

## THE INTERMEDIATE PRODUCT OF PYRRHOTITE ALTERATION

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### ABSTRACT

The "Zwischenprodukt" of Schneiderhöhn and Ramdohr (1931) has been identified in samples from Cerro de Pasco and Cobriza, Perú, associated with hexagonal pyrrhotite and pyrite-marcasite. A temperature of formation of less than 300°C, and possibly as low as 25°C, is indicated by the occurrence in these two deposits. Electron microprobe analysis yields 44.6 percent Fe and 52.5 percent S. No other elements were detected, suggesting the presence of 2.9 percent of some light element or combination of light elements.

### INTRODUCTION

The identity of the "Zwischenprodukt" of Schneiderhöhn and Ramdohr (1931) has been an unresolved problem since its first description by Nebel (1919). Nebel describes the replacement of pyrrhotite in the Duluth Complex by an unknown grayish-white phase having a lamellar, strongly cleaved appearance (page 376, plate 16c). Numerous investigators (Grondjic and Schouten, 1937; Frenzel, 1955; Ramdohr, 1960; Maucher, 1965; Cavagnino *et al.*, 1965; and Babkine *et al.* 1966) have noted this phase as an alteration product of pyrrhotite and have equated it with the "Zwischenprodukt". Others (Wright, 1966; Oelsner, 1966; and Chamberlain, 1967) have suggested that the intermediate product represents an incipient conversion of pyrrhotite to marcasite. Though this unknown sulfide does indeed resemble marcasite more closely than it resembles any other known sulfide, it has properties that are sufficiently distinct from marcasite to suggest that these two phases are not identical. This prompted the author to present new data on the intermediate product.

### OCCURRENCE

The intermediate product, not visible in hand specimens, occurs throughout the pyrrhotite-bearing portions of both Cerro de Pasco and Cobriza, Perú.<sup>1</sup> Its greatest development occurs in the partly oxidized outcrop of the Cobriza manto at elevation 2840m. It is less abundant in unoxidized portions of both ore bodies.

In both deposits, the intermediate product is present exclusively as oriented lamellae in both hexagonal and monoclinic pyrrhotite. The

<sup>1</sup> Cerro de Pasco is located 175 km NE of Lima, in the department of Pasco. Cobriza is located 280 km E of Lima, in the department of Huancavelica. A general reference to these two deposits is provided by Petersen (1965).

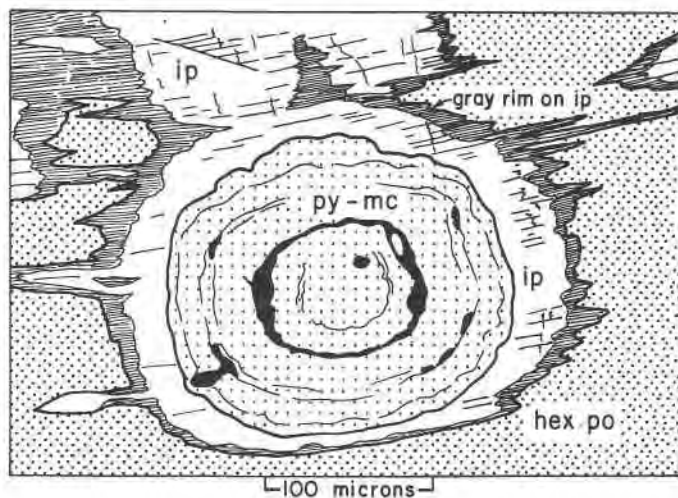


FIG. 1. The intermediate phase (ip) occurring as a shell between orbicular pyrite-marcasite (py-mc) and hexagonal pyrrhotite (hex po). A thin rim which possibly consists of a mixture of the intermediate product and iron oxides or hydroxides separates the intermediate product (*sensu stricto*) from hexagonal pyrrhotite. The elongation and cleavage of the intermediate product is parallel to (001) of pyrrhotite. Black zones in the pyrite-marcasite are voids. Tracing of microphotograph, Cobriza, Peru. Manto outcrop at 2840m.

lamellae, having a distinct cleavage parallel to their length, are oriented along the basal parting of pyrrhotite.

