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Pyrrhotite alteration—a study on Norwegian and Indian sulphide ores

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Abstract

Existence of an intermediate alteration product of pyrrhotite is confirmed in the sulphide ores of Kvikne, Norway and Kolihan, India. The alteration takes place due to change in oxygen potential by the introduction of atmospheric oxygen to pyrrhotite surface. Electron microprobe analysis of this intermediate product showed 44.2–45.1% (Fe) and 52.7-53% (S). Presence of no other element was detected.

Introduction

Fooslie (1950) described supergene marcasite replacing pyrrhotite from Norwegian sulphide ores. He identified an intermediate phase occurring between pyrrhotite and marcasite and antedating the formation of marcasite. Schneiderhohn & Ramdohr (1931) after a close study of this phase described it as a mineral, greyish in colour under reflected light and strongly anisotropic with excellent basal cleavage, being slightly harder than pyrrhotite. They termed the above phase as hydrosulphide and oxysulphide. Saebo *et al.* (1960) found marcasite to form along (0001) plane of pyrrhotite due to alteration of the latter. At the contact of pyrrhotite and marcasite, another unnamed mineral was found by them to form as the first alteration product of pyrrhotite. Taylor *et al.* (1971) established that consequent to oxidation pyrrhotite increasingly becomes iron deficient and with further oxidation, anomalous pyrrhotite (46.4 atomic % Fe) is formed. Progressive oxidation however, results in the formation of pyrite. Einaudi (1971) first reported an intermediate product of pyrrhotite alteration occurring as oriented lamellae along the basal parting of both hexagonal and monoclinic pyrrhotites. Fleet (1978) described marcasite as preferential replacement product of monoclinic (4c type) pyrrhotite. This preferred orientation has been noted to be a consequence of adjustment by the ordered removal of Fe atom from the pyrrhotite structure.

The present authors during their investigations on the Norwegian (Kvikne mine, Trondheim) and Indian (Kolihan mine, Rajasthan) sulphide ores, studied the preferential replacement of hexagonal pyrrhotite rather than monoclinic pyrrhotite by an intermediate product during oxidation of the former.

Analysis

Rao & Rao (1969) made an exhaustive study of pyrrhotite from Kolihan, India. Mukherjee (1968) attempted a minero-chemical investigation of pyrrhotite from Kolihan and Madan-Kudan, India. The detailed mineralogy of the sulphide ores from Kvikne, Norway and Kolihan, India were treated earlier by Nilsen & Mukherjee (1972) and Mukherjee (1966) respectively. Both monoclinic and hexagonal phases are present in these deposits, whereas the Kolihan ores contain troilite phase in addition. All these phases are confirmed by X-ray diffractometric studies.

Hexagonal pyrrhotite from these occurrences, in general, with the initiation of oxidation, usually reveal parallel planes of weakness, presumably 0001 planes. Along

