THE PYRRHOTITE – MARCASITE TRANSFORMATION

M. E. FLEET

Department of Geology, University of Western Ontario, London, Ontario N6A 5B7

ABSTRACT

Marcasite occurring as a replacement product of monoclinic $4C$ pyrrhotite in a specimen from Chihuahua, Mexico has a preferred orientation relative to the pyrrhotite substrate. There are three marcasite orientations related by 120° rotations about the pyrrhotite c-axis, and the complete relationship can be summarized as $a_{ma}||c_{po}$, $b_{ma}||a^*_{1po}$, $c_{ma}||a_{2po}$, where the crystallographic directions for pyrrhotite refer to the NiAs-type subcell. The orientation relationship is consistent with replacement by ordered removal of iron atoms from the pyrrhotite structure. The structural reorganization required to transform pyrrhotite to pyrite is much more complex, and this may account for the predominance of marcasite as the initial replacement product of pyrrhotite in supergene environments.

SOMMAIRE

La marcasite qui remplace la pyrrhotine monoclinique $4C$ dans un échantillon provenant de Chihuahua, Mexique, est orientée préférentiellement sur le cristal de pyrrhotine. Trois orientations sont possibles, reliées par rotations de 120° autour de l'axe c de la pyrrhotine (po). La relation complète peut être exprimée par $a_{ma}||c_{po}$, $b_{ma}||a^*_{1po}$, $c_{ma}||a_{2po}$, où les directions cristallographiques citées en notation hexagonale pour la pyrrhotine se rapportent à la sous-maille de type NiAs. Cette orientation est compatible avec une élimination ordonnée d'atomes de fer de la structure de la pyrrhotine. La réorganisation structurale requise pour transformer la pyrrhotine en pyrite est beaucoup plus compliquée, ce qui expliquerait la prédominance de la marcasite comme produit initial du remplacement de la pyrrhotine en milieux supergènes.

(Traduit par la Rédaction)

INTRODUCTION

The most common sulfide alteration product of pyrrhotite in supergene environments is marcasite or a mixture of marcasite and pyrite. This is discussed in some detail by Ramdohr (1969). In the present paper, marcasite replacement of a pyrrhotite is shown to have a preferred orientation. The orientation relationship is explained by comparison of the crystal structures of the two phases; the structural control on the reaction path of the pyrrhotite→Fe sulfide transformation is discussed.

EXPERIMENTAL

The material studied in the present investigation occurs in a hand specimen from Santa Eulalia, Chihuahua, Mexico (No. 2498 in the Dana Mineral Collection, University of Western Ontario). The hand specimen consists of pseudohexagonal columns of monoclinic pyrrhotite, approximately 0.3 to 1.5 cm wide and several cm long, on massive pyrrhotite with sparse chalcopyrite. The pyrrhotite columns have a pronounced basal parting and are decorated with minor chalcopyrite, galena, and more abundant calcite and radiating clusters of prismatic quartz. Single-crystal and powder X-ray diffraction analysis of unaltered material revealed only monoclinic $4C$ pyrrhotite. The range in composition of this pyrrhotite is evidently very small and the degree of crystal perfection quite high since the 102 reflection of the NiAs-type subcell resolves into a well-separated quadruplet in Jagodzinski focusing-camera photographs, as predicted by Corlett (1968). The pyrrhotite is twinned to produce the pseudohexagonal habit, and the intergrown monoclinic {001} faces impart a well-developed lineage structure to the basal growth surfaces.

