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RECORD 1972/77

DOLOMITIZATION AND THE GENESIS OF THE WOODCUTTERS LEAD-ZINC PROSPECT, NORTHERN TERRITORY, AUSTRALIA

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SUMMARY

The Woodcutters L.5 lead-zinc prospect in the Northern Territory, Australia, occurs in the Golden Dyke Formation, a sequence of carbonaceous siltstone, dolomite, and greywacke forming part of the Lower Proterozoic Goodparla Group, which was deposited on an Archaean granitic basement.

An attempt has been made to show how those factors which are considered to have been significant in the formation of dolomite were also important in the genesis of the Wooductters deposit.

These factors are:

1. An evaporitic environment which favoured dolomite formation concentrated lead and zinc in the overlying solutions.
2. The base metals were further concentrated, and fixed in the sediments, by co-precipitation with the precursors of dolomite, Mg-calcite and/or aragonite.
3. The formation of dolomite during diagenesis resulted in either a structural change if the precursor was aragonite, or an ordering if the precursor was Mg-calcite. The dolomite could not accommodate the relatively large amount of base metal associated with its precursors, and as a consequence, during dolomitization these were released to the pore solutions.

The metals in the pore solutions possibly complexed with organic materials such as those from the degradation of algal protein, and so remained in solution during lithification. During folding, the metal-enriched solutions were transported to fractures, and metal sulphides precipitated when the organic complexes became unstable.

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After lithification the carbonate-quartz-sulphide veins were zones of weakness along which shearing took place, probably over a considerable period of time. This shearing, as well as slight rise in temperature, resulted in fracturing, recrystallization, andreaction between the first-formed simple sulphides to produce the ore in its present form.

Zusammenfassung: Die Woodcutters L.5 Blei-Zink Lagerstätte im Northern Territory, Australien, tritt in der Golden Dyke Formation auf, die aus Kohlenstoffhaltigem Siltstein, Dolomit and Grauwacke besteht. Dieselbe bildet einen Teil der Unter-Proterozoischen Sedimente der Goodparla Group, welche auf einem Archaischen Granit-Untergrund abgelagert wurden.

In dieser Arbeit ist der Versuch gemacht worden zu zeigen, wie dies Faktoren welche als wichtig in der Bildung von Dolomit betrachtet werden auch bedeutend in der Genesis der Woodcutters Lagerstätte waren.

Diese Faktoren sind:

1. Die eindämpfende Umgebung, welche die Bildung von Dolomit begünstigt ebenfalls Blei-Zink in den darüberliegenden Lösungen konzentriert.
2. Die Metalle wurden weiter angereichert und mit den Sedimenten durch Co-Precipitation mit den Vorläufern des Dolomits, Mg-Calcit oder Aragonit, verbunden.
3. Die Bildung von Dolomit während der Diagensis führte entweder zu einem strukturellen Wechsel, wenn Aragonit der Vorläufer war oder zu einer Anordnung im Falle von Mg-Calcit. Der gut geordnete Dolomit war nicht in der Lage die verhältnismassig grosse Menge von Blei-Zink, verbunden mit seiner Vorläufern, zu behalten und demzufolge wurden diese wahrend der Dolomitisierung an die Porenlösungen abgegeben.

Die Metalle in der Porenlösungen, möglicherweise zusammengesetzt mit organischem Material, wie diejenigen von der Degradation von Algen Protein, verblieben löslich während der Konsolidation. Wahrend der Faltung wurden die mit Metall angereicherten Lösengen zu Spalten Transportiert und als Metall-sulphide niedergeschlagen als die organischen Komplexe labil wurden.

Nach der Verfestigung wurden die Karbonat-Quarz-Sulphid Gänge Schwächezonen, entlang denen Scherung stattfaund, wahrscheinlich über ein grosse Zeitspanne hinweg. Diese Scherung sowohl als auch ein leichter

Temperaturanstieg verursachten Brüche, Re-Kristallisierung, und Reaktion zwischen den zuerst geformten, einfachen Sulphiden um das Erz in seiner jetzigen Form zu bilden.

Introduction

The Woodcutters lead-zinc prospect lies about 80 km south of Darwin, and about 13 km east of the Rum Jungle uranium mine (Fig. 1) in the Northern Territory of Australia.

Interest in the area began when the Bureau of Mineral Resources found a number of radiometric anomalies during air-borne surveys conducted in 1957. In 1964 the Bureau carried out reconnaissance geological, geophysical, and geochemical surveys which extended from the Giants' Reef fault to the south of the Batchelor Road. These were along east-west lines spaced 2,400 feet apart. The results of this work defined an elongated zone of geochemical, geophysical, and radiometric anomalies in what is now known as the Woodcutters' area. Inferred reserves calculated from B.M.R. drilling up to 1967 were 500,000 long tons containing 8% lead, 16% zinc, and 7 ounces of silver per ton. The prospect was then handed over to a private company for further exploration, and, if warranted, development. This exploration is continuing at the time of writing, and the bulk of the drill cores used in this investigation were obtained from the company, Geopeko Ltd.

Geological and Tectonic Framework

The deposit is located in the Golden Dyke Formation on the western edge of the Lower Proterozoic Pine Creek Geosyncline. It consists of several near-vertical fissure fillings in the axial part of a north-pitching anticline (Fig. 2).

In the Rum Jungle area, the sedimentary succession, which was laid down on an Archaean granitic basement, consists of the following formations in order of increasing age (WALPOLE, CROHN, DUNN, RANDAL, 1968 ((see Fig. 1):

Burrell Creek Formation: Siltstone, greywacke.

Golden Dyke Formation: Black shale and slate, sericitic and chloritic schist, minor intercalated limestone, dolomite, chert, and pyritic quartzite.

Masson Formation: Quartz greywacke, quartz sandstone, siltstone.

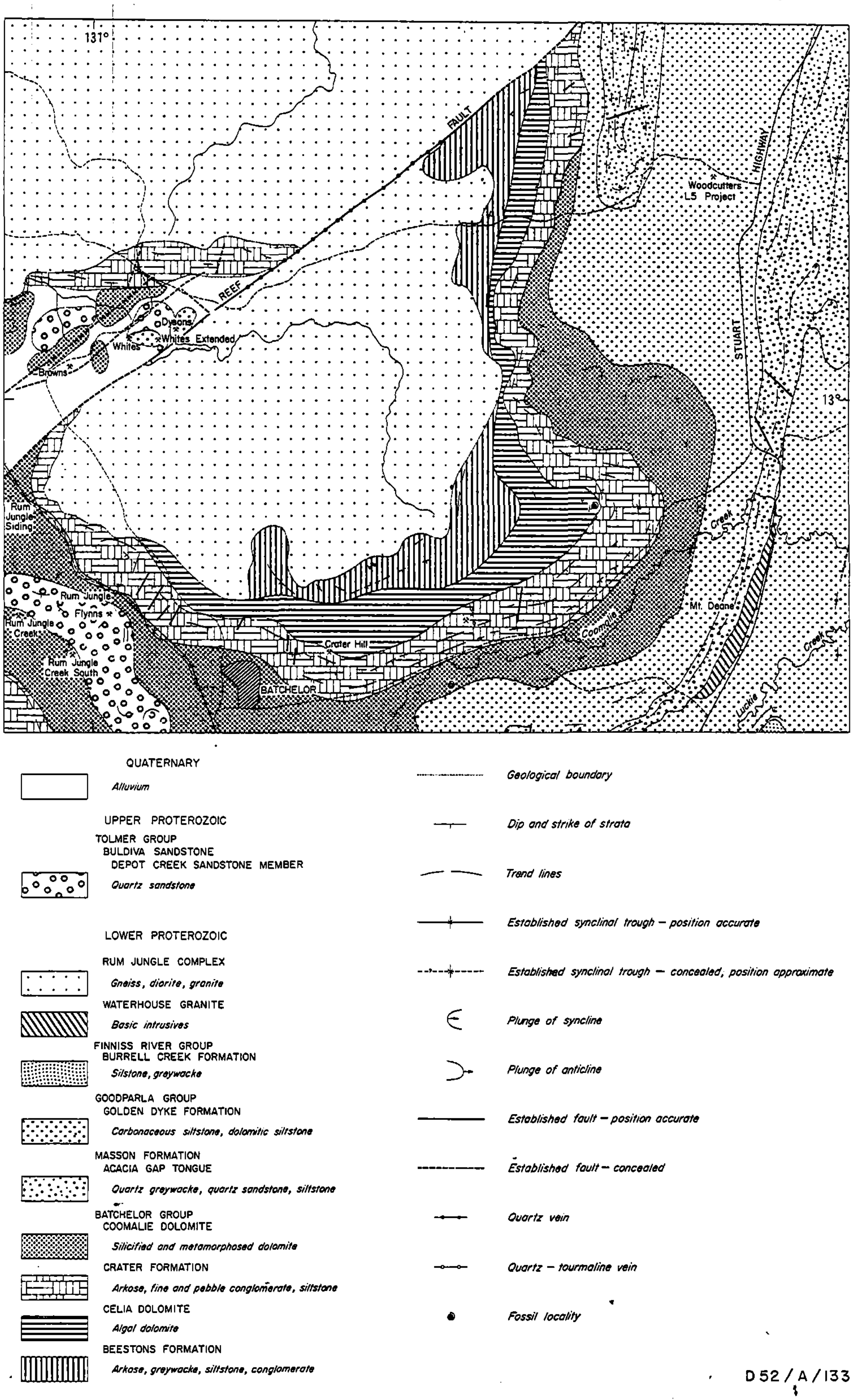

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FIG. 1

Solid geology, southern part of Rum Jungle complex and neighbouring Pine Creek Geosyncline succession. After Rum Jungle District Special Sheet, Bureau of Mineral Resources, 1960.

