SUPERGENE MARCASITE, REPLACING PYRRHOTITE

BY

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Most occurrences of marcasite seem to be of supergene origin. An interesting mode of occurrence is in connection with pyrrhotite-bearing ores at the border between the oxidation- and cementation zones, the marcasite here representing the first stage in the process of secondary enrichment. Secondary iron sulfides, deposited under these conditions, are not very common. It is generally only pyrrhotite, which undergoes this sort of replacement, because it is most easily soluble among the ordinary sulfides.

The process had been occasionally recorded from several deposits, when Gilbert first proved its real significance.[1]

The primary ores of Ducktown consist of pyrrhotite, chalcopyrite, sphalerite and varying amounts of pyrite. The gossan is 30 m thick. Below the gossan, secondary marcasite is observed in the pyrrhotite, partly as small ellipsoids (birds eye structure), partly as microscopic veinlets, which may ultimately replace the pyrrhotite completely. In most cases pyrrhotite is the only mineral attacked, the veinlets stopping abruptly against the surrounding minerals. Sometimes the sphalerite is also involved in the process, while chalcopyrite and pyrite remain unaffected. The veinlets of hard and white marcasite in some cases are said to show a transitional zone towards the pyrrhotite, being "softer, browner and more easily affected by reagents".

In the opinion of Gilbert it is the new-formed marcasite, which is replaced at the next stage by the rich, secondary copper minerals (chalcocite etc.). Thus it should play an important part in the process of secondary enrichment.

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[1] Geoffrey Gilbert: Oxidation and Enrichment at Ducktown, Tenn. Trans. American Inst. Min. Eng. LXX (1924), p. 998.

From the oxidation zone, solutions with sulfuric acid and ferric
sulfate seep down into the fresh ore, rapidly attacking the pyrrhotite
and liberating hydrogen sulfide and some free sulfur. The newly
formed hydrogen sulfide reduces the ferric sulfate, firstly to ferrous
sulfate with formation of more free sulfur. The further reaction with
H_2S and S produces marcasite practically in situ, provided the solu-
tions are cold and acid.

Interesting from a mineralogical point of view is the intermediate
zone between pyrrhotite and the marcasite veinlets, antedating the
marcasite formation. It has been more closely studied by Ramdohr,[1]
founded on better polished specimens, but even he does not attain a
definite conclusion as to its real nature. He describes it as follows:

The mineral is greyish white in reflected light, strongly aniso-
tropic with excellent basal cleavage, slightly harder than pyrrhotite.
It grows from fissures and cleavage planes into the pyrrhotite with
orientated growth, is more easily tarnished and more easily attacked
by chemical reagents, e. g. HNO_3, HCl, NH_4OH.

The Copper Prospects of Håfjellstuva.

Replacement of the above-mentioned type has scarcely been
observed form Norwegian deposits, where surface oxidation is gener-
ally scarce.[2] It was therefore surprising to find it in typical devel-
opment in some small copper prospects, belonging to the government,
in the southern slope of Håfjellstuva, Ofoten.

The oxidation of the narrow ore is here relatively deep. Below it,
marcasite veinlets in the pyrrhotite are plainly visible, even in ordinary
thin sections, but only near the surface. They disappear very soon
towards depth. Excellent relief-free polished sections (according to
the Vanderwilt polishing method) made a close study of the veinlets
possible and disclosed new details of the structure.

The ore deposit contains as primary minerals *pyrrhotite, chalco-
pyrite* and *sphalerite,* rather coarse-grained and nearly contemporane-
ous. It is traced for a length of 120 m, but always narrow, never
exceeding some few dm. It is embedded in a very thick series of

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[1] Schneiderhöhn-Ramdohr: Lehrbuch der Erzmikroskopie, p. 138, 196 and
    fig. 62.
[2] Ödman has described it from Kaveltop in Sweden. Olof Ödman: Sulfiderze
    von Kaveltorp. Geol. Fören. Förh. 55 (1933), p. 594.

calcite marble of a dark grey colour, slightly dolomitic. Near the ore
the marble is more banded and completely dolomitic. Within this dark
dolomite are parallel streaks and narrow bands of a colourless car-
bonate, more coarse-grained and partly interwoven with sulfides. Its
refringeance is $\omega = 1.683$, corresponding to a dolomite, very poor
in iron. It is obviously associated with the process of ore deposition,
and together with some quartz forms the only gangue minerals
accompanying the ore. No silicates occur. In crossing fissures we
find cavities with crystals of clear calcite ($\omega = 1.660$), younger than
the ore minerals.