The columnar pyrrhotite shows incipient surficial alteration to marcasite varying from a discontinuous film and crust on column faces to extensive replacement on fractured surfaces. Marcasite may extend or protrude outward as an overgrowth, and this is particularly apparent along column edges and on fractured surfaces. In fact, on fractured basal surfaces, euhedral marcasite crystals with prominent {101} faces are observed with a binocular microscope. These have a preferred orientation relative to the pyrrhotite substrate, with the b axis parallel to the pyrrhotite basal plane and in three orientations related by 120° rotations about the pyrrhotite c axis.
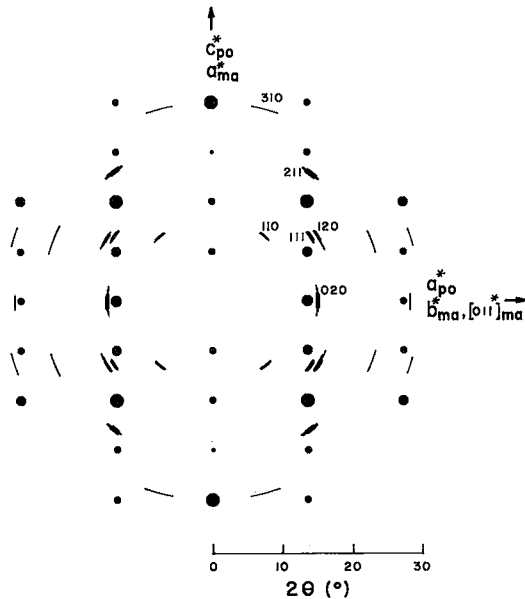
In polished sections cut parallel to the basal

FIG. 1. Reproduction of central part of a-axis precession photograph of a fragment of monoclinic $4C$ pyrrhotite partly replaced by marcasite. Dots are pyrrhotite subcell reflections (superstructure reflections have been omitted); crystallographic directions for pyrrhotite refer to the NiAs-type subcell; arcs are marcasite reflections. $\mu=25°$; Zr-filtered MoKα radiation; 35 kV, 20 mA; 1 day exposure.
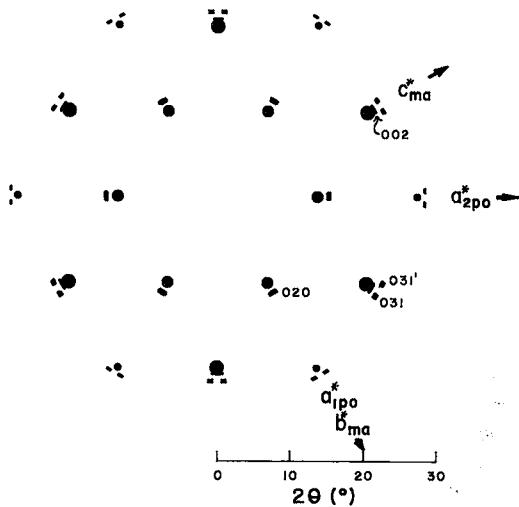

FIG. 2. Reproduction of central part of c-axis precession photograph of a fragment of monoclinic $4C$ pyrrhotite partly replaced by marcasite; legend as in Figure 1.

plane of the columnar pyrrhotite the marcasite is developed as localized embayments that extend 100 to 200 μm into the pyrrhotite. The contact between the two phases is sharp and the 'intermediate product' of Ramdohr (1969) does not appear to be present. Also, the optical properties of marcasite are consistent with those reported in the literature; these, together with the X-ray diffraction data, suggest that this is a normal marcasite of stoichiometric FeS$_2$ composition. Individual marcasite grains are in one of three orientations, related by 120° rotations. The marcasite grains are usually complexly intergrown but grains in any one orientation are in optical continuity across the replaced area. One marcasite area is sector-twinned, with 60° sectors; its interface with the unreplaced pyrrhotite has a near-hexagonal outline.