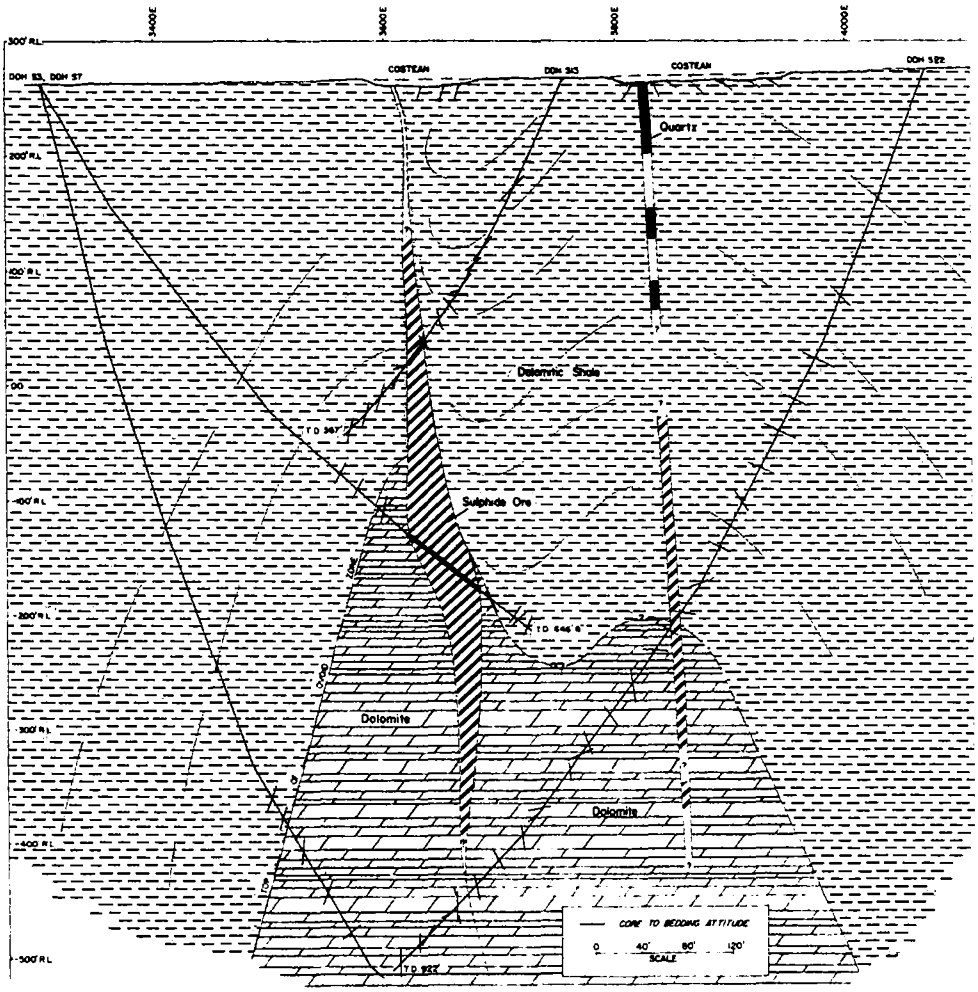

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FIG. 2

Section through the Woodcutters lode. Geology inferred from drill core information. After A. Taube, Geopeko Ltd.

Coomalie Dolomite: Dolomite, magnesite, and calcilutite.

Crater Formation: Mainly greywacke and pebble conglomerate.

Celia Dolomite: Dolomite and algal dolomite.

Beeston's Formation: Arkose, greywacke, quartz sandstone, and conglomerate.

Host Rocks

Carbonate analyses show that the host rocks range from about 90% sericite to about 97% dolomite (Fig. 3), indicating that the rock types are dolomitic shale to almost pure dolomite with a maximum in the region of strongly argillacous dolostone. Some specimens of dolomitic shale have a poorly developed slaty cleavage.

In thin section the rocks are seen to consist of very fine-grained (1-5 μ) dolomite and sericite, together with varying quantities of fine-grained quartz and chalcedony. The alignment of sericite flakes in some of the less dolomitic rocks has caused a pronounced bedding plane foliation, probably representing a plane of flattening, as suggested by DUNNET & MOORE (1969), who state that marl and limestone may undergo about 25% to 30% compaction before foliation becomes visible in hand specimen. Carbonaceous material forms thin bands and lenses parallel to the foliation, and in places it is sufficiently concentrated to make the rock virtually opaque in thin section. RAMDOHR (pers. comm., 1970) terms the material "Vorgraphit", a precursor of true graphite.

Patches of anatase up to 1.5 m across are common; these appear to have been derived by the alteration of titano-magnetite or ilmenite which could have had a detrital origin. Small apatite crystals up to 1 mm long commonly occur aligned parallel to the bedding, apparently these formed during diagenesis.

No calc-silicate minerals were seen in thin section, and the host rocks have therefore not been metamorphosed to any appreciable extent. Both 1M and 2M polymorphs were identified in the micas separated from several samples. The presence of the 1M polymorph indicates that the rock has not reached temperatures

CLASSIFICATION BASED ON CARBONATE ANALYSES OF 91 SAMPLES OF ROCKS FROM WOODCUTTERS L5 PROSPECT

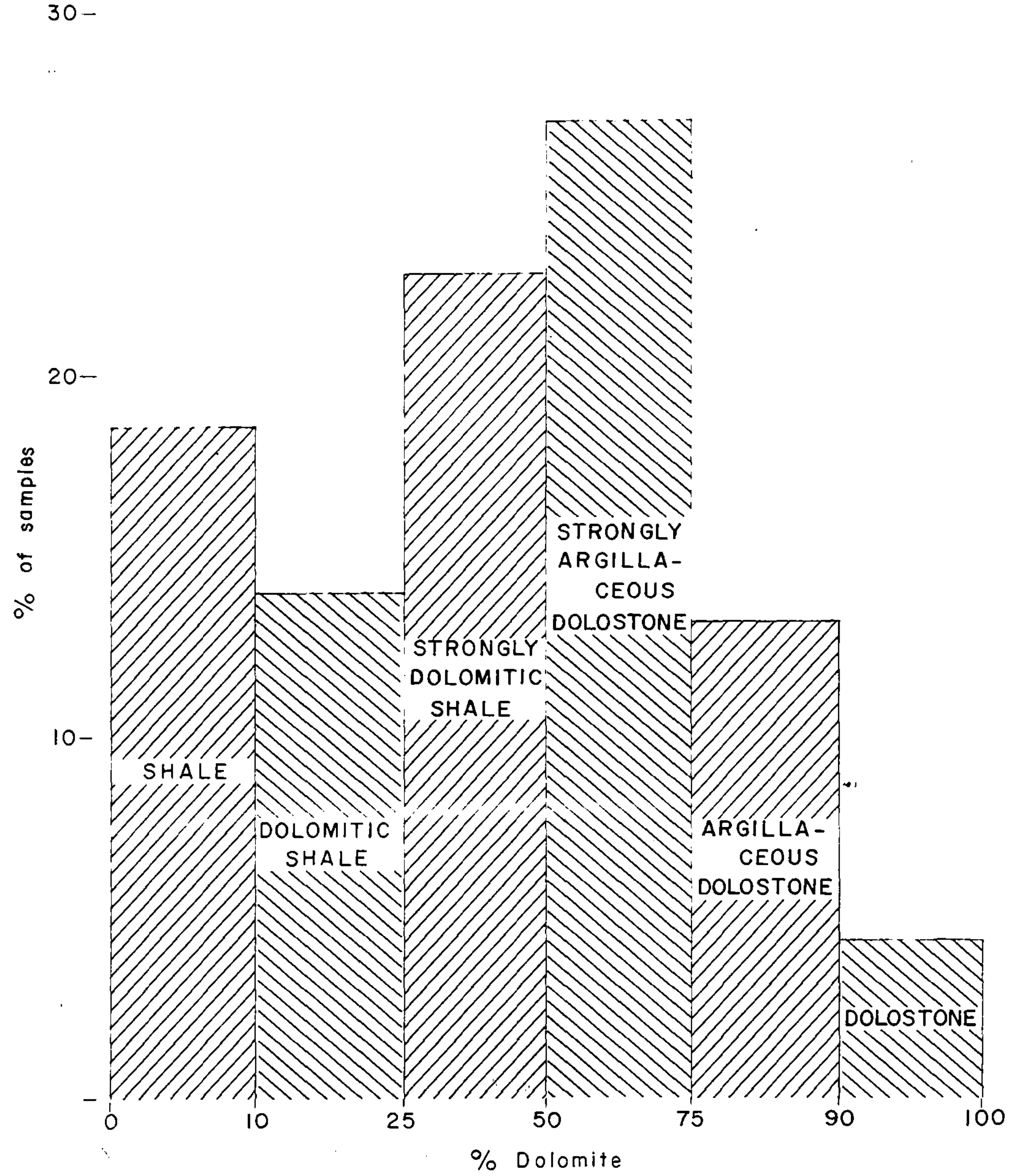

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FIG. 3

above 180°C (YODER & EUGSTER, 1955). The 2M polymorph is probably of detrital origin.

The presence of chalcedony also indicates that the temperature of the rock has not been above 250-300°C, as this mineral inverts to quartz in this temperature region (KENNEDY, 1950). The presence of soft, low-reflecting nickeliferous pyrite in the lodes indicates formation at a temperature below 200°C (RAMDOHR, pers. comm., 1970). Furthermore, blaubleibender covellite which is enclosed in grains of galena, will not form above 157°C (MCH, 1971).

It is therefore apparent that the rock has been subjected to no more than moderate burial metamorphism, and that the highest temperature reached was about 160°C, and certainly no higher than 200°C.

Small veins of coarse grained dolomite, silica, and sulphide are common; they frequently have margins of carbonaceous material, and are arranged at random angles to the bedding. These veins have apparently been formed early in diagenesis, as the more steeply dipping ones are strongly folded through later compaction of the rock.

Ore Mineralogy and Fabrics

One hundred and twenty four polished sections and 36 thin sections were examined, and the following sulphide minerals were identified:

Mineral	Frequency of Occurrence in specimens (%)	Minerals	Frequency of Occurrence in specimens (%)
Pyrite	100	Meneghenite	10
Sphalerite	80	Chalcopyrite	16
Galena	80	Greenockite	8
Arsenopyrite	75	Jamesonite	5
Bournonite	44	Digenite	5
Boulangerite	52	Marcasite	4
Tetrahedrite	20	Pyrrhotite	6
Geochronite	24	Bornite	2
Stannite	20	Covellite	2

The textures and paragenetic features of the individual minerals are described below.

