (S. GRAFENAUER, 1966) igneous activity. Yet, the distribution of orebodies in a distinct part of the Middle Permian sequence, ore fabrics, absence of hydrothermal alterations, as well as geochemical characteristics of ore minerals speak in favour of diagenetic origin (M. DROVENIK, 1968, 1970).

The ore bearing beds were covered by Upper Permian, Mesozoic and Tertiary sedimentary rocks with a total thickness of some 5,000 m. Practically no mobilization appeared in the mineralized beds while lying in the region of higher pressure and temperature. But this process started when the Permian beds were uplifted during the Alpidic orogeny. Some detrital components as well as minerals grown in diagenesis were mobilized. In such a manner originated several generations of ore and gangue minerals.

Orogenic movements caused fissuring and fracturing of Permian sedimentary rocks. The pressure was lower in the fissured and fractured zones than in the intact parts of rocks. Thus the mobilization started. First were formed metasomatic quartz veins and veinlets, which often cut sandstone beds, but terminate on the contact with shales. Even megascopically, the striped texture caused by platy, parallel lying quartz grains can be visible here and there. The orientation of quartz grains changes often in individual veins, which proves that the beds rotated during the orogeny, or that the pressure changed its direction. Under the microscope the platy quartz grains are somewhat troubled (Fig. 1). The contact between veins and wallrock is usually blurred. In larger veins, especially under crossed nicols, the striped texture is well visible (Fig. 2). Some quartz veins include younger, also platy carbonate grains (Fig. 2).

Later numerous metasomatic quartz veins and veinlets were crushed. Individual quartz fragments have undergone aggradational recrystallization. Although the striped texture is somewhere still visible, at least under the microscope. Now first the younger generation of quartz crystallized, forming thus a cement of crushed veins and veinlets. Its grains are perfectly clear (Fig. 3) and grow on older quartz grains in optical continuity (Fig. 4).

More or less simultaneously with quartz ore minerals were mobilized, especially chalcopyrite and bornite, which also represent the cement of crushed quartz veins (Fig. 3). With the younger generation of quartz and with sulfides are quite often associated idiomorphic and hypidiomorphic albite grains. In some veins are present only isolated albite grains, in others they are accumulated in groups; individual grains are dispersed in the younger generation of quartz or in the sulfide patches (Fig. 5). Under higher magnification the twinning lamellae are well visible (Fig. 6). Albite grains are often slightly corroded by copper sulfides, otherwise they are perfect clear, even in the case when surrounded by copper sulfides (Fig. 7). Mutual relationships indicate that albite grains are younger than quartz, but older than copper sulfides. In mineralized siltstone also albite-chalcopyrite veinlets occur (Fig. 8).

Beside the mentioned veins and veinlets in the Škofje deposit also up to 0,5 m large ore veins have been observed, cutting several beds of mineralized sandstones, siltstones and shales. They contain the youngest generation of quartz as well as newly formed carbonates, albite and ore minerals. All minerals occur predominantly in small xenomorphic grains. However, the walls of cavities are encrusted with very well developed crystals of quartz, calcite, dolomite, albite and of sulfides; chalcopyrite crystals attain even 3 cm. No such chalcopyrite crystal was found, to my knowledge, in the famous copper deposit Bor, Eastern Serbia. By their appearance these veins are similar to the veins occurring in the magmatic hydrothermal copper deposits. Therefore it is not surprising that in the past they have been presented as a proof for magmatic hydrothermal origin of Škofje.

Finally it should be stated, that in the Škofje deposit also the Upper Permian carbonate rocks are mineralized. But the ore minerals have been found only at their contact with the mineralized Middle Permian Val Gardena sandstones. Copper sulfides spread at most 1,5 to 2 meters into the Upper Permian dolomites. It can be therefore concluded that the ore minerals and quartz were mobilized from the Middle Permian into Upper Permian sedimentary rocks.

Uranium Deposit Žirovski vrh

As the copper deposit Škofje, also the uranium deposit Žirovski vrh is situated in the western part of Sava folds. However, opposite to Škofje, the orebodies in

Žirovski vrh lie in the lower part of the Middle Permian Val Gardena clastic sedimentary sequence, where the gray coloured varieties are by far the most common (V. OMALJEV, 1967; E. LUKACS, A. P. FLORJANČIČ, 1974; T. BUDKOVIČ, 1980). Uranium mineralization originated during the diagenesis of clastic sediments. Beside pitchblende and coffinite also several sulfides precipitated. The most common are pyrite, galena, sphalerite, chalcopyrite and arsenopyrite.

During the Alpidic orogeny also in Žirovski vrh numerous quartz and quartz-carbonate veins were formed (T. DOLENEC, 1979) which, grosso modo, have the same characteristics as the veins from Škofje. When they cross the orebodies, sulfides are also present. Anyway, practically no pitchblende or coffinite were found in mentioned veins or veinlets, which indicate that the conditions were not appropriate for mobilization of these two minerals.