Two fundamental associations are noted in these deposits. The unknown sulfide commonly occurs in thin rims separating pyrrhotite from pyrite or marcasite. This type of occurrence is especially well-developed at Cobriza (Figure 1), where shells of the intermediate product averaging  $25\ \mu\text{m}$  in width completely enclose orbicular pyrite-marcasite intergrowths in hexagonal pyrrhotite. The intermediate product also occurs without pyrite or marcasite along cracks and grain boundaries in pyrrhotite (Figure 2). At Cerro de Pasco, where this second type of occurrence is characteristic, the intermediate product has developed to a greater degree in hexagonal rather than monoclinic pyrrhotite (Figure 2).

#### PHYSICAL, OPTICAL, AND CHEMICAL PROPERTIES

The color of the intermediate product in reflected light is grayish white, distinctly grayer than marcasite and whiter than pyrrhotite. At the contact with pyrrhotite it may develop a darker gray tinge (Figure 1). The anisotropism of the intermediate product is strong, like pyrrhotite; polarization colors are yellowish-brown, grayish-blue, similar to marcasite but weaker.

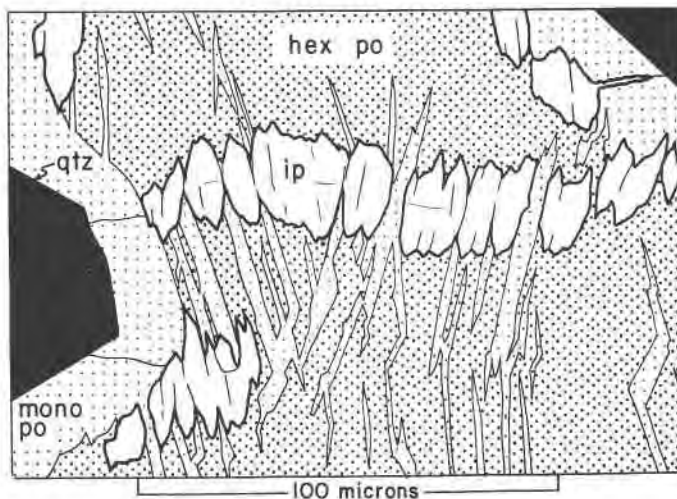


FIG. 2. The intermediate phase (ip) preferentially replacing hexagonal pyrrhotite (hex po) in an intergrowth of hexagonal and monoclinic pyrrhotite (mono po). The pyrrhotite intergrowth was brought out by staining with ammonium dichromate. Cracks continue into the monoclinic form but the intermediate product terminates (on left) or is reduced in development (upper right). Tracing of microphotograph, Cerro de Pasco, Perú. Pyrrhotite pipe, 1800 level.

1:1  $\text{HNO}_3$  decomposes the intermediate product with strong effervescence and the fumes produce a brown tarnish. Marcasite reacts less strongly to the same reagent. All other standard etch reagents have no effect on either mineral.

The hardness of the intermediate product was tested with a Leitz Miniload microhardness tester using a 25 gram load. Due to the small size of the lamellae and the perfect cleavage, the majority of indentations were distorted and were therefore discarded. The range of Vickers hardness of five perfect indentations was 572 to 734 with an average of 650. Published Vickers hardness values for pyrrhotite are 230–259, for pyrite 1027–1240, and for marcasite 941–1288 (Bowie and Taylor, 1958).

The difficulty in separating a clean fraction of the intermediate product for X-ray analysis has been the main deterrent in attempts to conclusively characterize this phase. The author met with results similar to those of Frenzel (1955) and Maucher (1965): the powder patterns were extremely variable, but consistently included some of the strong pyrrhotite and marcasite lines.

Chemical analysis of the intermediate product by all conventional techniques is difficult due to the minute development of this phase. How-

TABLE 1. COMPOSITION OF THE INTERMEDIATE PRODUCT AND RELATED COMPOUNDS

Phase	Wt % Fe	Wt % S	Other
"Zwischenprodukt" <sup>a</sup>	40.0	52.1	7.9 <sup>b</sup>
FeS <sub>2</sub>	46.6	53.4	0.0
Intermediate phase <sup>c</sup>	44.6	52.5	2.9 <sup>d</sup>
Dark gray fringe <sup>e</sup>	45.4	31.5	23.1 <sup>d</sup>
Fe <sub>7</sub> S <sub>8</sub>	61.3	38.7	0.0

<sup>a</sup> Ramdohr, 1960.