Pyrite

The formation of pyrite has been a continuous process beginning with early sedimentation, continuing through diagnesis, and ending with precipitation along with the other sulphides in the ore veins.

Penecontemporaneous pyrite has formed very fine grained layers in the host rock, and part of it was later mobilized into large, irregular masses transgressing the bedding (Fig. 4). Diagenetic pyrite has also crystallized as euhedral crystals, most of which have pressure shadows of various sizes (Figs. 5, 6) expressed as chalcedony, dolomite, coarser-grained sericite, galena, or sphalerite.

The bedding is distorted around only a few of the crystals, indicating that these were formed during diagenesis and before compaction. Other crystals, around which the beds are not distorted, apparently formed after compaction of the rock was complete.

Many pyrite crystals are partly replaced by chalcedony and dolomite, and randomly oriented dolomite-chalcedony veins are lined in places with a new generation of euhedral pyrite crystals which are not corroded, and which were probably derived from the earlier pyrite. These veins frequently have a central zone of sphalerite, galena, and lead sulpho-salts.

Irregular masses of pyrite containing silicate inclusions frequently have rims of inclusion-free pyrite with well-defined crystal outlines (Fig. 7). This secondary pyrite frequently has other sulphides associated with it.

Irregular masses of pyrite are commonly closely associated with patches of anatase derived from what appears to have been either titano-magnetite or ilmenite. The frequency of this association suggests that the circulation of a sulphide-bearing solution was responsible for the alteration of the iron oxides. According to GRUNER (1959), the reactions

$$FeTiO_2 + H_2S \rightarrow TiO_2 + FeS + H_2O$$

$$FeS + H_2S \rightarrow FeS_2 + H_2$$

proceed at 300°C, but he suggested that they would take place at lower temperatures, given sufficient time.

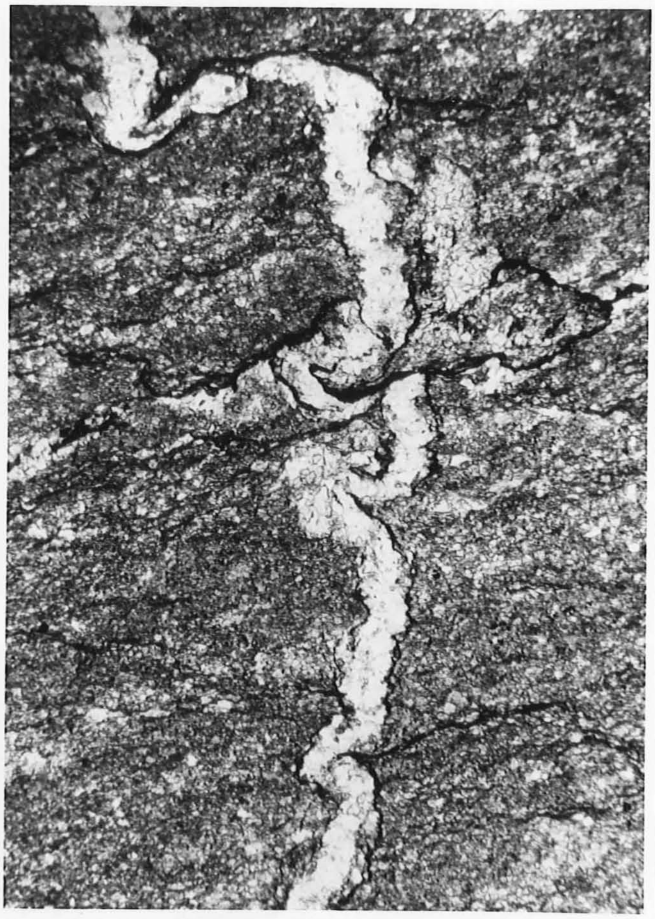


FIG. 4

Compaction of quartz and dolomite vein during diagenesis. The black material is graphite. D.D.H. S17 887'. x 10. Thin Section.

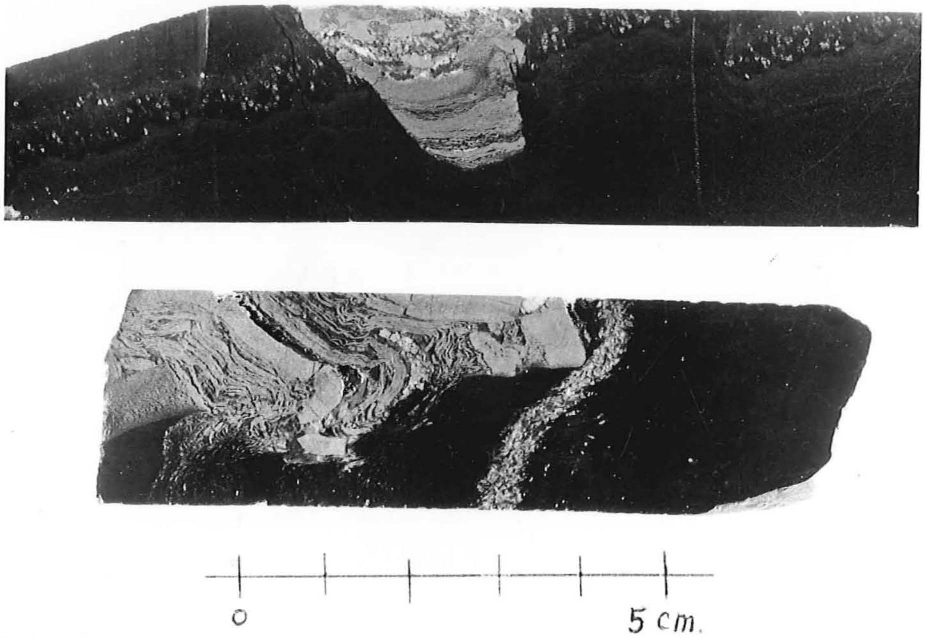


FIG. 5

Massive pyrite transgressing bedding. In the top photo the crenulated beds roughly parallel to the long axis of the core contain a high proportion of very fine grained penecontemporaneous pyrite.

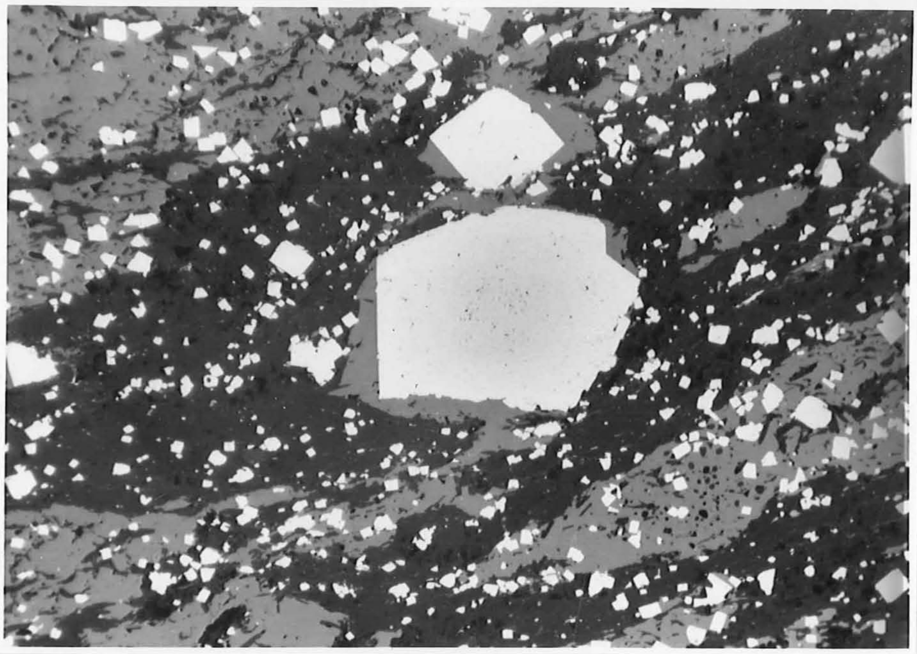


FIG. 6

Pressure shadows on pyrite filled with sphalerite. D.D.H. S36, 353'. x 32. Pyrite, white; sphalerite, mid-grey. Polished section.

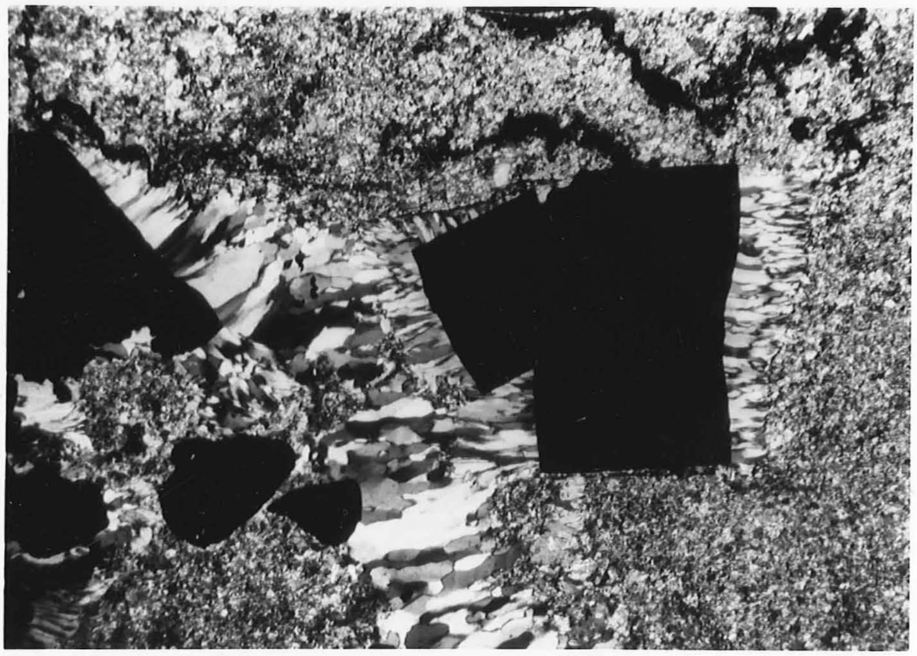


FIG. 7

Pressure shadows on pyrite filled with chalcedony. D.D.H. S23, 666'. x 10. Pyrite black. Thin section.