The youngest are calcite-pyrite veins. Calcite grains include or are encrusted by pyrite (Fig. 9). In the vugs occur very well developed calcite scalenohedrons, covered by tiny pyrite crystals. These veins are tectonically undisturbed. Both minerals, calcite and pyrite very probably are crystallizing in the deeper part of the deposit even today.

Mercury Deposit Idrija

Detailed explorations show that the mercury deposit Idrija originated during the Middle Triassic magmatic-tectonic evolution (B. BERCE, 1958, 1977; I. MLAKAR, M. DROVENIK, 1971). Two phases of mineralization can be distinguished. In the first one along subvertical faults in the Carboniferous-Permian, Permian, Scythian and Anisian sedimentary rocks metasomatic and network mercury orebodies were formed. During the second phase the hydrothermal solutions additionally mineralized the mentioned sedimentary rocks, as well as the Langobardian conglomerate. Then they issued to the bottom of the sedimentary basin, situated just above the deposit, where also clastic and pyroclastic material, together with organic remnants were deposited. In this way originated the highly mineralized Langobardian Skonca beds. They contain several types of syngenetic mercury ores, but the most characteristic is the so-called steel ore, forming conformable beds and lenses, and composed mainly of organic matter (sapropelite) and cinnabar. Microscopic observation reveals botryoidal colloform masses of cinnabar, intimately intergrown with gangue, or tiny impregnations of cinnabar in organic matter. Due to the variable concentration of cinnabar in particular layers the bedded structure is usually well visible.

In the overlying Langobardian tuffs and tuffites have been found two ore bearing horizons, showing the graded bedding of syngenetic ore; individual grains are composed of cinnabar and chalcedony.

Also Idrija was covered by Upper Triassic, Jurassic, Cretaceous and Tertiary sedimentary rocks in total thickness of about 4,500 m, and then uplifted during the Alpidic orogeny. Post Triassic tectonic movements caused fissures and fractures in the "steel ore". In the open spaces were mobilized cinnabar and organic matter.

Especially the cinnabar veinlets crossing discordantly the "steel ore" beds and lenses are often present (Fig. 10). The cinnabar ore lying in the Langobardian tuffs and tuffites contains quartz-cinnabar and cinnabar veinlets (Fig. 11), which originated by mobilization of mercury from intact parts of the ore into the fractured ones.

The youngest mineralized beds in the Idrija deposit are Cordevolian dolomites. However, it should be stated, that the cinnabar veinlets appear only close to the contact with mineralized Carboniferous-Permian beds; cinnabar was very probably removed from these beds.

No other proofs have been found for mercury mobilization in Idrija deposit, in spite of the fact that beside cinnabar also the more mobile native mercury is present in the ore. The Upper Triassic sedimentary rocks (with exception of the cited Cordevolian dolomits), as well as Jurassic, Cretaceous or Tertiary beds in Idrija deposit, its surroundings and on the whole territory of Slovenia, are completely free of mercury mineralization.

Lead-zinc Deposit Mežica

Thus we come to our economically most important and geologically most interesting mineral deposit, to the lead-zinc deposit Mežica, situated in the Northern Karavanke. Here were mineralized the Middle Triassic Wetterstein limestones and dolomites. In the upper part of more than one thousand meter thick Ladinian carbonate rocks sequence several types of orebodies can be distinguished, but the most important are the concordant and discordant orebodies.

The origin of the Mežica deposit is still controversial, as it is the case with several other lead-zinc and zinc-lead deposits of the Eastern Alps. If overlooking the opinions of geologists which have visited Mežica for a short time only, and taking into account the opinions of geologists which worked in Mežica for a longer period, thus having possibility to study the ore deposit in detail, then five theories could be mentioned:

(1) The first one (A. Zorc, 1955) suggests that "the ore deposit is of Triassic age most probably and has been formed syngenetically out of the submarine hydrothermal solutions. Later it has been influenced by tectonic, metasomatic, and oxidation changes."

(2) The second theory favors the syngenetic-sedimentary origin of concordant orebodies, but did not determine precisely the source of lead and zinc. Discordant orebodies are of post Triassic age. They may have been formed by hydrothermal activity related to post Jurassic, most probably to Tertiary igneous events which gave tonalite, tonalite-porphyrite and dacite on the Pohorje mountain and tonalite in the Železna Kaplja-Črna zone (I. Štrucl, 1965).

(3) The third theory explains the origin of the concordant orebodies in the same way as the second one. For the formation of the discordant orebodies, which are of post Triassic age, it proposes however a hydatogenic resedimentation (I. Štrucl,

1971). "Whether diagenetic processes i.e. recrystallization, resedimentation, redeposition played an important role can just be proved when further investigation yield results."

(4) The basic assumption of the fourth theory is that the Mežica deposit, according to the hypothesis of H. SCHNEIDERHÖHN, is of regenerated type (S. GRAFENAUER, 1958). "The principal phase of mineralization took place in the time of the Variscic orogenesis. Through the orogenesis during the Alpine phase the ore content of the old Variscic deposit was put in motion and a posttectonic regenerative ore deposit was formed."