Small fragments of the columnar pyrrhotite with marcasite replacement were removed for examination with an X-ray precession camera (Figs. 1 and 2). The marcasite (ma) has a preferred orientation relative to the pyrrhotite (po) substrate, with $a_{ma}\|c_{po}$, $b_{ma}\|a^*_{po}$ and $c_{ma}\|a_{po}$ (the crystallographic directions for pyrrhotite refer to the NiAs-type subcell). The orientation relationship is complex, as there are three equivalent orientations of marcasite related by 120° rotations about the pyrrhotite c-axis; for an individual orientation, as suggested by Figure 2, $a_{ma}\|c_{po}$, $b_{ma}\|a_1^*_{po}$, $c_{ma}\|a_{2po}$, and so on. The apparent second preferred orientation of marcasite with [011]$^*_{ma}$ sub-parallel to a^*_{po} and [031]$^*_{ma}$ sub-parallel to a_{po} results from the close dimensional and positional correspondence of the marcasite and pyrrhotite structures.

DISCUSSION

The X-ray diffraction studies (Figs. 1 and 2) confirm the hand-specimen and polished-section observations that there are three orientations of marcasite developed on pyrrhotite, related by 120° rotations about the pyrrhotite c axis. Similar results are obtained from fragments with both twinned and untwinned monoclinic $4C$ pyrrhotite substrates. Hence, the preferred orientation reflects the hexagonal symmetry of the NiAs-type subcell and seems to be independent of superstructure symmetry.

The oriented replacement of pyrrhotite by marcasite can be accounted for quite readily by comparison of the crystal structures of the two phases (Figs. 3 and 4, Table 1). The structure of the subcell of pyrrhotite consists of a hexagonal close-packed array of S atoms with Fe atoms in octahedral interstices arranged in layers
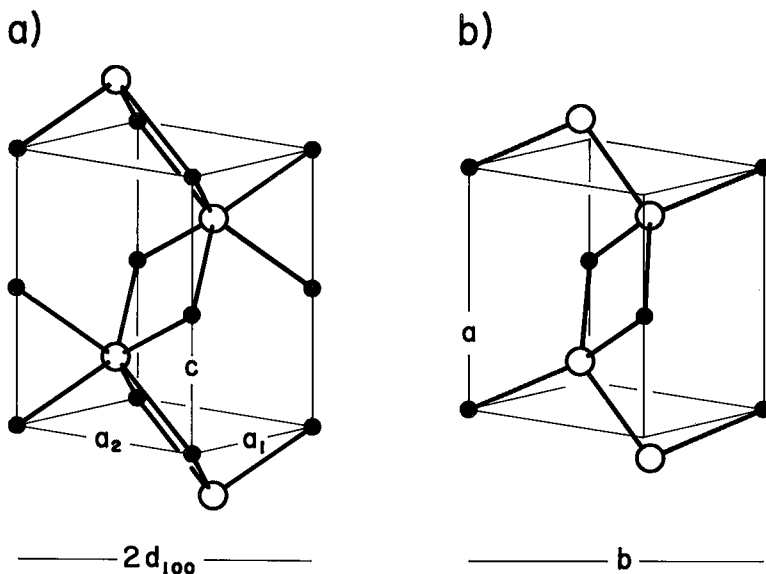
FIG. 3. a) Crystal structure of NiAs-type subcell of pyrrhotite; b) part of crystal structure of marcasite with reference hexagonal unit-cell outline. Large open circles, S atoms; small solid circles, Fe atoms.

parallel to (00.1). Nonstoichiometry results from vacancies in alternate Fe layers, and ordered arrangements of these vacancies (*e.g.*, Fleet 1971; Tokonami *et al.* 1972) are responsible for the pyrrhotite superstructures. In pyrrhotite there is no direct association between the S atoms. In contrast, the structure of marcasite contains covalently bonded disulfide groups, and whereas the Fe atoms are octahedrally coordinated to S, each S atom is tetrahedrally coordinated to one S and three Fe atoms. The marcasite structure can be derived from the ideal NiAs-type structure by ordered removal of half of the metal atoms from each (00.1) layer. This has also been pointed out by Pearson (1972). Of course, for transformation from monoclinic 4C pyrrhotite with ideal composition Fe_7S_8, only one-third of the remaining Fe atoms in the vacancy layers need be removed. Collapse of the semi-vacated structure in the pyrrhotite c-axis direction accompanied by some contraction in the pyrrhotite $[1\bar{1}.0]$ direction (marcasite b axis) moves the paired S atoms close enough together to associate into disulfide groups.