At high magnification pyrite in the lodes commonly shows zoning and multiple twin-like intergorwths of a slightly softer, less strongly reflecting mineral which proved to be nickeliferous pyrite. RAMDOHR (pers. comm., 1970) suggested that the larger atomic radius of nickel, which has substituted for iron in the pyrite structure, could cause the lower reflectivity and hardness. He also stated that the presence of nickeliferous pyrite indicates a temperature of formation of about 150°-200°C. At higher temperatures nickel would combine with arsenic, which is abundant in the ore.

Sphalerite

Sphalerite typically occurs in epigenetic veins formed during the folding of the rocks. It is commonly moulded on pyrite and arsenopyrite. It is generally closely associated with galena and lead sulpho-salts, and shows evidence in places of fairly pronounced shearing and recrystallization (Fig. 8). Masses of sphalerite crystals are, in places, outlined by pyrite and chalcopyrite, which appear to have been expelled from the sphalerite as a consequence of recrystallizatio This does not imply that the copper and iron were present originally in solid solution. ROBERTS (1965) has shown that a homogeneous mixture of sphalerite and chalcopyrite precipitates will recrystallize at temperatures as low as 130°-150°C at 2000 bars, and during this recrystallization textures result which could be interpreted as being formed by unmixing from solid solution (Fig. 9), but which in fact are the result of crystal growth in a mixture of very fine-grained precipitates. Stannite and tetrahedrite are commonly dispersed throughout sphalerite as small irregular grains and fine-grained streaks which in places show a strong orientation along what appears to be a shear direction (Fig. 10). Galena and lead sulpho-salts less commonly form similarly oriented streaks in sphalerite.

At high magnification small rounded blebs of sphalerite may be observed in the host rock; these range from 0.001 mm to 1 mm, and were probably formed by precipitation from the circulating fluids which formed the lodes.

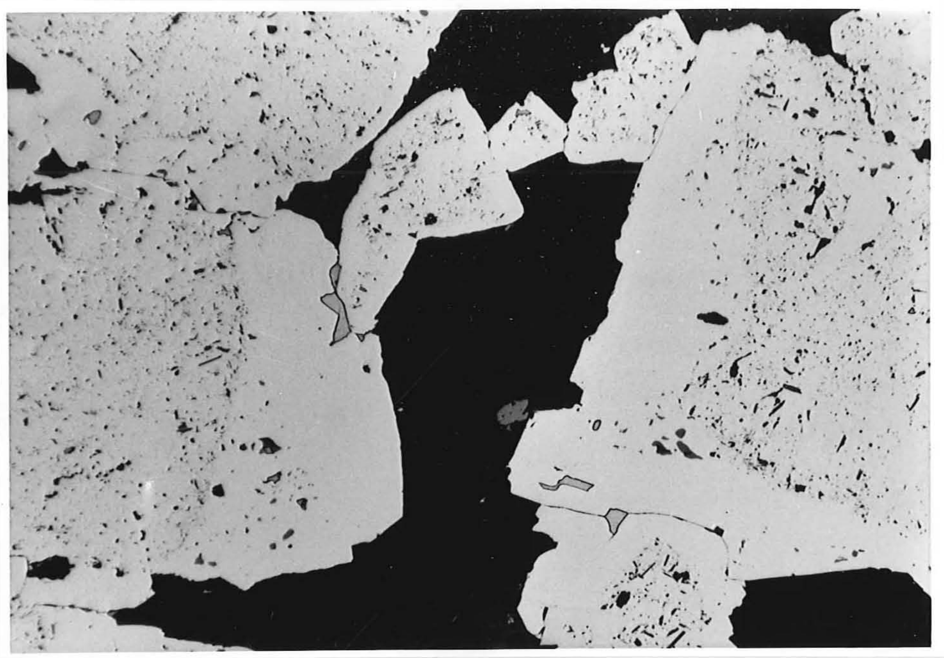


FIG. 8

Overgrowth of inclusion-free pyrite on earlier pyrite with abundant silicate inclusions. D.D.H. S35, 251'. x 32 Polished section.

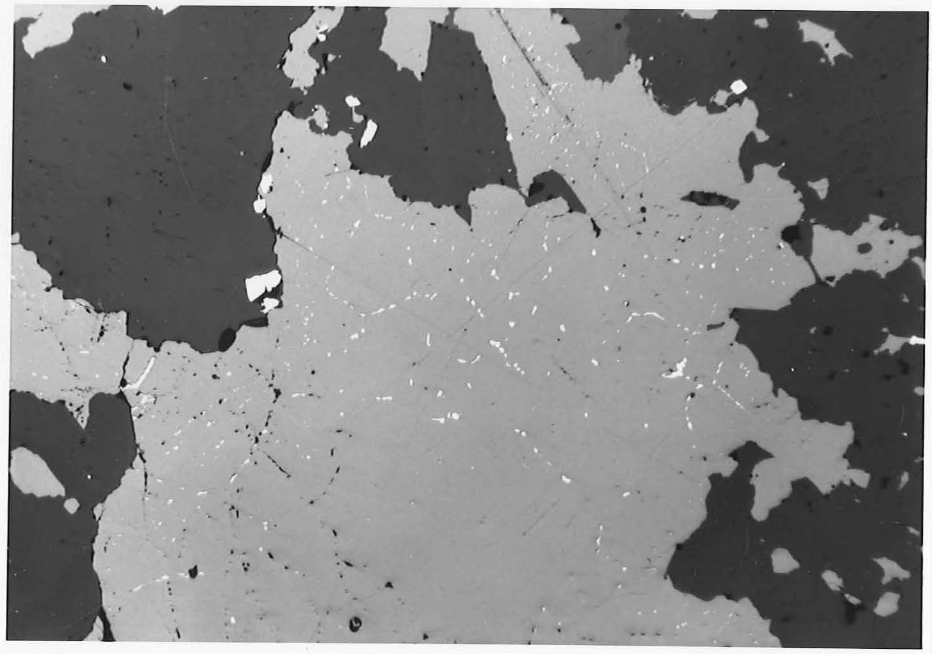


FIG. 9

Chalcopyrite outlining polygonal crustals of sphalerite. D.D.H. S28a 684'6". x 10. Chalcopyrite, white; sphalerite, mid-grey; quartz, dark grey. Polished section.

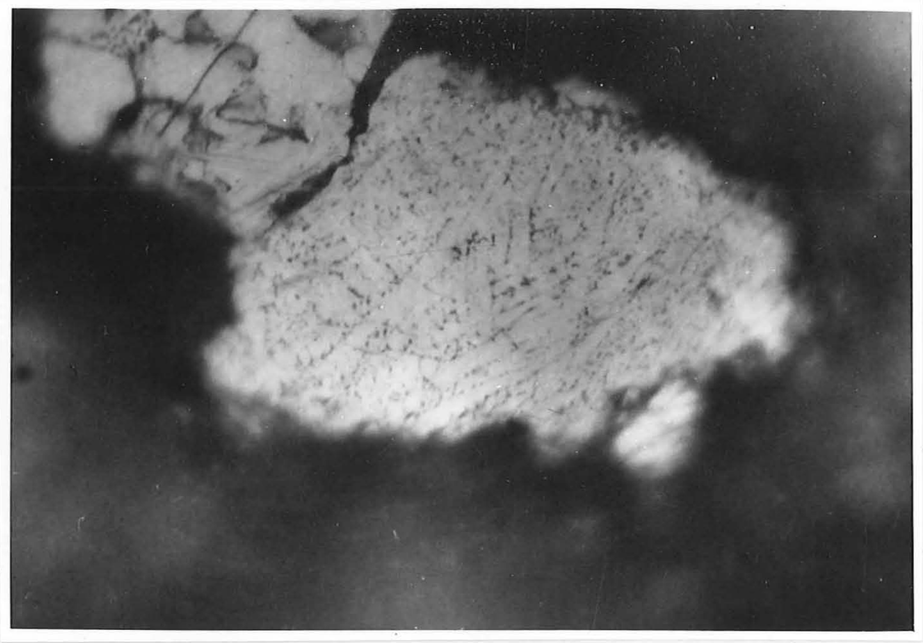


FIG. 10

Sphalerite formed along crystallographic directions in chalcopyrite during recrystallization x 1200. Polished section.

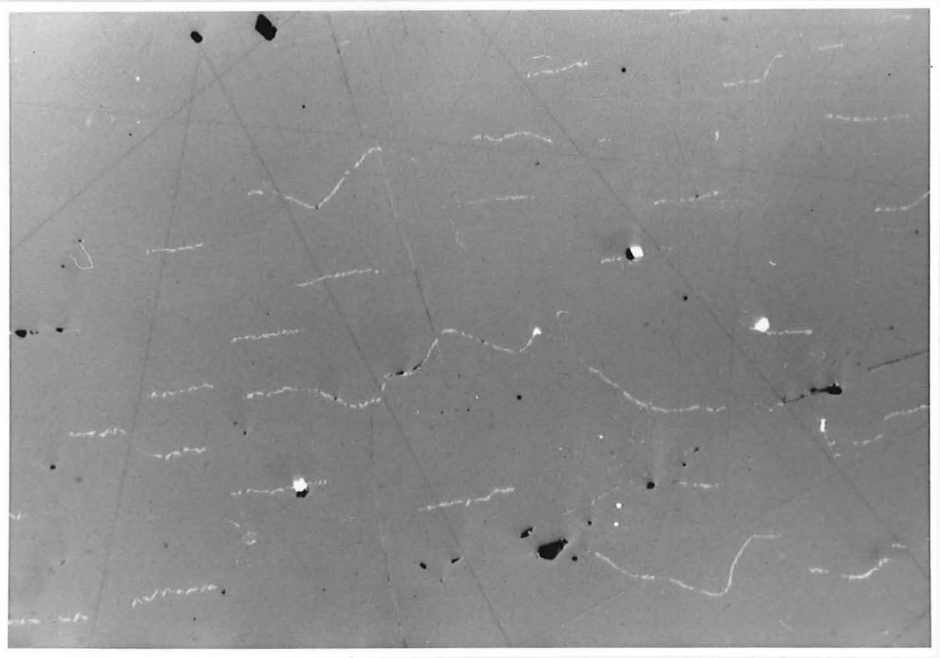


FIG. 11

Stannite marking the deformation of sphalerite D.D.H. S36, 382' x 64. Polished section.