(5) The fifth theory advocates the epigenetic hydrothermal origin in connection with the Middle Triassic Wengenian magmatism (S. GRAFENAUER, 1965, 1969).

In the frame of this paper, I would only like to call attention to some facts which can be used for the interpretation of origin of the concordant and discordant orebodies, and shall help us to answer the question about the mobilization of ore and gangue minerals in this deposit.

The *concordant* orebodies (called also conformable or stratabound sill type orebodies) are situated 10–15 m, 20–25 m, 50–60 m, 90 m and 130–150 m below the Raibler shale, which indicate the affiliation of orebodies to definite horizons of the Ladinian lithologic sequence. The ore shows predominantly epigenetic metasomatic replacement structures, but in several orebodies the ore fabrics are present, which can be interpreted as sedimentary ones. Very characteristic are the so-called "Bodenerze" consisting of rhythmic, thin lamellar ore minerals-dolomite layers. By mass-spectrometric analyses it was found that the sulfide sulfur is enriched in ligther isotope and that $\delta^{34}S$ values oscillate in broad range. So for example the $\delta^{34}S$ value for the sulfides from the Navršnik section varies from –1,70‰ to –20,93‰ (M. DROVENIK et al., 1980 b). Galena has only a few trace elements, and even those in small quantities: Ag values reach 35 ppm, Cu values vary from 1 to 100 ppm, and the Sb values from 37 to 260 ppm (M. DROVENIK et al., 1980 a).

The *discordant* orebodies (named also unconformable orebodies or Union system orebodies) are situated along post Triassic faults and fault zones. They contain predominantly ore breccias, often showing crustifications, as well as cocarde and replacement structures. The breccia fragments are represented by barren and mineralized limestones and dolomites; even limestone fragments with sphalerite and fluorite laminae displaying rhythmic structure have been found. In some cases the wall rock limestone shows a somewhat more pronounced recrystallization, detectable only under microscope, but no typical hydrothermal alterations have been reported. The sulfur is also enriched with the lighter isotope, however in opposite to the sulfur in ore minerals from concordant orebodies, the range of $\delta^{34}S$ is usually essentially smaller. Typical example offer the data for Union section, where $\delta^{34}S$ values vary from –5,38‰ to –10,80‰, and Stari Fridrih section, where they are arranged between –14,78‰ and –19,74‰ (M. DROVENIK et al., 1980 b). Galena is extremely pure. This is, as far as I know, the purest galena of all lead-zinc or zinc-lead deposits of Yugoslavia. It is practically free of Ag and Sb, only the Cu values reach 22 ppm.

Advocates of the syn- or diagenetic origin of the concordant orebodies base their assumption mainly on the distribution of the ore in definite horizons of the

Ladinian carbonate rocks sequence, as well as on the mentioned sedimentary fabrics. Let us add that the sulfide sulfur isotope composition speaks in favour of biogenic sulfur. It appears that the concordant orebodies were indeed formed during the diagenesis of the carbonate rocks. It should be anyway stated that on the origin of metals there are no more than unproved speculations.

Discordant orebodies were formed along the faults. It is, in my opinion, very significant that galena from these orebodies is poorer in trace elements than its varieties from concordant ones. Therefore it is hard to believe, that the faults and fault zones were the conducting ways for ascending hydrothermal solutions, which might then penetrate into the lithologically favorable carbonate beds and cause the formation of the concordant orebodies. The direction of solutions was probably just opposite – the ore and gangue material was mobilized from the mineralized Ladinian carbonate rocks into the faults and fault zones. This process included geochemical differentiation and the following crystallization of very pure galena, as well as homogenization of sulfur isotopes. Against the origin of the discordant orebodies from magmatic hydrothermal solutions speaks also the absence of typical hydrothermal alterations.

If this hypothesis is correct, then during the post Triassic time, most probably in the Tertiary period, in Mežica mobilization processes were active not only on the decimeter or meter, but on several 100 meter scale.

But if our interpretation is wrong, and the discordant as well as concordant orebodies originated epigenetically from magmatic hydrothermal solutions, there still remains the very delicate question of the source of these solutions, since no Yugoslav lead-zinc or zinc-lead deposit associated with Triassic or Tertiary igneous activity has such mineralogical and geochemical characteristics as Mežica.