Optical spectrograms of the ore minerals, taken by Dr. I. Oftedal,
show:

Sphalerite	Chalcopyrite	Pyrrhotite with marcasite
Cd 0.1—0.3 %	Mn 0.1 %	Mn trace
	Ag 0.00x	Ni 0.1 %
	Ni, Sn traces?	Co 0.1 %

Microscopic studies of polished specimens show:

Sphalerite. The black, iron-rich sphalerite is completely homogenous,
without exsolutions of any sort.

Chalcopyrite. It shows faint twinning lamellae. At very high magni-
fication are seen some sparse and minute spindles of a mineral
with extremely high reflection pleochroism, creamy white —
nearly black, and very strong anisotropism. It is undoubtedly
valeriite. Cubanite is not present.

Pyrrhotite. It occurs as grains up to 2 mm diameter. In the still fresh
parts of the grains, it is completely homogenous and without
visible cleavage or parting.

Marcasite. As seen from Fig. 1 the pyrrhotite is cut by numerous
veinlets of marcasite, partly along cracks in different directions,
partly as seams along grain boundaries. The marcasite is easily
recognized by its creamy colour in reflected light (paler than
pyrite), its great hardness and its marked anisotropism with
distinct colour effects.

The marcasite veinlets and seams have a thickness of 0.1 mm or
less, and occur in all the pyrrhotite grains without exception. The
sphalerite and chalcopyrite, on the contrary, are completely fresh and
unaffected. Against them the veinlets either stop abruptly or continue

as a narrow border seam.   Against dolomite grains are always found border seams of macrasite.

As seen from the microphotos, the ordinary marcasite and the fresh pyrrhotite are never in direct contact with each other. They are separated by double garlands or marginal zones of a combined thickness of 0.05 mm or less. The minerals of both zones are distinctly different from the sulfides just mentioned. In reflected light they have grey colours, the outer zone distinctly lighter than that of sphalerite, the inner zone distinctly darker.

The sequence is the following:

> Pyrrhotite.
> Outer marginal zone, light grey.
> Inner marginal zone, dark grey.
> Marcasite.

The Light Grey Marginal Zone.

This mineral, representing the first alteration of the pyrrhotite, has a marked anistropism, stronger than either pyrrhotite or marcasite. To all appearance it has also a marked cleavage, which seems, however, to be only imaginary.

The habit of the zone is fibrous or lamellar, with a seismogram-like contact against the pyrrhotite and with single rays proceeding far into it. Fig. 1. Within each individual pyrrhotite grain their direction is quite uniform, independent of the direction of the marcasite veinlets, to which they may happen to run parallel. It seems therefore, that it is the basal parting of the pyrrhotite, invisible in ·the fresh mineral, which is elicited by the alteration.

Moreover, under crossed nicols, its optical orientation is parallel to that of the pyrrhotite, independent of that of the marcasite. The new-formed mineral therefore seems to be closely related to the pyrrhotite, with more or less retention of the space lattice.

In polished specimens the mineral is not easily tarnished in air. It is somewhat harder than pyrrhotite. The polishing scratches are numerous and distinct on pyrrhotite, few and narrow on the grey border zone and nearly absent on marcasite.

The character of the mineral corresponds very well with the description, given by Ramdohr (loc. cit.). As to the nature of the mineral, we may conclude from the spectrogram, that iron is the only

cation contained. Much further we can not get, so long material for chemical analysis is not available. One might think of some sort of oxysulfide [1] or hydrosulfide.[2]

M. Saksela [3] mentions a mineral replacing pyrrhotite, and designated by him "Wasserkies". Its properties seem to be similar in many respects to those observed in our light grey border zone.

The chemical investigations of L. Lokka [4] on a black, sulfidic material from the Otravaara pyrite mine proved the existence of a hydrous sulfide besides melnikowite and minute grains of pyrite. The total composition was 39.5 % Fe, 51.5 % S and 7.95 % H_2O. S : Fe $= 2.27$. As the water could be driven out already below 100° C and most of the hydrous part of the sulfide could be extracted by water (S : Fe $= 1.2$), it is scarcely comparable with our mineral.

The Dark Grey Marginal Zone.

This zone generally is narrower than the foregoing and in some places may taper out completely, but on the whole it has a very regular extention.