Galena

Galena occurs mainly in epigenetic veins, where it contains lead sulpho-salts, with which it forms irregular intergrowths. It commonly fills fractures in sphalerite and pyrite, and the rare copper sulphides in the ore are frequently associated with galena.

Like sphalerite, galena is distributed throughout some specimens of the country rock as very small rounded blebs, similar in size to the sphalerite growths, and probably of the same origin.

Lead sulpho-salts (boulangerite, geochronite, meneghenite, and jamesonite)

The lead sulpho-salts are generally associated with galena and sphalerite, mostly as irregular intergrowths, but in places boulangerite forms stellate clusters and isolated blades in the quartz-dolomite gangue. Boulangerite forming veins in pyrite is twinned parallel to traces of shearing in the pyrite; "horse tail textures are also common in this mineral.

The sulpho-salts themselves, especially boulangerite and geochronite, are frequently intergrown as a recrystallised mosaic of equidimensional grains. Geochronite shows the typical fine twining commonly associated with this mineral.

Because geochronite is so similar to jordanite in its optical properties, as well as having an X-ray diffraction pattern which is indistinguishable from that of jordanite (GRAESER, 1965), it was identified by X-ray fluorescence analysis which established that antimony and arsenic were present in equal amounts.

Jamesonite and meneghenite commonly form small (0.15-0.25 mm) inclusions in galena.

Bournonite

Bournonite is widespread; it is mostly associated with the lead sulpho-salts and with galena. It has recrystallized in many places as a mosaic of equidimensional grains, some of which have bent twin lamellae.

Very rarely chalcopyrite and bornite are associated with bournonite, and in some specimens very small grains of greenockite are included in it.

Arsenopyrite

Arsenopyrite has a distribution similar to that of pyrite except that it does not appear to be bedded. It forms euhedral crystals and masses of subhedral crystals distributed throughout the rock; these are frequently strongly fractured and corroded. It is commonly closely associated and intergrown with pyrite, it has been dissolved and reprecipitated as shown by galena - filled fractures which have selvedges of arsenopyrite crystals adjacent to masses of corroded arsenopyrite, and stellate groups of crystals are contained in some quartz areas.

Tetrahedrite and stannite

Tetrahedrite and stannite are widespread as irregular small grains in sphalerite.

In several specimens tetrahedrite forms areas, up to 1 mm across, with anomalous anistropism and a strong undulose extinction, indicating that it has been strongly stressed. It is improbable that this mineral has unmixed from a solid solution in sphalerite, as neither the rock nor the ore has reached temperatures sufficiently high for solid solutions to form.

Marcasite

Marcasite appears very rarely as minute grains in pyrite, and along fractures in this mineral where it gives the impression of having formed by alteration.

Chalcopyrite

The little chalcopyrite that there is in the ore is almost exclusively associated with sphalertie and galena, both as small randomly distributed grains. Very rarely it forms small round blebs in pyrite.

Pyrrhotite

Pyrrhotite was observed only as small irregular grains enclosed in pyrite, and rarely in chalcopyrite.

Greenockite

Most of the greenockite occurs as fine intergrowths, about 1 to 2 microns across, in bournonite. A small quantity is intergrown with tetrahedrite, sphalerite, galena, and, very rarely, with boulangerite. Its presence was established by its deep carmine internal reflections, and its bluish colour in plane polarised light. In addition, one drill core contained small carmine red crystals which were identified as greenockite by X-ray diffraction (A. TAUBE, pers. comm.).

Blaubleibender covellite, digenite, and bornite

These three minerals are commonly closely associated as small grains and veinlets in galena and pyrite.

Gangue Minerals

The gangue minerals in order of decreasing abundance are: dolomite, quartz, graphite, tourmaline, anatase, chalcedony, sericite, and muscovite (rare).

Dolomite

Dolomite typically forms large crystals in the ore veins; where the ore has recrystallized the dolomite has a finer, saccharoidal texture.

Quartz

Quartz is usually associated with dolomite, and occurs in a similar manner, frequently in the centre of veins whose margins are lined with dolomite. In places the quartz grains show strong undulose extinction; in others they have recrystallized as gains with sharp extinction.

Tourmaline

Colourless tourmaline is widespread in the ore, in places forming densely packed masses of interlocking crystals in a matrix of sulphide. In many specimens the crystals show subparallel orientation (Fig, 12). Nests of very fine crystals are frequently enclosed in the gangue minerals.

The presence of this mineral does not necessarily indicate that high temperatures were reached during ore formation. KRYNINE (1964) has shown that tourmaline can form in cold water on the sea floor, and that this low temperature variety is usually colourless to pale blue, indicating a magnesian variety with possibly some Ca or Na. Its presence in the ore is probably the result of mobilization of the consitituents of tourmaline from the sediments by circulating fluids.

Anatase

Anatase is widely distributed throughout the ore and the country rock. It usually forms a fine mesh of crystals resulting from the alteration of titano-magnetite or ilmenite; in places the crystal form of the original mineral is still preserved. (Fig. 13).

Sericite and Muscovite

Sericite is present in the ore mainly as residual patches of country rock, which frequently retain their banded appearance. Very rarely in veins of sulphide, sericite has recrystallised into flakes of muscovite.

Chalcedony

Chalcedony forms occasional fillings in carbonate veins, and more frequently infillings in pressure shadows around pyrite crystals.

Graphite

Graphite is widespread throughout the ore and country rock; in the ore it is commonly associated with residual areas of sericite. The mineral is

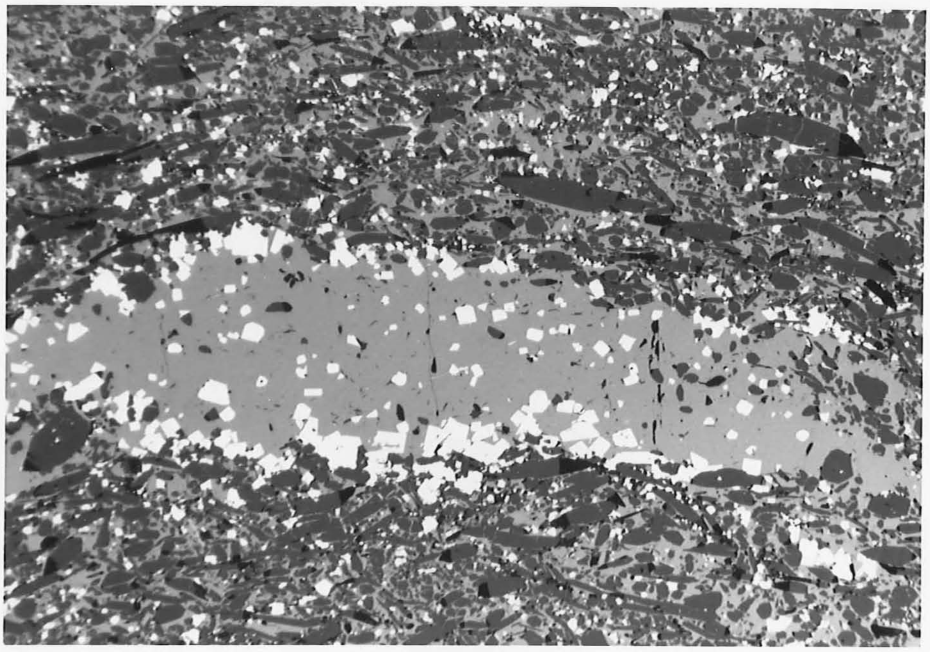


FIG. 12

Subparallel tourmaline crystals in massive sulphide ore. D.D.H. S23, 647'. x 16. Tourmaline, Dark Grey.

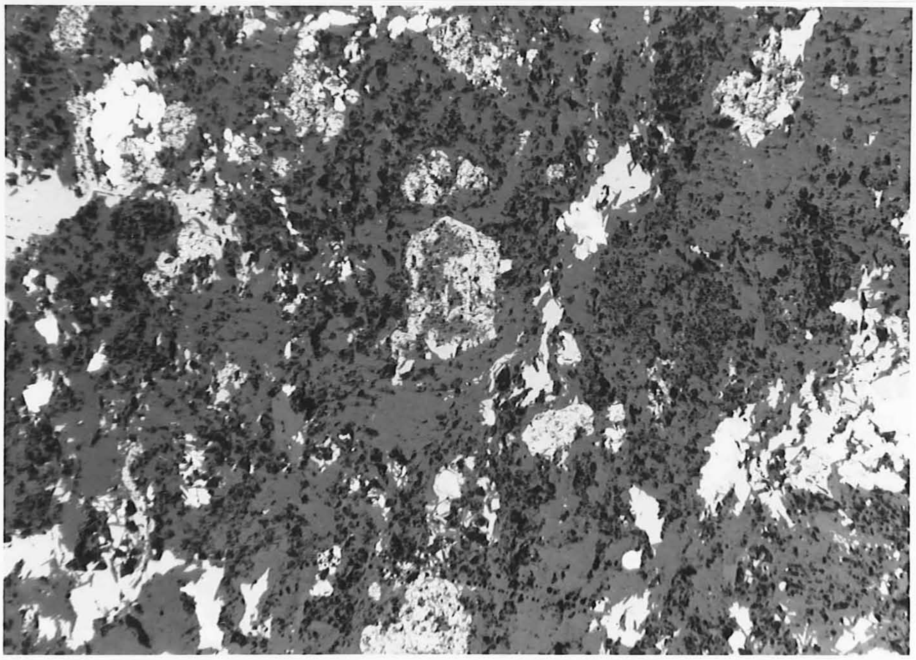


FIG. 13

Alteration of titanomagnetite (white) to anatase (grey). D.D.H. S38, 228'. x 16. Polished section.

not true graphite: it has low reflectivity, and is brownish in plane-polarized light; its pleochroism is strong, and its anisotropism differs from that of true graphite in that its colours range from yellowish cream to dark grey. RAMDOHR (pers. comm, 1970) terms the material "Vorgraphit", and suggests that it does not survive at temperatures about 150°C.

It has been suggested (TAUBE, 1969) that the dolomite veins containing the ore are carbonatites.