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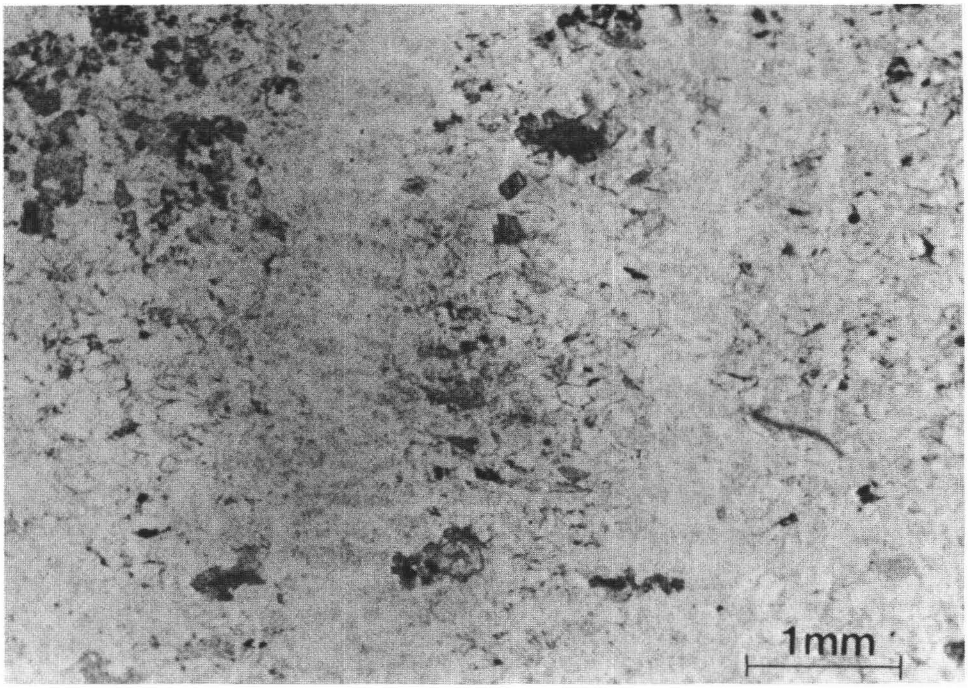

Fig. 1. Two metasomatic quartz veins with troubled grains cutting medium grained sandstone. Transmitted polarized light.

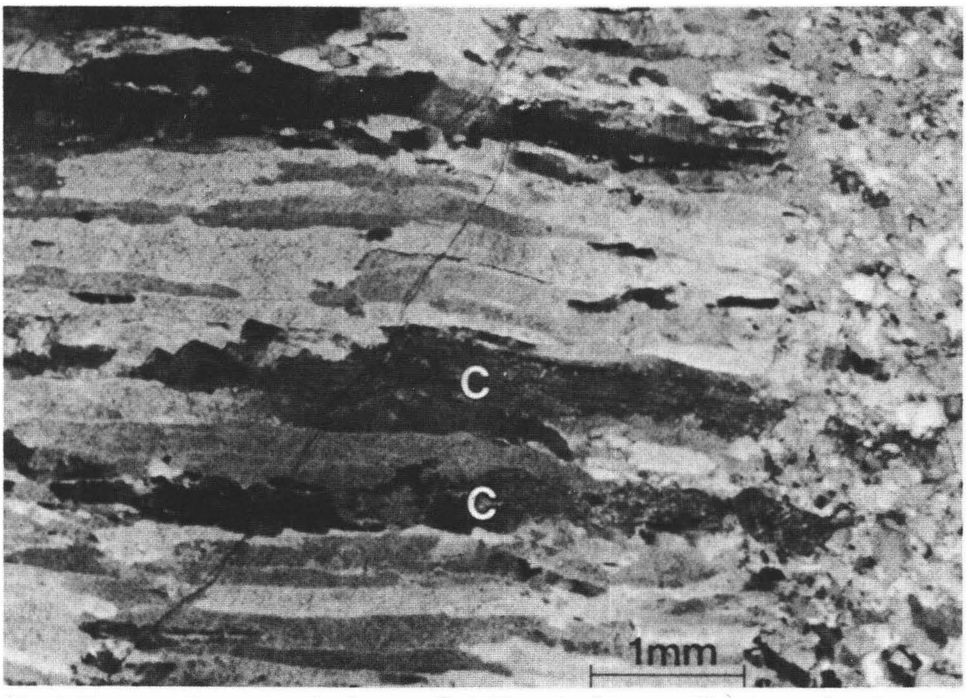

Fig. 2. Metasomatic quartz vein shows well visible striped texture. Note two carbonate grains (c)! Transmitted polarized light, + nicols.