The 29% volume reduction associated with this transformation is relatively large and markedly anisotropic. Thus the extent of displacement of the individual marcasite crystallites from their ideal orientations is directionally dependent. It is minimal in the basal plane of pyrrhotite (*b,c* plane of marcasite) as the dimensional fit of the two structures is best in
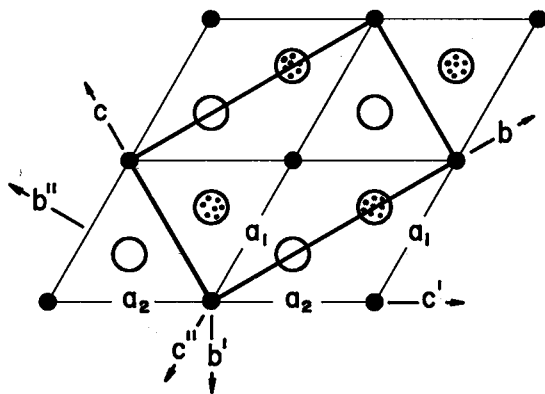

FIG. 4. Crystal structure of NiAs-type subcell of pyrrhotite projected down c axis with reference marcasite unit-cell outline (heavy lines) in one of the three preferred orientations of marcasite replacement in pyrrhotite. Large stippled circles, S at $z=\frac{3}{4}$; large open circles, S at $z=\frac{1}{4}$; small solid circles, Fe at $z=0, \frac{1}{2}$.

TABLE 1. RELATED CRYSTALLOGRAPHIC DISTANCES (Å) IN MONOCLINIC 4c PYRRHOTITE* AND MARCASITE

pyrrhotite	marcasite
$a = 3.43$	$a = 3.39$
$2d_{100} = 5.95$	$b = 5.43$
$c = 5.70$	$a = 4.46$

*Pyrrhotite data refer to the NiAs-type subcell.

this plane. Photographs precessed about the pyrrhotite c axis (Fig. 2) show virtually no misalignment between related crystallographic directions, in spite of the rather large contraction (10%) in the pyrrhotite $[1\bar{1}.0]$ direction. The marcasite reflections are diffuse but near-equivalent, transformation-related $0kl$ reflections (e.g., 031) occur as well-separated paired diffraction nodes. In contrast, as the pyrrhotite c axis contracts by 22% during the transformation, precession photographs which include the pyrrhotite c^* axis (e.g., Fig. 1) show the greatest mosaic spread, the marcasite crystallites being rotated up to $\pm5°$ from ideal orientations.

The areas of marcasite replacement are rather porous, which suggests that the mechanism of the transformation is one of Fe removal (consistent with the present crystallographic argument) rather than S addition. The excess Fe maintains the aqueous solution saturated with respect to marcasite and is reprecipitated as marcasite overgrowths on replacement marcasite. Although nonstoichiometry can be very extensive in chalcogenides belonging to the NiAs-CdI₂ structure series (e.g., Jeannin 1970), Fe deficiency in Fe sulfides with the NiAs-type structure has not been demonstrated beyond the composition of monoclinic $4C$ pyrrhotite, and Fe sulfides with the CdI₂-type structure have not been reported. Thus, the actual structural transformation in the replacement of pyrrhotite by marcasite is considered to proceed fairly directly from the Fe_7S_8 composition rather than from that of a more Fe-deficient intermediary. Also, marcasite and pyrite phases are not markedly nonstoichiometric and the transformed product most probably is stoichiometric marcasite. The 'intermediate product' discussed by Ramdohr (1969) gives marcasite X-ray diffraction patterns and its anomalous optical properties may be attributable to defects in poorly crystalline material (localized changes in composition, stoichiometry, stereochemistry, and so on) rather than to appreciable nonstoichiometry. Although an 'intermediate product' specimen from Peru was reported to contain (in wt.%) 44.6 Fe, 52.5 S, 2.9 light elements (Einaudi 1971), this composition was determined by electron microprobe analysis of small and somewhat porous lamellae intimately intergrown with pyrrhotite; thus it cannot be regarded as significantly different from ideal FeS_2. A similar mineral substance to the 'intermediate product' with an apparent variation in composition from $FeS_{1.2}$ to $FeS_{1.8}$, has been reported by Ivanitskiy et al. (1973). However, whereas the unit cell parameters for it are, generally, slightly greater than those of stoichiometric marcasite, the relative intensities of