Several factors argue against a carbonatite origin for the dolomite veins:

Carbonatites are usually associated with alkaline igneous activity. There is no evidence of such acitivty in the Woodcutters area. According to HEINRICH (1966), apatite is abundant and widespread in carbonatites; in fact, its presence is a highly characteristic feature of all carbonatites. Although undoubtedly diagenetic apatite is present in the country rock, no apatite was observed in the dolomite vein material examined in this study.

With the exception of pyrite, sulphides are uncommon to very rare in carbonatites. The majority of carbonatite complexes are surrounded by a fenitized halo. Those that have no such haloes have other forms of metasomatic alteration in the wall rocks. No such alteration has been observed in rocks from the Woodcutters area.

Oxygen isotope studies (HEINRICH, 1966) support the assumption that carbonatites have a magmatic origin, although some isotope investigations indicate that some "carbonatites" have been deposited at temperatures as low as 250°C; these have been formed by the carbonatization of periodotites had serpentinites, neither of which is present in the sequence at Woodcutters. In addition, the presence of blaubleibender covellite in the veins is evidence that they have not been heated above about 160°C. Experimental evidence by WYLLIE (1966) suggests that carbonatites are emplaced at temperatures in the region of 600°C.

As the petrological and mineralogical examination of the country rocks and the ore at Woodcutters provides strong evidence that the rocks have not been subjected to temperatures over about 200°C, and there is no evidence of any fenitization of the fine-grained argillaceous material adjacent to the veins such as would be expected to result from intrusion, the suggestion that the ore veins are carbonatitic can be dismissed. In addition, chemical analyses of eleven samples of country rock gave the dolomite formula $Ca_{52-54}Mg_{48-46}(CO_3)_{100}$, and X-ray analyses of dolomite from five ore vein samples by the method of GOLDSMITH, GRAF, and JOENSUU (1965) gave the composition $Ca_{55}Mg_{45}(CO_3)_{100}$.

The Depositional Environment of the Woodcutters Deposit

The formation of dolomite has been the subject of intensive study in recent years, and works by GRAF and GOLDSMITH (1956), ALDERMAN and SKINNER (1957), CHILINGAR and BISSEL (1963a), DEGENS and EPSTEIN (1964), PATERSON and VON DER BORCH (1965), FRIEDMAN and SANDERS (1967), MÜLLER and IRION (1968), FRIEDMAN (1968), and MÜLLER (1970) are some of the many which refer to the conditions necessary for the formation of dolomite.

A review of the world-wide association of Pb-Zn ores with dolomite has been presented by HEWITT (1928). More recently SANGSTER (1970) has reviewed Canadian lead-zinc deposits which are associated with carbonate rocks, most of which are dolomites.

On the evidence available, it appears that dolomite is unlikely to be precipitated directly, and forms from either aragonite or Mg-calcite only under certain conditions. As will be suggested later, the formation of dolomite by dolomitization of either Mg-calcite or aragonite is a significant factor in the formation of dolomitic Pb-Zn ores. Studies on the formation of dolomites at the present time indicate that the two most necessary conditions are high pH and high Mg/Ca ratio. Somewhat high to high salinity, evaporitic conditions, and high temperatures, though apparently not essential to dolomite formation, probably speed the process. The effect of CO_2 pressure is not clear from the theoretical and experimental evidence.

There are no typical evaporitic minerals in the Woodcutters deposit. According to FRIEDMAN and SANDERS (1967) the association of dolostones with terrigenous sediments containing no evaporites is an indication that they were deposited under conditions of lower salinity than sediments associated with evaporitic minerals. The $CaCO_3$ excess in the Woodcutters dolomites also indicates a lower salinity of the environment of deposition. MARSCHNER (1968) in her study of the carbonate rocks of the Lower Keuper has observed that the $CaCO_3$ excess in the early diagenetic dolomites of this sequence decreases upwards, and attributes this to lower salinity at the start of deposition.

Although the evidence indicates that high salinities, evaporitic conditions, and higher temperatures are not essential for the formation of dolomite, the observations made on recent dolomites show that such conditions commonly apply. In the Coorong, South Australia, dolomite is forming from aragonite in a shallow restricted marine environment which undergoes an annual evaporative cycle (ALDERMAN & SKINNER, 1957). DEGENS & EPSTEIN (1964) quote the unpublished work of BAJOR who considers that the Steinheim Basin sediments of southern Germany were deposited in a continental evaporative environment. GRAF et al. (1961) state that radiocarbon dating of the dolomites in Lake Bonneville showed an age of 11,300 years, and that this corresponds to a period of reduced lake level, i.e., greater aridity.

Therefore it seems reasonable to assume that the Woodcutters dolomite was formed in a restricted basin type of invironment which developed during the deposition of the Golden Dyke sediments on the western margin of the Pine Creek

Geosyncline. The basin or large lagoon was partly cut off from the sea and periodically dessicated; the water would increase in salinity, the pH would be high, and the Mg/Ca ratio would be such that Mg-calcite or aragonite could precipitate.

On the question of depth of water during deposition and subsequent diagenesis, the studies of GRAF et al. (1961) at Bonneville, and of DEGENS, KNETSCH & REUTER (1960) on the Buntsandstein in southern Germany, showed that dolomite commonly forms in fairly shallow water. The dolomite at the base of the Muschelkalk was deposited under shallow marine conditions; in deeper and more open water, a limestone gradually takes over from the dolomite.

Origin of the Ore

Although it is here suggested that the Woodcutters deposit is sedimentary origin, it is obvious that the ore shoots themselves are not a primary depositional feature.

FRIEDMAN & SANDERS (1967) remark that the widespread association of lead-zinc deposits with dolomitic rocks suggests that the commonly accepted hydrothermal hypothesis to explain their origin requires examination.

It will be suggested in this paper that a hydrothermal event caused the mobilisation of the ore solutions, but that this event was preceeded by sedimentational and diagenetic processes which concentrated metals in the sediments and formed the ore solutions.

These events can be divided into four stages:-

1. Concentration of metals in the basin water
2. Fixation of metals in the sediments
3. Transport of metal solutions
4. Precipitation of metallic sulphides

Later tectonism has re-textured the ore in places, and in some cases changed the mineral assemblage.

The suggestion advanced in this paper is that the conditions which resulted in the dolomitization at Woodcutters have been of considerable significance in the first three of these events.

Concentration

The concentration of lead and zinc in seawater is 0.00003 and 0.01 PPM, respectively (GOLDBERG 1963), so normal seawater does not appear to have been a likely source for the metals. To obtain 1 PPM of lead in solution a concentration of 33,000 times would be necessary, a quite unrealistic factor for normal evaporation at the Earth's surface to achieve.

LERMAN (1970) gives the mean global evaporation rate as 0.8-1.0 metres/year. At this rate he calculates that a 100-metre column of 0.2 molal NaCl would be reduced to about 5 metres in 95 years, with an increase of NaCl concentration to 5.5 molal - a concentration factor of 27.5. Thus, even if the metals were not removed during sedimentation, the concentration of lead in a 100-metre column of seawater in 95 years would be only 0.0009 PPM, and that of zinc 0.3 PPM. It does not appear likely that this amount of metal in the basin water would be great enough to produce in the sediments a concentration sufficient to eventually enrich the pore solutions sufficiently for them to be a potential ore fluid. This leads to the conclusion that water containing above-background amounts of dissolved base metals must have been entering the basin. If 1 PPM zinc and 0.5 PPM lead were present in this water, and no other water with lower concentrations of these metals were being added to the basin, mild evaporation would increase these concentrations by a factor of two in a short time; for example, the Red Sea brines contain up to 0.7 PPM lead and up to 71 PPM zinc (BROOKS, KAPLAN & PETERSON 1969). The ability of these metals to stay in solution in such concentrations would depend upon a variety of factors, the most important of which would be pH and the anionic composition of the water.

Fixation in the Sediments

Although the above figures are low in comparison with the final concentration required for ore-grade mineralization, the efficient removal of metals from solution could result in a much higher concentration in the sediments.

The efficient removal and the fixation of the base metal ions in the sediments could have been achieved by their co-precipitation with the precursors of dolomite, either aragonite or Mg-Calcite. This is a highly efficient method of removing metal ions from solution, and is used in radiochemistry for the removal of radioactive tracers from solutions even when their concentration is so low that their solubility products are not exceeded (BONNER & KAHN, 1951). The co-precipitatio is effected either by the formation of mixed crystals or by adsorption. $CaCO_3$ will carry 97% of Pb^{212} out of solution, so that if the basin water contained 1 PPM of lead, it could very efficiently be concentrated in the sediments by this method. The final concentration in the sediment would depend on the amount of carbonate produced relative to the volume of the basin water and on the amount of detritus locally entering the basin. SKINNER, SKINNER & RUBIN (1963), in calculations based on precipitation of carbonate in the Coorong, South Australia, showed that, from a mean water depth of 50 cm, carbonate sediment accumulates at a rate of 0.5 mm per year. Therefore if 1 PPM lead were fixed with an efficiency of 97%, a concentration of nearly 1000 PPM would be achieved in the sediments.

Although a concentration of 1 PPM of lead in solution in the presence of carbonate ions would exceed the solubility product of either the carbonate or the basic carbonate, this amount of lead (and zinc) could be stabilized in solution as chloride or carbonate complexes, or as organic complexes formed from algal degradation products. If the metals are present as bicarbonate complexe as suggested by GOLEVA et al. (1970), any rise in temperature or in pH which would result in the precipitation of carbonates would make the bicarbonate complexes unstable, and allow the metals to co-precipitate with the carbonates.

Both lead and zinc may substitute for calcium in the aragonite structure; 2 to 6 weight percent lead is fairly common, but the range of solubility must extend well beyond the latter figure, as PALACHE, BERMAN & FRONDEL (1951) report a specimen from Serbia as containing 15 percent PbO. Zinc has been reported to substitute for calcium in aragonite in amounts ranging from 0.9 to 3.0 weight percent (PALACHE et al.,1951).

ZWIERZICKI (1948) states that the dolomite of the Upper Silesian lead-zinc deposits has a low MgO content (15%), and it commonly contains about 3-5% Fe, 0.5-1.5% Zn, up to 0.2% Pb, and 0.5% Mn. He suggests these metals may be present as double salts.