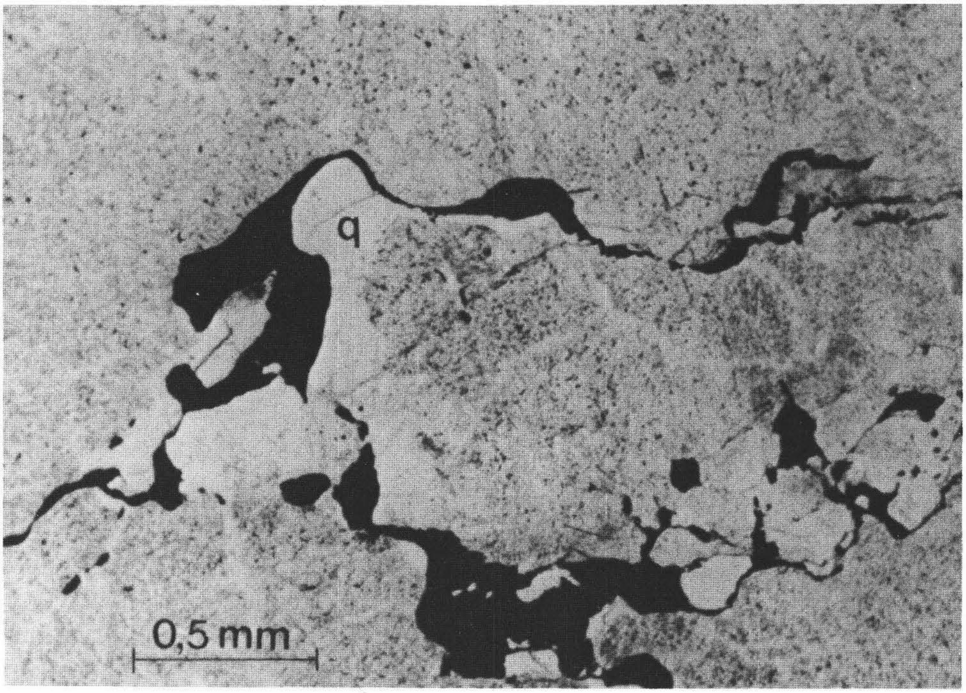

Fig. 3. Rims of younger clear quartz (q) on fragments of metasomatic quartz. Black patches are copper sulfides. Transmitted polarized light.

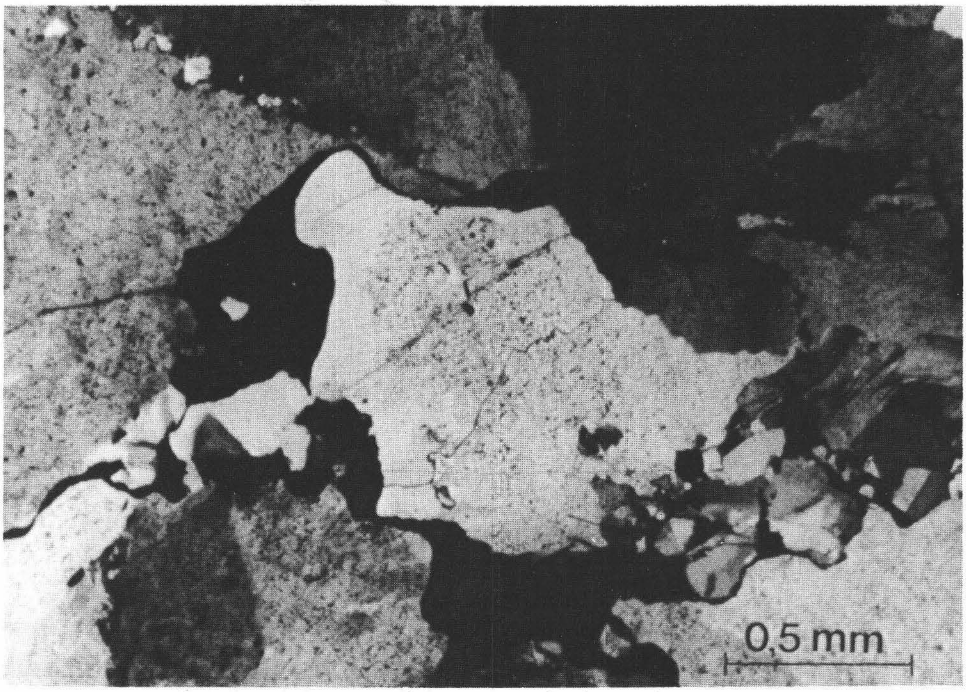

Fig. 4. Growth of younger quartz in optical continuity on older quartz fragment is well visible under, + nicols.