the characteristic diffraction lines are virtually identical to equivalent marcasite lines, and more detailed and systematic work on this substance seems warranted. Smythite is not a possible intermediate in the pyrrhotite-marcasite transformation since the layers of S atoms in its derivative NiAs-type structure do not form hexagonal close-packed arrays. However, its structure suggests that it may be an intermediate in the alteration of pyrrhotite to violarite, as reported by Nickel et al. (1974) and Misra & Fleet (1974).

The structural reorganization required to transform pyrrhotite to pyrite is much more complex and less direct than that required to transform pyrrhotite to marcasite. In addition to the reorganization required for the latter transformation, the disulfide group in alternate layers of the pyrrhotite (11.0) plane (Fig.4) must be rotated approximately 90° about the pyrrhotite $[1\bar{1}.0]$ direction. Hence, the predominance of marcasite rather than pyrite as the initial replacement product of pyrrhotite may reflect kinetic rather than equilibrium factors. Much of the pyrite in these assemblages must be derived through inversion of earlier marcasite. Pyrite formed in this way may show two preferred orientations relative to the marcasite substrate (Fleet 1970) so that, theoretically, it could show a total of six preferred orientations relative to the original pyrrhotite substrate. However, the orientation of pyrite crystallites in the material examined in the present study was random.

ACKNOWLEDGEMENT

REFERENCES

CORLETT, M. (1968): Low-iron polymorphs in the pyrrhotite group. Z. Krist. 126, 124-134.

EINAUDI, M. T. (1971): The intermediate product of pyrrhotite alteration. Amer. Mineral. 56, 1297-1302.

FLEET, M. E. (1970): Structural aspects of the marcasite-pyrite transformation. Can. Mineral. 10, 225-231.

————— (1971): The crystal structure of a pyrrhotite (Fe₇S₈). Acta Cryst. B27, 1864-1867.

IVANITSKIY, T. V., AKHVLEDIANI, R. A., KAKHADZE, E. I. & TSEPIN, A. I. (1973): New variety of replacement product of pyrrhotite. Dokl. Akad. Nauk SSSR 213, 688-691.

JEANNIN, Y. P. (1970): Recent progress in the investigation of nonstoichiometry. *In* Problems of Nonstoichiometry (A. Rabenau ed.). North-Holland, Amsterdam.

MISRA, K. C. & FLEET, M. E. (1974): Chemical composition and stability of violarite. *Econ. Geol.* **69**, 391-403.

NICKEL, E. H., ROSS, J. R. & THORNBER, M. R. (1974): The supergene alteration of pyrrhotite-pentlandite ore at Kambalda, Western Australia. *Econ. Geol.* **69**, 93-107.

PEARSON, W. B. (1972): *The Crystal Chemistry and Physics of Metals and Alloys.* Wiley-Interscience, New York.

RAMDOHR, P. (1969): *The Ore Minerals and Their Intergrowths.* Pergamon, Oxford.

TOKONAMI, M., NISHIGUCHI, K. & MORIMOTO, N. (1972): Crystal structure of a monoclinic pyrrhotite (Fe_7S_8). *Amer. Mineral.* **57**, 1066-1080.