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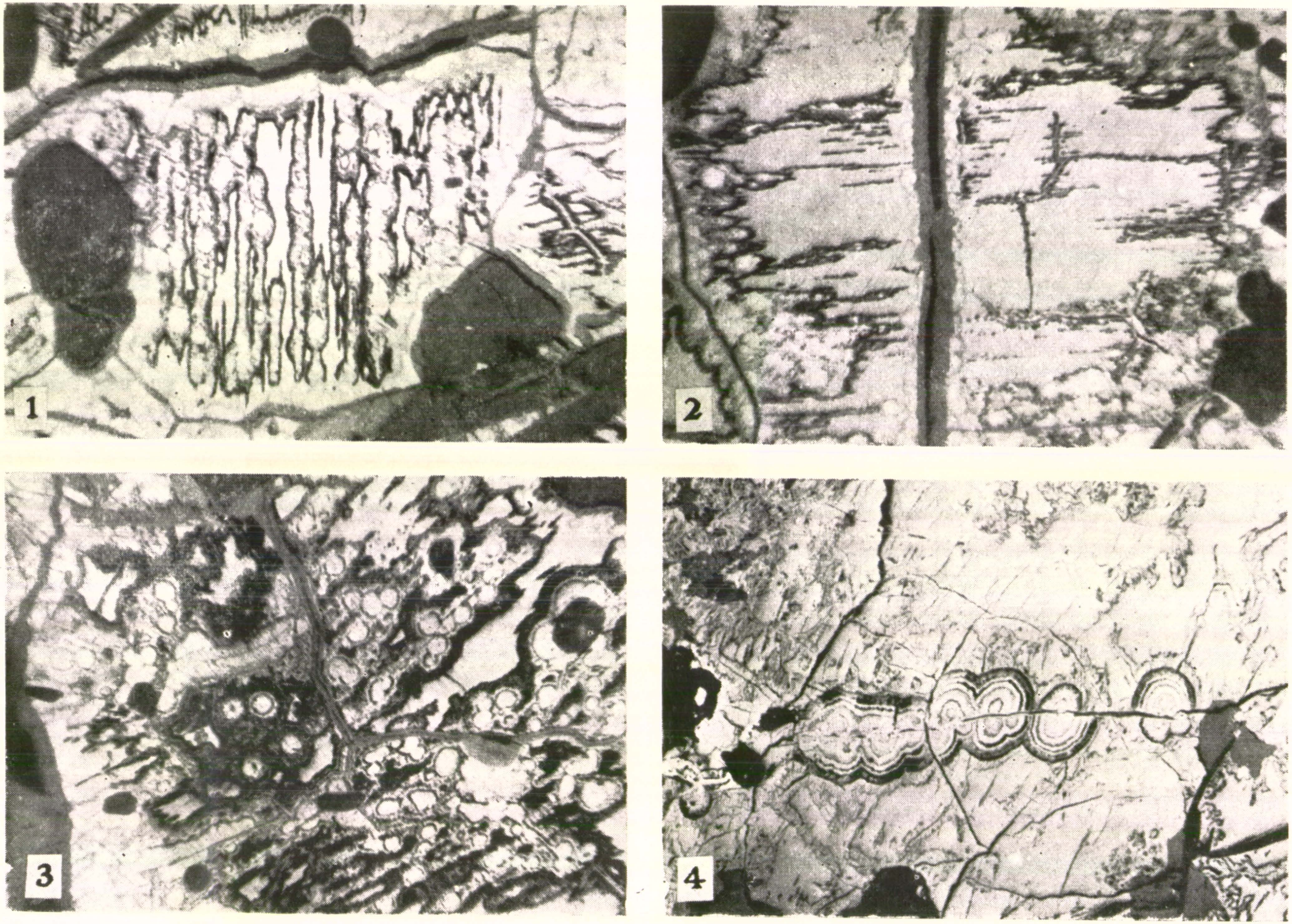
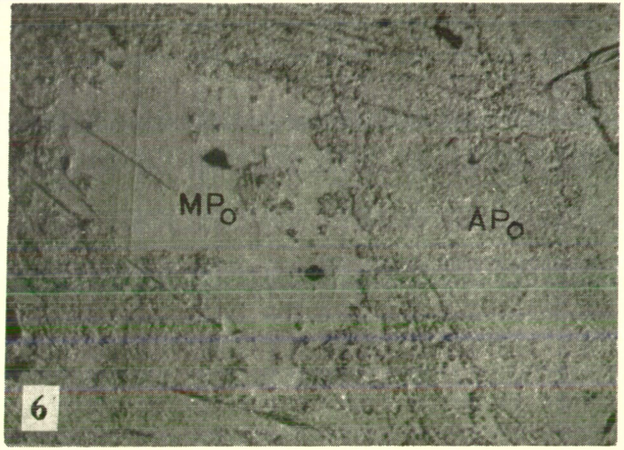
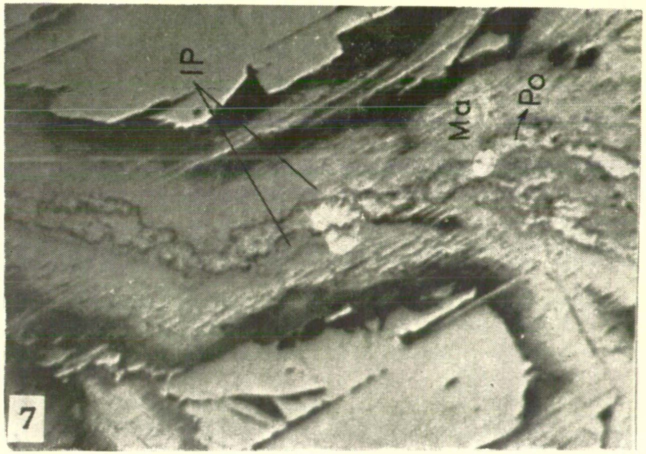
EXPLANATION OF FIGURES