The contact against the outer zone also reminds of a seismogram, with hairlike offshoots into it, still better marking its fibrous or lamellar habit (see white rays in Fig. 3). Towards the marcasite, the contact is more abrupt, but still reminding of short-cut hair. Fig. 2. Thus the direction of the pyrrhotite parting is prevailing also in this zone.

The mineral of the dark zone only partly shows a smooth surface, in reflected light darker than sphalerite and with weak anisotropism. Most of it, with dark-field illumination shows a shimmering surface, probably due to porosity. Fig. 3. In transmitted light of very thin sections the mineral is seen to be *limonite* of a reddish brown colour.

One might perhaps suspect, that the limonite were due to an entirely younger oxidation. Besides the intimate connection of the

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[1] In analogy with *voltzite*-formation on sphalerite and wurtzite.

[2] *Hydrotroilite* so far is only known in the amorphous state. Laudermilk and Woodford: Hydrous iron sulphide in California crystalline limestone. Am. Min. 25 (1940), p. 418.

[3] Martti Saksela: Über eine antimonreiche Paragenese in Ylöjärvi. Bull. Comm. geol. Finlande, 140 (1947), p. 208.

[4] Lauri Lokka: Beiträge zur Kenntnis des Chemismus der finnischen Minerale. Bull. Comm. geol. Finlande, 129 (1943), p. 48.

different zones, this idea is disproved by a small offshoot of marcasite, cutting the whole zone, and thus younger. (See left side of Fig. 2.)

Co-occurrence of marcasite and limonite under similar conditions is known from several deposits, *e. g.* Rossland, B. C. (Gilbert loc. cit., p. 1019). It is explained by varying acidity of the descending solutions. A drop in the concentration of sulfuric acid allows part of the ferric sulfate to hydrolize to ferric hydroxide.

The marcasite veinlets.

The texture is here quite different, without any preferred direction. From Fig. 1 it appears, that the veinlets often have more or less remiform borders, which may work outwards forming small semicircular bodies or spheroids, everywhere accompanied by the double marginal zone.

It is therefore apparent, that the marcasite has originally been deposited as a gel. The narrow fissures, generally following the central part of the veinlets, are contraction cracks formed by the following crystallization.

A closer study of the marcasite also shows, that it is by far not as uniform as the pyrrhotite. Only a rim on both sides of the veinlet is compact with a smooth surface, the central part is more or less pitted and stained in rythmic zones, parallel to the borders. (Fig. 2, 3.) This may be due to porosity with or without deposition or limonite.

For deposition of marcasite, an acid character of the descending solutions is generally demanded. Within a dolomitic rock this can only be maintained within a short vertical section, within a calcite marble it would scarcaly be possible at all.

There is a striking analogy between this supergene formation of marcasite from pyrrhotite and the corresponding formation of bravoite (or violarite) from pentlandite under similar conditions. Yet in most cases they do not seem to bee simultaneous. In the nickel deposit of Lillefjellklumpen [1] and several others, the pentlandite near the surface to a great extent has been changed to bravoite, but the pyrrhotite has remained fresh. In the nickel deposits of Vlakfontein in South Africa, according to Wagner,[2] the pyrrhotite to a great extent has

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[1] S. Foslie and M. Høst: Platina i sulfidisk nikkelmalm. Norges Geol. Unders. nr. 137 (1932), p. 21, 64.

[2] Percy Wagner: Magmatic nickel deposits of the Bushveld Complex. South Africa Geol. Surv. Mem. 21 (1924), p. 155.

been replaced by marcasite, but the patches and veinlets of pentlandite have not been affected, and are now found as very distinct inclusions within the marcasite. No indication of bravoite formation is mentioned in the description.

It is possible that the two processes are associated with different pH-conditions of the solutions.