<sup>b</sup> H<sub>2</sub>O.

<sup>c</sup> Probe analysis, average of double intensity determinations on 8 separate lamellae, from Cerro de Pasco, Perú. Represents chemically homogeneous material.

<sup>d</sup> Not determined.

<sup>e</sup> Probe analysis, average of double intensity measurements on 12 separate areas, Cobriza, Perú. Represents chemically inhomogeneous material.

ever, Ramdohr (1960) quotes an analysis by Saksela of exceptionally coarse material: Fe/S = 1/2.27, H<sub>2</sub>O = 7.95 percent. If the Fe/S is an atomic ratio, recalculation yields approximately 40 weight percent iron and 52 weight percent sulfur. Electron microprobe analysis (ARL-EMX in the Department of Geological Sciences, Harvard University) of the intermediate product from Cerro de Pasco, using synthetic pyrrhotites and chemically analyzed pyrite from Bingham as standards, yielded similar results. The 5 × 25 μm lamellae, optically homogeneous under oil immersion of 1000X, were intimately intergrown with hexagonal pyrrhotite. The analysis yielded 44.6 (5) weight percent iron and 52.5 (5) weight percent sulfur, giving a total of 97.1 percent. Scanning with both LiF and ADP crystals failed to reveal any additional elements. The remainder, 2.9 percent, would appear to be a light element (O, H, F, C) not detectable in such low quantities by electron probe techniques.

The first standard deviation of double sulfur and iron intensity measurements on eight separate grains was 1.2 and 0.5 percent of the counts, respectively. This represents the precision of the method and demonstrates that the intermediate product is chemically homogeneous on a micron scale. Analysis of material of progressively darker gray shades indicates that iron remains approximately constant, while sulfur decreases sharply (Table 1).

#### DISCUSSION

The preferential replacement of the hexagonal rather than monoclinic form of pyrrhotite by the intermediate product reveals as regards the relative stability of these two pyrrhotites. Under the conditions of forma-

tion of the intermediate product, presumably low temperature and low pH, monoclinic pyrrhotite is more stable than hexagonal pyrrhotite.

The mode of occurrence and apparent composition of the "Zwischenprodukt" lead Ramdohr (1960) to conclude that it forms through the disintegration of pyrrhotite and the incorporation of water or oxygen. Such a conclusion is supported, in principle, by the present study.

A low temperature of formation, possibly as low as 25°C, is inferred from the occurrence of the intermediate product in the two deposits. The upper temperature limit at Cerro de Pasco is fixed by the upper thermal stability of monoclinic pyrrhotite at 308°C (Clark, 1966). The temperature at which the intermediate product formed had to be lower than 308°C, because this phase is preferentially formed in hexagonal rather than monoclinic pyrrhotite. Had it formed prior to exsolution of monoclinic pyrrhotite from hexagonal pyrrhotite, it would not show this preferential distribution (Figure 2). The close association of the intermediate product with marcasite (Figure 1) may also indicate temperatures below 300°C. The fact that the intermediate product occurs most abundantly in the oxidized portion of the Cobriza ore body suggests that it formed there during the low temperature oxidation of pyrrhotite.

The observation that the intermediate product occurs only in pyrrhotite suggests that pyrrhotite acts as a seed crystal and that the structure of the intermediate phase may be a layer structure closely related to the NiAs-type.

#### ACKNOWLEDGMENTS

The author wishes to thank Professor Ulrich Petersen of Harvard University for introducing him to the problem of the "Zwischenprodukt" and for his guidance during the course of this investigation. A National Aeronautics and Space Administration grant (#NSG-282-63 to C. Frondel, Department of Geological Sciences, Harvard University) defrayed the cost of the electron microprobe analyses.

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*Manuscript received, November 2, 1970; accepted for publication, February 5, 1971.*