Because lead carbonate is isostructural with aragonite, lead would more readily substitute for calcium than would zinc, and from the figures quoted above this appears to be the case. On the other hand, zinc carbonate is isostructural with calcite, and as a result, according to PALACHE et al. (1951), a limited series may exist between $ZnCO_3$ and $CaCO_3$. Natural calcites are reported to contain up to at least 4.0 weight percent ZnO, whereas lead, according to PALACHE et al. (1951), substitutes in significant though relatively small amounts. Co-precipitation of lead and zinc with aragonite and Mg-calcite could thus fix in the sediments quantities of these metals which could represent a significant step towards the development or ore-grade mineralization.

Transport and Precipitation

The fine grainsize of the dolomite indicates the dolomitization commenced during late sedimentation and continued through early diagenesis (FRIEDMAN & SANDERS 1967). In the conversion of the precursors to dolomite, aragonite undergoes a structural change, and Mg-Calcite changes from a less ordered state to the well-ordered dolomite. In both cases the end-product, dolomite, would not be able to accommodate in its structure the base metal ions held by the precursors, and they would thus be released to the pore solution.

From the description of the diagenetic pattern of the Wettersteinkalk by GERMANN (1968), this early stage of diagensis probably took place under conditions of shallow burial - about 20 to 500 metres.

LARSEN & CHILINGAR (1967) describe the early diagenetic processes in detail. These are summarized below.

They begin with the consumption of free O_2 by organisms, after which the reduction of $Fe,^{3+}Mn,^{4+}$ V, Cr, and SO_4^{2-} begins. Eh becomes lower, and pH rises. The solid phases in the sediments - SiO_2, $CaCO_3$, $MgCO_3$, etc - dissolve in the interstitial water. Organic matter decomposes, forming gases (CO_2, H_2S, H_2, NH_3, N_2, etc), and water-soluble compounds. Larsen and Chilingar further state that, as a result, waters become depleted in sulphates and enriched in Fe^{2+}, Mn^{2+}, SiO_2, organic matter, phosphorus, and minor elements. Oxygen disappears, and H_2S, CH_4, CO_2, NH_3, etc, are accumulated. The alkalinity becomes high (6.8-8.5), and Eh decreases (-150 to -330).

The release of metal ions to the pore solution during dolomitization, even if not complete, would create a fairly concentrated potentially ore-forming solution, provided that the metals would remain in solution, and hence be available fo later removal to an invironment where precipitation could take place. This solubilization could have been achieved by the formation of metal-organic complexes.

Graphitic material is a common constitutent of the Woodcutters rocks, which contain up to 1.6% organic carbon. Both the underlying Celia and Coomalie dolomites contain stromatolites, so it is probable that algae were the source of the organic material in the dolomite. The degradation products of this organic material would, during diagenesis, be able to form complexes with the metals released to the pore solutions.

The possibility that metals may also have been transported as carbonate or chloride complexes cannot be ignored, but it is probable that, in the presence of decomposing organic material, inorganic complexes would assume less importance as a means of metal solubilisation than would organic complexes.

EVANS (1964) has shown that both rock-forming minerals and metal sulphides can be dissolved by organic materials. Whether chelation or simply solubilisation is the mechanism involved, the figures he quotes for solubulities of various minerals are strong evidence in support of the suggestion that organic complexes could be a very important factor in the transport of metals in evnironments where there has been biogenic activity.

EVANS (1964) quotes experiments done by NEUBERG & MANDL (1948), in which zinc dissolved in L-alanine could not be precipitated by Na_2S. These workers also observed that L-alanine and all α-amino acids that they tested were able to dissolve the sulphides of Mn, Co, Ni, Fe, Cu, and most other metals. ABELSON (1957) has shown that the principal amino-acids present in a fossil clam 25,000,000 years old were alanine, glutamic acid, glycine, isoleucine or leucine, proline or valine - all α-amino acids.

EVANS (1964) also found that a group of minerals, including galena, was completely soluble in sodium-adenosine triphosphate. These minerals could not be precipitated from the solution by addition of the usual reagents, and remained in solution until the Na-ATP decomposed.

ROEDDER (1967) states, from fluid inclusion evidence, that ore fluids which formed a number of Mississippi-type deposits were Na-Ca-Cl brines containing abundant organic matter. In these inclusions he found gas, which he presumed to be mainly methane, and an oily material.

BONDARENKO (1968) has shown that lead is 10 to 60 times more soluble in fulvic acids than in water at the same pH, and because of this suggests that fulvate complexes are possible forms in which this metal may migrate.

The results summarized above suggest that organic complexes may play an important part in he transport of metals.

OWEN (1964) states that the degree of compaction of many carbonate sediments during minor loading before lithification is comparatively slight, that the expulsion of pore fluids during diagenesis is only slight, and that early lithification of carbonate rocks under some conditions favours the continued retention of such fluids. This early lithification, according to HUNT (1967), is accompanied by the hydrolysis and solubilization of any proteinaceous matter they may contain. ABELSON (1957) reports on the work (unpublished) of CONWAY, who investigated the thermal degradation of alanine, and found that, at 80°C, the time required for the degradation of 63 percent of this material is about 10^6 years, and at 60°C the figure is 10^8 years. Oxygen also shortens the lifetime of alanine.

OWEN'S study on carbonate lithification, and CONWAY'S work on the stability of alanine suggest that retained pore fluids containing organo-metallic complexes would be preserved even under conditions of relatively deep burial. At Woodcutters, their expulsion under the influence of pressures developed during the formation of the anticlinal structure in which the ore is now situated, would allow their movement into tension fractures. This movement would take place along solution channels along fractures and joints, which according to OWEN (1964) are commonly developed in dolomitic rocks.

On reaching zones of relatively low pressure, gases such as CO_2 and NH_3 would escape causing the organo-metallic complexes to become unstable, and the metal sulphides to precipitate.

At first the metals would precipitate as simple sulphides in the low-temperature environment, and would in part react fairly quickly with one other to form lead sulpho-salts. Reaction between PbS and Bi_2S_3 has been shown by MOH (pers. comm., 1970) to take place at low temperatures. He found that after two years lead sulphide and bismuth sulphide commence to react (to form lead-bismuth sulpho-salts) in aqueous solution at 200°C.

Re-texturing and further mineralogical modification in the lode would take place over a period of time as a result of changing physical and chemical conditions.

Summary of suggested mode of origin of the deposit

The first stage of the development of the deposit was the formation of a shallow restricted basin on the western edge of the Pine Creek Geosyncline. Evaporitic conditions and a heavy growth of algal material resulted in the seasonal co-precipitation of small amounts of lead and zinc with the dolomite precursors.

Intimately associated with the precipitated carbonates was a large quantity of algal material now partly represented by carbonaceous matter. Early in diagenesis this material was completely degraded, and the products of this degradation were complexed with metal ions released to the pore solutions during dolomitization of the carbonates, and probably also with any sulphide ions produced in the upper layers of the sediment by bacterial sulphate reduction. In this way the formation of metal sulphide precipitates would be inhibited.

As with oil-producing rocks (OWEN, 1964), the sediments would lithify early in diagenesis by cementation. This process would result in a porous rock capable of retaining the metal-rich solutions formed during dolomitization.

During this period of lithification, some movement of fluids took place, and veins of dolomite and quartz were formed both parallel to and at angles to the bedding, and were compressed during compaction of the sediments (Fig. 4). In places the fluids carried some sulphide (mainly pyrite) in solution , and the quartz-sulphide bodies formed from them were moulded by the compacting sediments (Fig. 14).

Some time after lithification, while the pore fluids were still retained in them, the rocks were folded. Tension in the crestal parts of the anticline produced fractures parallel to the axial plane and more or less normal to the bedding, and compression produced a high pressure area towards the deeper parts of the fold.

The pressure gradient developed caused the pore-solutions to move along fractures and solution-cavities into the tension fractures, where the metal sulphides precipitated after the organic complexes became unstable as a result of a change of composition of the solutions brought about, at least, in part, perhaps, by the release of gases in response to diminished pressure. Evidence for the post-lithification movement of fluids containing silica, dolomite, and sulphide may be seen in Figs. 6 and 7, which show pressure shadows developed on diagenetic pyrite crystals. The outlines of the pyrite crystals are preserved, indicating that the rock had virtually reached its final level of compaction and lithification at the time of folding. Fluids moving into the open spaces precipitated dlolomite, chalcedony, quartz, and sulphides.

According to the criteria set out by SYNDER (1967), the deposit would be classed as epigenetic. However, if its origin were ascribed to epigenetic processes it could create a misleading impression through disregarding the importance of the parts played by sedimentary and diagenetic processes.

Because both sedimentation and diagenetic processes were responsible for the concentration of the ore components, it would perhaps be more accurate to say that the deposit had a sedimentary origin, and that it has been formed by tectonic mobilization.

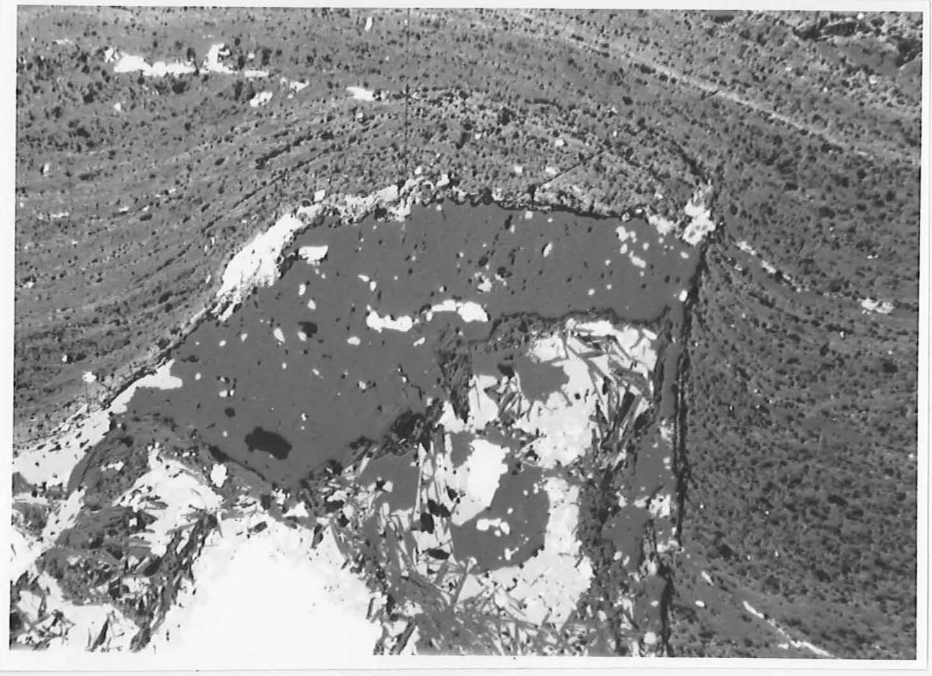


FIG. 14

Compaction of sediments over a quartz/pyrite mass. D.D.H. S38, 283'6". x 16. Polished section.