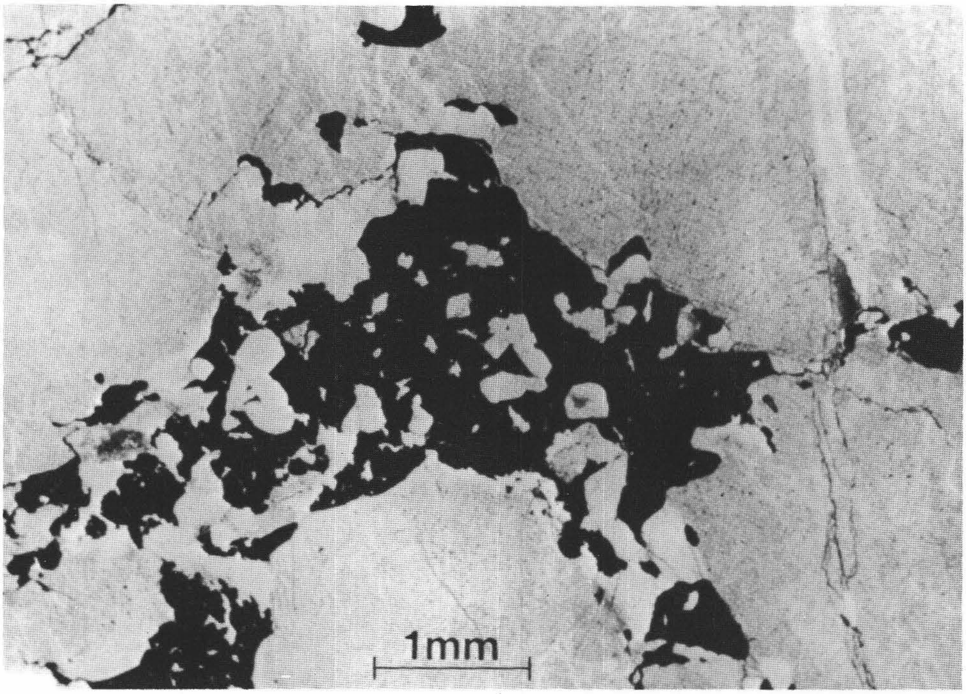

Fig. 5. Sulfide patch including albite grains. Transmitted polarized light.

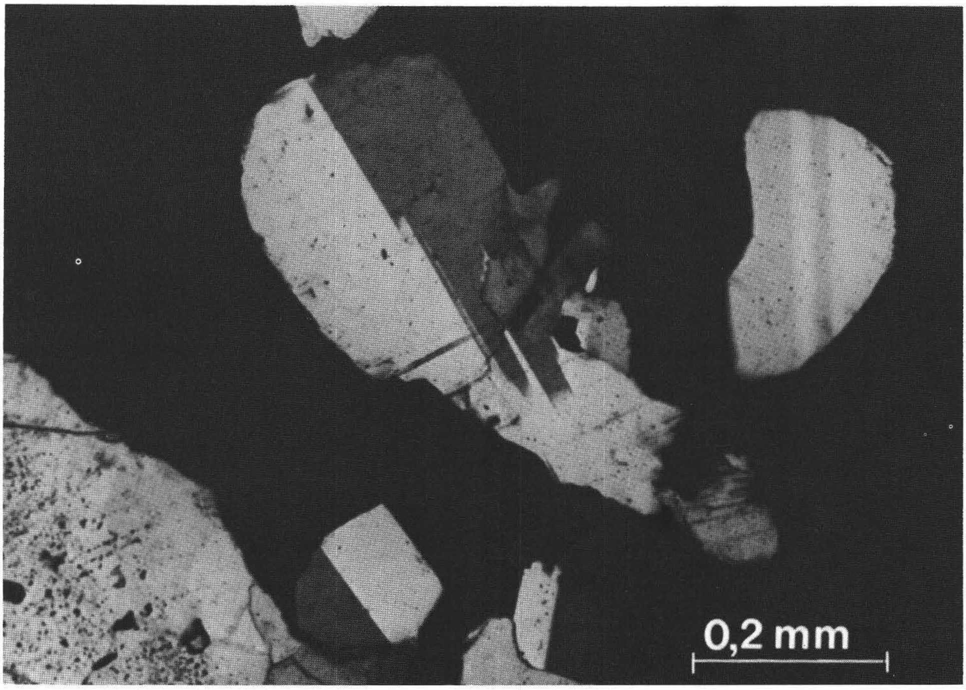

Fig. 6. Twinned albite grains from the Fig. 5. Transmitted polarized light, + nicols.

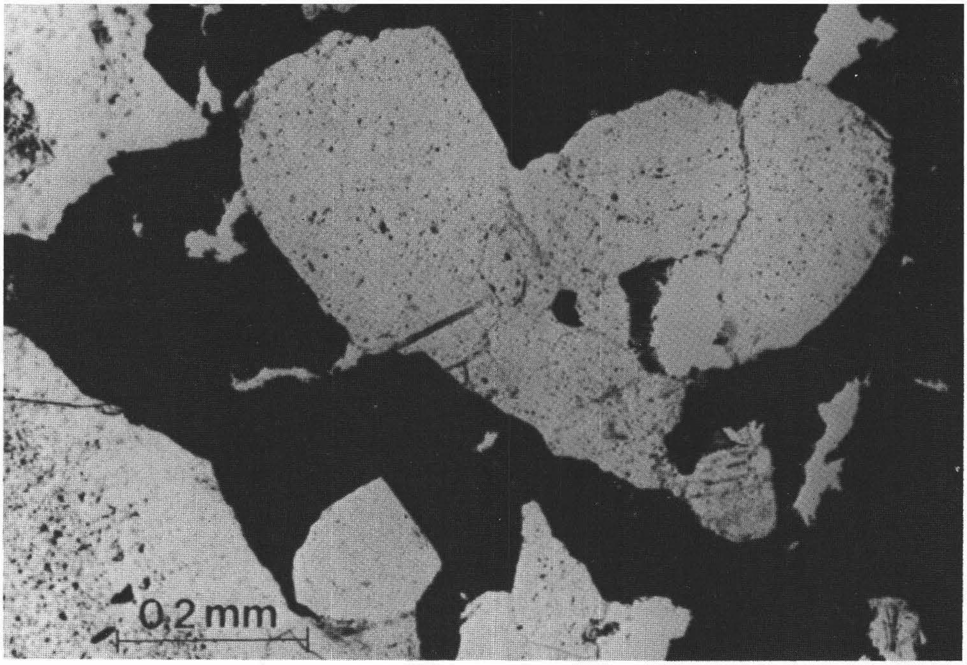

Fig. 7. Albite grains surrounded and corroded by copper sulfides. Transmitted polarized light, + nicols.