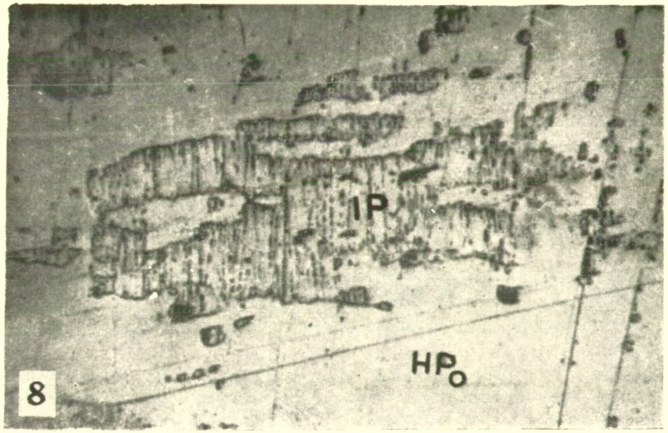
1. Alteration of pyrrhotite along (0001) planes; Kvikne Mine. ×200.
2. Initiation of alteration along fractures; Kvikne Mine. ×150.
3. Spheroidal and concentric growth of Bird's eye texture; Kvikne mine. ×200.
4. Alteration along fractures in the form of colloform aggregates; Kolihan mine. ×200.



Figures 1 to 4.







Figures 5 to 8.

these planes and grain boundaries the alteration extends (Figs. 1 and 2). Bird's eye textures are also produced due to alteration of hexagonal pyrrhotite. The Bird's eyes are found to grow perpendicularly to the parting planes along which transformation was initiated. The bird's eyes are spheroidal in appearance and show concentric growth (Fig. 3). During their growth the eyes may coalesce and form irregular bands along fracture of parting/cleavage planes. Occasional alteration also takes place in the form of colloform aggregate along the fractures (Fig. 4). Ellipsoidal altered zones are sometimes found along fractures in pyrrhotite and these ellipsoids join together and develop banding structures (Fig. 5). Monoclinic pyrrhotite was found to alter around its periphery (Fig. 6), producing anomalous pyrrhotite. Anomalous pyrrhotite is confirmed by X-ray diffractometric studies (FeK radiation) where it showed $\bar{4}08$ peak higher than 408 peak. This phenomena was described earlier by several workers and recently by Taylor (1971). The phase in question has probably formed by oxidation of pyrrhotite.

It is known that pyrrhotite generally alters to marcasite, gradually producing pyrite as the final product. Presence of an intermediate product is well-known though its true nature is not fully understood (Nebel, 1919, Frenzel 1965). In the present case, one intermediate product of alteration in between pyrrhotite and marcasite is found (Figs. 7 and 8). This intermediate product also occurs as oriented lamellae/patches in hexagonal pyrrhotite and not too infrequently as rims or bands enveloping the hexagonal pyrrhotite. The colour of this product was found to be greyish white to light greyish white with anoisotropism in shades of greyish blue. Since the initial work of Fooslie (op. cit.) the characteristic features of this intermediate product, reported so far from different localities of the world, are shown below:

Location	*Optical properties*	*Chemical composition*
Norway Fooslie (op. cit.)	Light grey with marked cleavage	39.5% (Fe), 51.5% (S) and 7.95% (H_2O)*
Italy Enaudi (op. cit.)	Light greyish white decomposes with 1 : 1 HNO_3	44.6% (Fe), 52.5% (S) and 2.2% (H_2O ?)**
Norway Present authors	— do —	(44.2% (Fe), 53% (S) and 2.8% (H_2O ?)***
India Present authors	Greyish white decomposes with 1 : 1 HNO_3	45.1% (Fe), 52.7% (S) 2.2% (H_2O ?)***

*Chemical analysis; **EMP Analysis; ***EMP Analysis by ARL-EMX Model using chemically analysed pyrrhotite as standard.

Emperical observations thus reveal that the degree of alteration depended on the availability of fresh surfaces (fracture planes or basal partings/cleavages, besides

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EXPLANATION OF FIGURES

5. Ellipsoidal altered zones along fractures forming bands; Kolihan mine, ×200.
6. Alteration of monoclinic pyrrhotite (MP_o) around its periphery to anomalous pyrrhotite (AP_o); Kolihan mine. ×200.
7. Intermediate product (IP) of alteration in between pyrrhotite (P_o) and marcasite (M_a), Kvikne mine. ×600.
8. Intermediate alteration product (IP) occurring as oriented lamellae and patches in hexagonal pyrrhotite (HP_o); Kolihan mine. ×600.

the external surface) of pyrrhotites that were exposed to the external environment. Once altered along the exposed fresh surfaces the alteration products protected pyrrhotites from further decomposition. This implies quick equilibration of the altered product to the charged surrounding p_{fluid}, the f_S being internally controlled.

Conclusion

The intermediate product between pyrrhotite and marcasite delineated in the present case is similar in many respects to the characteristic alteration products of Enaudi (op. cit.) and Fooslie (op. cit.). It is confirmed to be an altogether different phase from marcasite or anomalous pyrrhotite. Ramdohr's conclusion as also suggested by Enaudi (op. cit.) that the intermediate product forms through the disintregation of pyrrhotite with incorporation of H_2O/O_2 has thus been held by the present authors.

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