The distance over which the fluids would have to move to reach the site where the sulphides were finally deposited also needs consideration.

It is probable that for the formation of the Woodcutters deposit the fluid moving through its parent rock along secondary pore spaces need not have travelled far.

Assuming that the fluids that contributed to the lode at Woodcutters moved a distance of not more than 500 metres a sphere of this radius would have a volume of -

$(5 \times 10^2)^3 \times 4/3 \times 22/7$ metres^3.

Assuming that at the time of fluid movement the rock had 20% porosity, and that half of the pore fluids were able to reach the fractures, the volume of this fluid would be -

$(5 \times 10^2)^3 \times 4/3 \times 22/7 \times 10^{-1} \times 10^6$ ml.

If the fluids contained 0.1% Pb they would contribute -

$(5 \times 10^2)^3 \times 4/3 \times 22/7 \times 10^{-1} \times 10^6 \times 10^{-3}$ gm of Pb

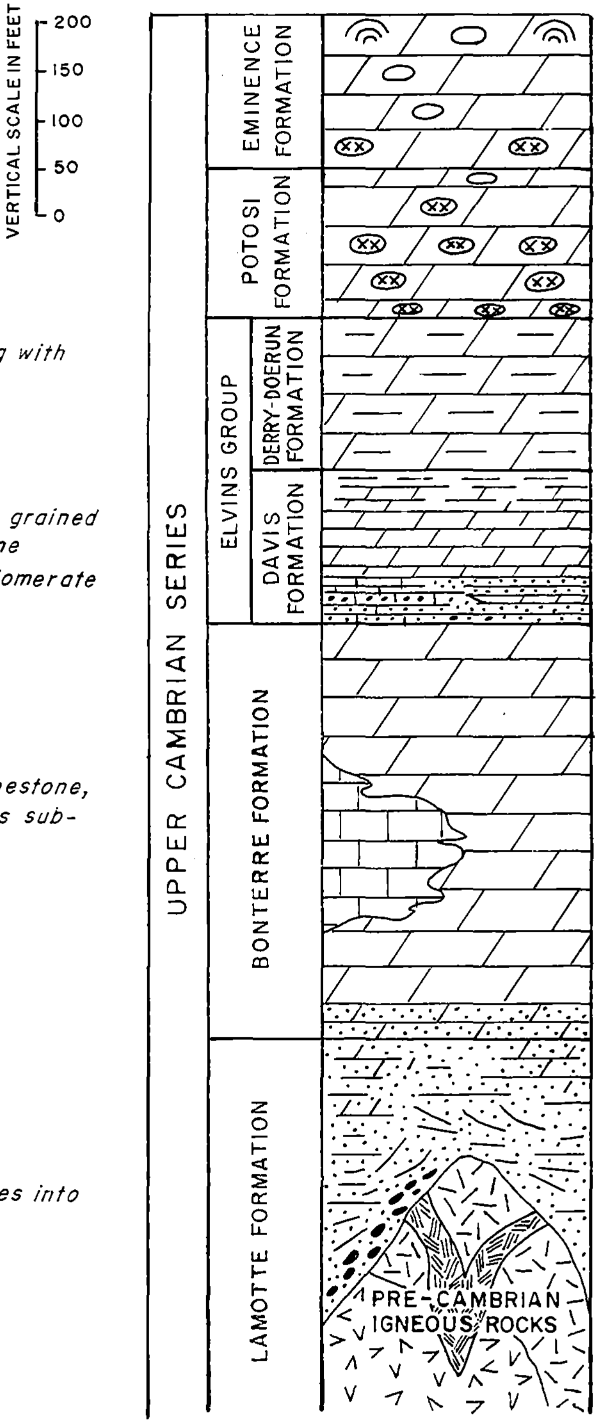
$= 500 \times 10^8$ gm or 500×10^2 metric tons Pb,

or 1,000,000 metric tons of 5% Pb ore.

If the pore fluids contained 0.05% Pb, a sphere of radius 600 metres would contribute the same quantity of lead. Two million tons of 5% Pb ore would require a sphere of radius 800 metres to supply the volume of solution under the stated conditions at 0.05% Pb.

Considering that oil may migrate over distances as great as 100 miles (BARBAT, 1967; KVENVOLDEN & SQUIRES, 1967), the distances that the ore fluids moved in the formation of Woodcutters are well within the bounds of possibility.

Subsequent to their deposition in the fractures, recrystallization of the lodes by shearing, compressional effects, and possibly heating has taken place; this recrystallization is particularly evident in the polygonal sphalerite shown in figure 9. Shearing has resulted in the formation of tetrahedrite with an anomalous anisotropism, and the lineations of stannite in sphalerite (Fig. 11).



Dolomite containing nodules and beds of chert, cryptozoans

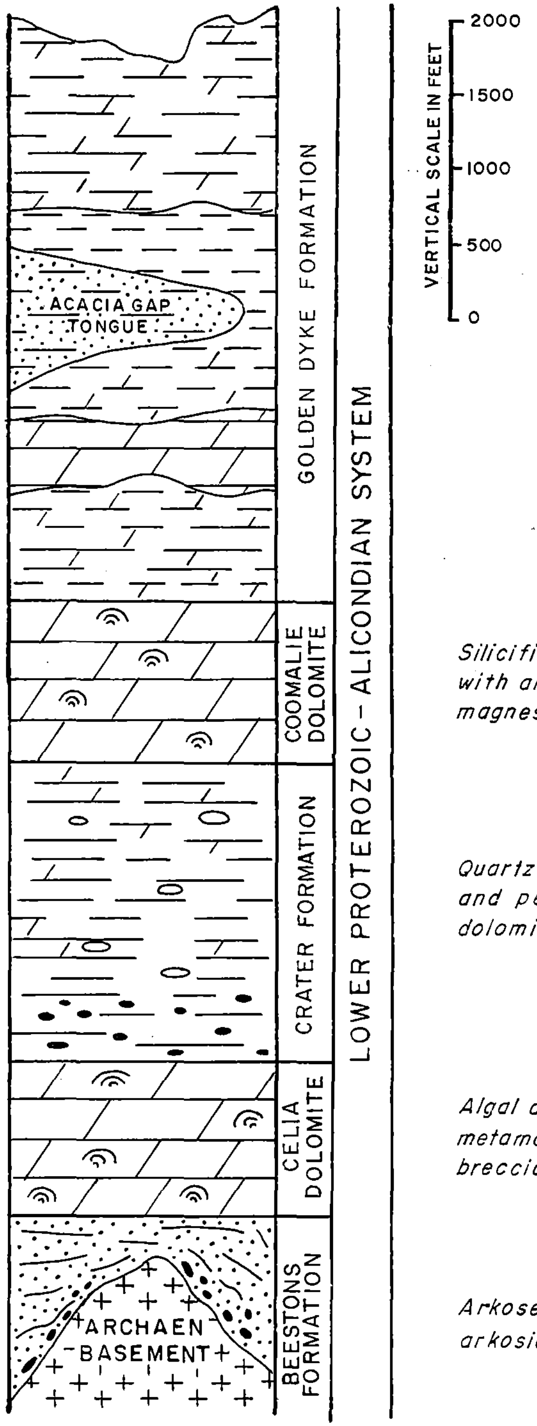
Dolomite and quartz druses

Thin bedded dolomite alternating with thin bedded siltstone and shale

Glauconitic shale, siltstone, fine grained sandstone, dolomite and limestone conglomerate

Medium bedded dolomite, some limestone, some glauconite, algal structures submarine breccia

Mainly quartzose sandstone grades into arcose and conglomerate



Quartz, siltstone and carbonaceous siltstone in places, pyritic marl and dolomite; silicified dolomite breccia

Quartz greywacke and s/s pyritic carbonaceous siltstone

Silicified and metamorphosed dolomite with algal bioherms in places, calcilutite-magnesite in places

Quartz greywacke, greywacke arkose, fine and pebble conglomerate, siltstone, dolomitic marl with chert lenses

Algal dolomite in places silicified and metamorphosed, silicified dolomitic breccia, tremolite schist

Arkose greywacke, siltstone conglomerate, arkosic conglomerate, friable quartz sandstone

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Although from this interpretation of its genesis, the Woodcutters deposit has some similarities to the Mississippi type lead-zinc deposits, it could not be classed strictly as a deposit of this type if the features characteristic of these deposits listed by JACKSON & BEALES (1967) are considered. However, the sedimentary sequence in which the deposit is situated has marked similarities to that which contains the southern Missouri lead-zinc deposits (HOWE, 1961, Fig. 15). In addition, the widespread occurrence of primary bedded pyrite (Fig. 5), and the virtual restriction of galena and sphalerite to suitable structural situations, which, according to SNYDER (1967), are features of Mississippi type deposits, are also features of the Woodcutters lodes and country rocks.

The similarity of Woodcutters to the southern Missouri deposits, coupled with the probable significance of dolomite and its precursors in the formation of lead-zinc deposits, suggests the possibility that ore may also be found in the Celia or the Coomalie Dolomites. The search for such deposits should also be carried out in the dolomitic facies of the Golden Dyke Formation, especially in places where there is evidence that fluid movement has taken place; it should be centred about fracture-zones and anticlinal zones which may indicate the existence of pressure gradients and accompanying tension fractures similar to those which contain the ore at Woodcutters.

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