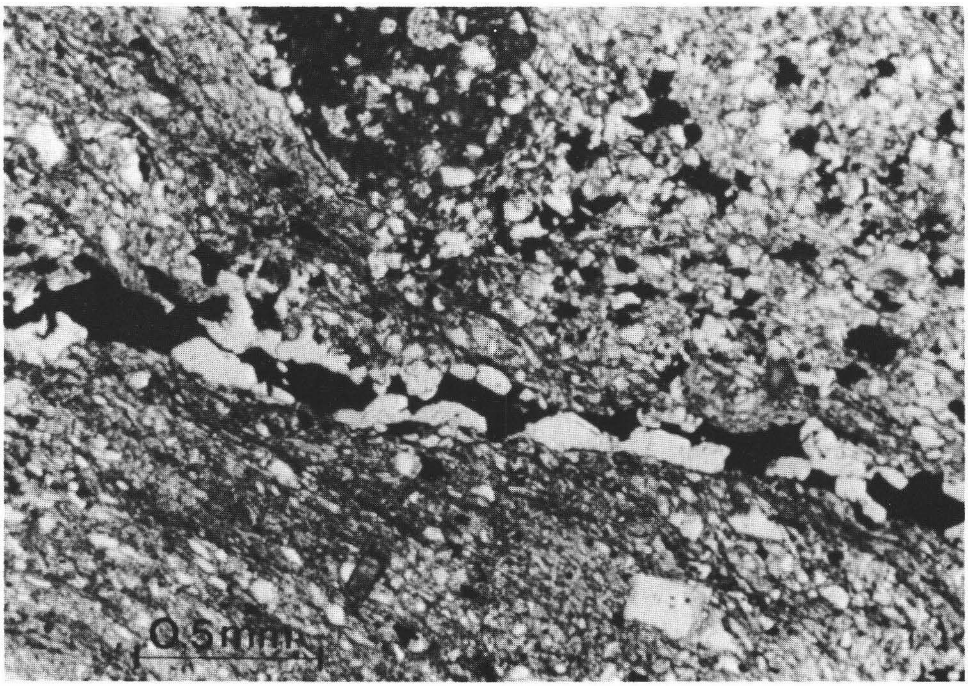

Fig. 8. Albite-chalcopyrite veinlet cutting the mineralized siltstone. Transmitted polarized light.

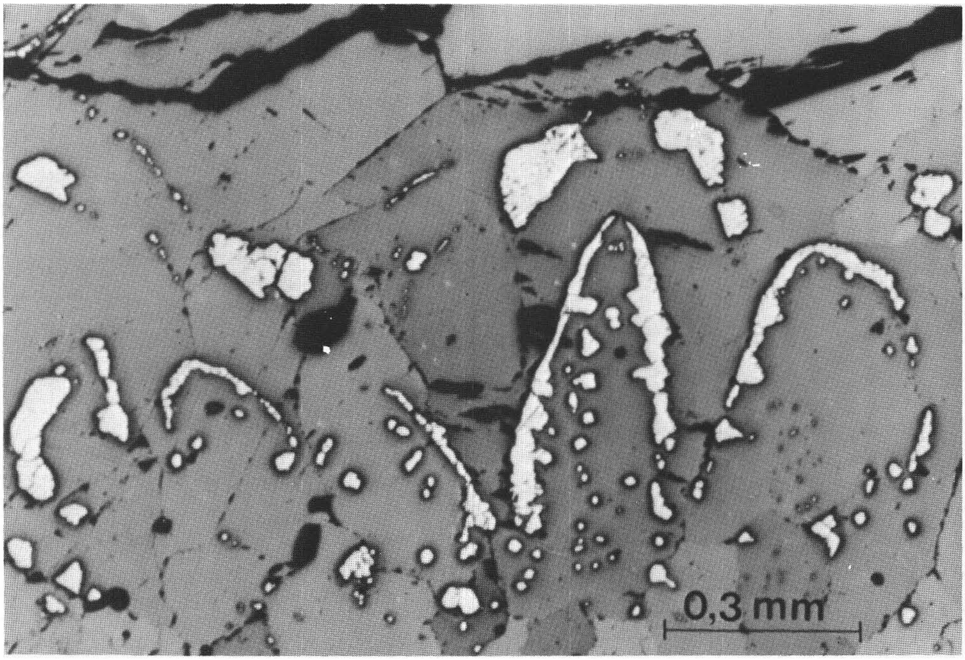

Fig. 9. Calcite grains peppered and encrusted by pyrite. Reflected polarized light.