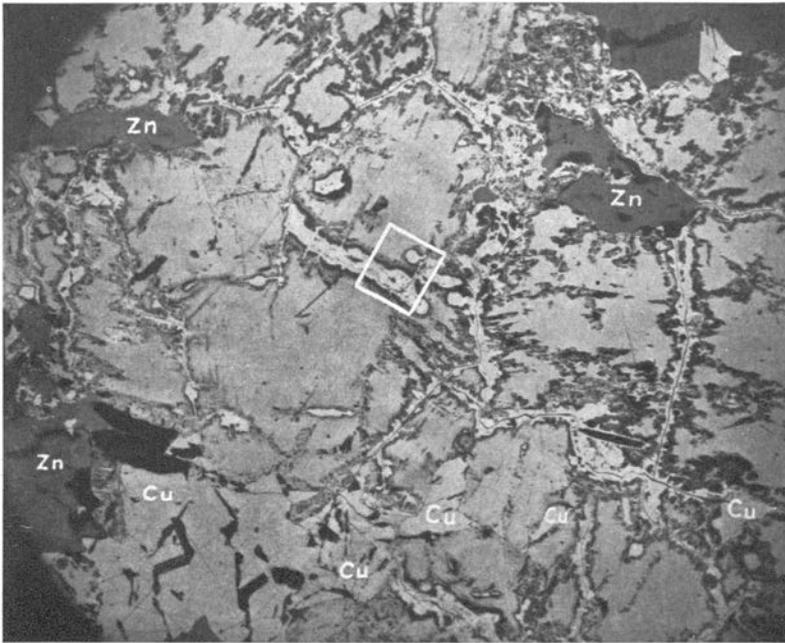Norges Geologiske Undersøkelse, 22 desember 1948.

Fig. 1. Pyrrhotite (medium grey) with veinlets of marcasite (white). Some grains of sphalerite (dark grey, Zn) and chalcopyrite (light grey, Cu). Small square enlarged in Fig. 2, 3. Pol. sec., ord. light. 25 ×.

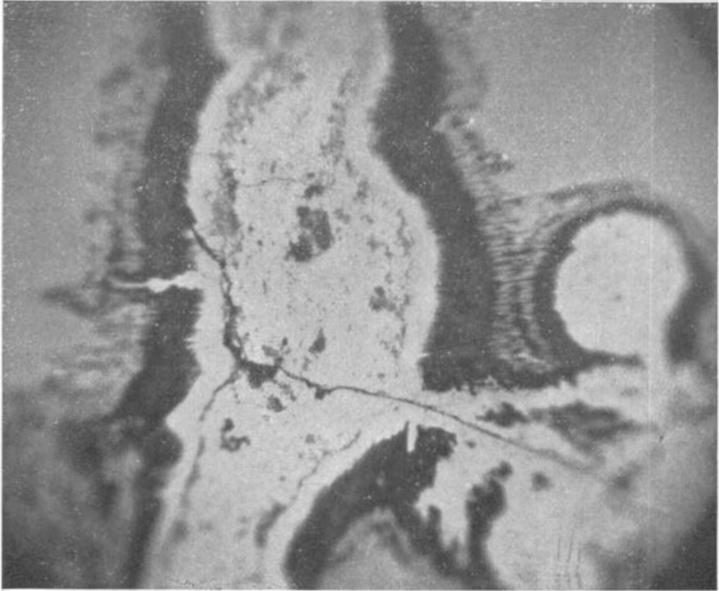*Steinar Foslie: Supergene marcasite, replacing pyrrhotite.*

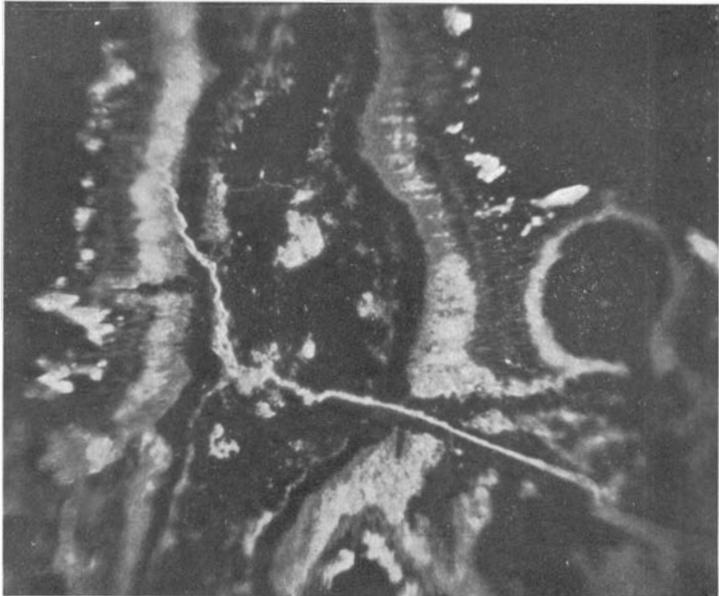Fig. 2. Detail of marcasite veinlet and spheroid (white) with double marginal zone. On both sides is pyrrhotite (medium grey). Pol. sec., ord. light. 250 ×.

Fig. 3. Same as Fig. 2, but dark field illumination.