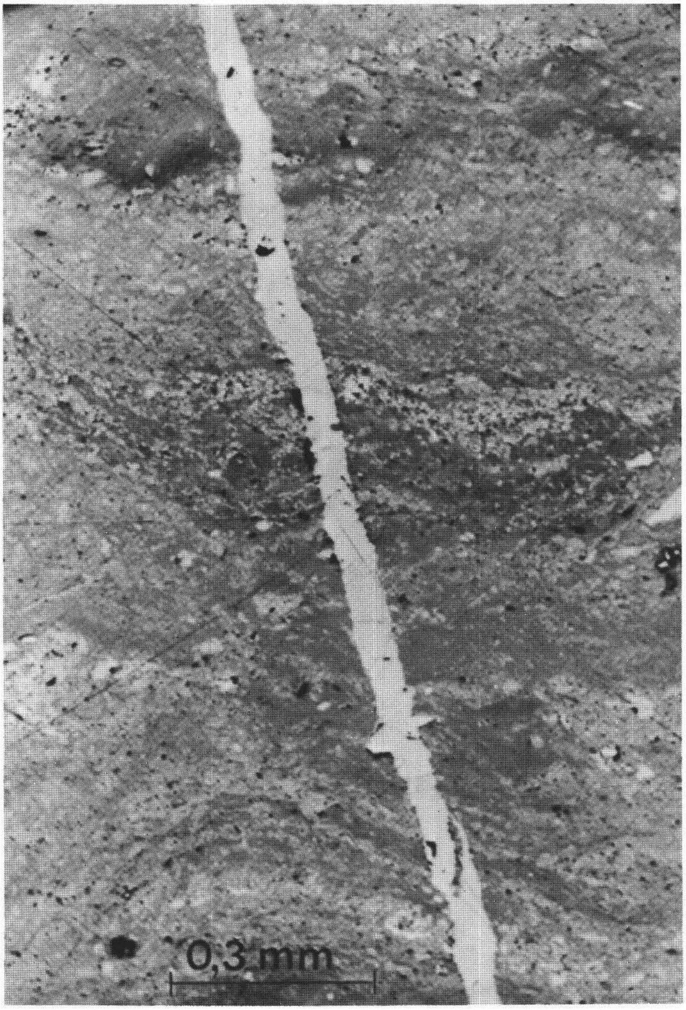

Fig. 10. Cinnabar veinlet cuts “stell ore” showing bedded structure. Reflected polarized light.

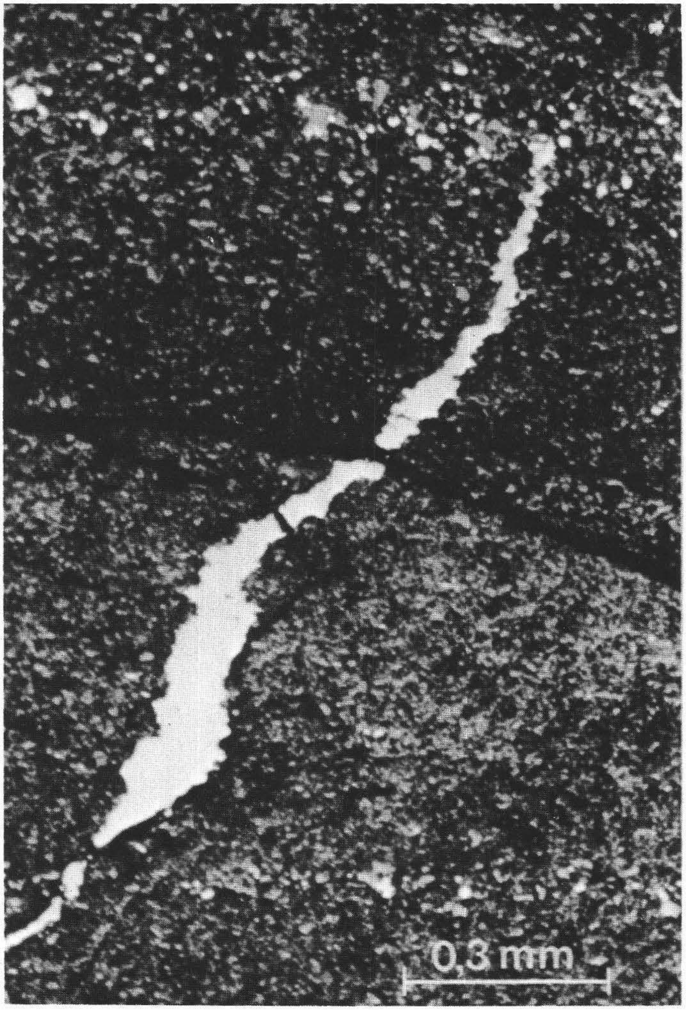

Fig. 11. Cinnabar veinlet crossing syngenetically mineralized tuff. Reflected polarized light.