

THERMAL DECOMPOSITION OF ARSENOPYRITE

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One phase of a recent investigation of the crystal structure of arsenopyrite, which has been described elsewhere,¹ was an attempt to cause a high temperature order-disorder inversion from the arsenopyrite unit cell to one of the marcasite type. The attempt was unsuccessful because the mineral decomposed. It was felt, however, that the decomposition and its theoretical implications were worth reporting.

The arsenopyrite used in the investigation was from Spindelmuhle and from a specimen believed to have come from Saxony. In the early part of the work, small single crystals suitable for rotation photographs were used. The term "single crystal" is misleading as optical evidence later showed that what appeared to be single crystals were in reality built up of polysynthetic twins.^{2,3} When it became apparent that no inversion could be brought about below the decomposition temperature, it was decided to determine approximately what this temperature was. For convenience, powdered material was used.

The samples were sealed in evacuated silica tubes and heated in an electric furnace which could be maintained at a uniform temperature. Various temperatures and periods of time were tried in the attempt to bring about the inversion. Table 1 is compiled from the data recorded:

TABLE 1

<i>Locality</i>	<i>Temp (°C)</i>	<i>Time</i>	<i>Form</i>	<i>Result</i>
Spindelmuhle	543	4h 10m	Crystal	No effect
Saxony (?)	597	3h 0m	Powder	No effect
Spindelmuhle	646	0h 15m	Crystal	Partial decomp.
Saxony (?)	657	2h 47m	Powder	No effect
Saxony (?)	707	2h 57m	Powder	Decomposition
Saxony (?)	738	2h 45m	Powder	Decomposition
Saxony (?)	849	2h 57m	Crystal	Decomposition
Saxony (?)	852	0h 16m	Crystal	Decomposition
Saxony (?)	856	167h 31m	Crystal	Decomposition
Spindelmuhle	857	0h 15m	Crystal	Decomposition
Spindelmuhle	857	2h 25m	Crystal	Decomposition

The experiments were not performed in order of increasing temperatures as listed in the table. In general, the higher temperature tests were made first.

¹ Buerger, M. J.: *Zeits. Krist. (A)*, **95**, 83-113, 1936.

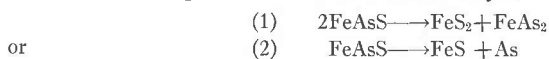
² Buerger, M. J.: *Op. cit.*

³ Buerger, M. J., and Lukesh, J. S.: *Am. Mineral.*, **21**, 667-669 (1936). See Fig. 4, p. 669.

It can be seen from the table that the decomposition begins to be detectable at about 650°C. The apparent inconsistency occasioned by the fact that a crystal from Spindelmühle was partially decomposed after fifteen minutes of heating at 646° and powder from Saxony (?) was unaffected at 657° after two and three-quarter hours may perhaps be due to variations in composition. Unfortunately, no analyses of the materials are available. All of the temperatures recorded above were measured with a thermocouple whose cold junction was kept at room temperature, and hence the values are not precise.

Rotation photographs taken before and after heating the single crystals showed that essentially a powder resulted. In cases of low temperatures and short periods of time, the outward appearance of the crystals was unchanged except for a microscopic pitting. Crystals which were heated at high temperatures for long periods of time were actually separated into two components. The same was true of all of the powdered material which was affected at all. One of the products of decomposition was in the form of silvery hexagonal plates, and the other consisted of yellowish, non-magnetic lumps. When crystals were used, the yellow material was in apparently residual lumps, left after the distillation of the other component; when powder was used, the yellow component was in the form of very small, well-formed crystals.

Powder photographs of the two components were taken and compared with those of all possible decomposition products as well as the original arsenopyrite. It is clear from a brief consideration of the composition of arsenopyrite and from the fact that it was heated in the absence of air that there are only four possible products: pyrite (at the temperatures involved marcasite is unlikely), löllingite, pyrrhotite, and arsenic. The reaction could proceed in one of two ways:



The composition of arsenopyrite is known to be highly variable;^{4,5} the formula can be written $\text{Fe}_x\text{As}_y\text{S}_z$ where x , y and z are approximately equal to one. A departure from the ideal composition of the original material would, of course, have an effect on the end products. Of the two alternative reactions, the more probable should be that in which such variations could be more easily accommodated. Greater flexibility is offered in reaction 2, pyrrhotite being highly variable and the amount of arsenic being unlimited. The reaction would be: $\text{Fe}_x\text{As}_y\text{S}_z \rightarrow \text{Fe}_x\text{S}_z + y\text{As}$. Actually, comparison of powder photographs identified the silvery

⁴ Doelter, C., and Leitmeier, H.: *Handbuch der Mineralchemie*, Bd. IV, Erste Hälfte, Dresden and Leipzig, 610-618 (1926).

⁵ Buerger, M. J.: *Op. cit.*

hexagonal plates as arsenic and the yellow material as pyrrhotite (see Figs. 1 and 2).

Since no analyses of the materials used are available, no values can be assigned to x and z . Some indication of the relative proportions of iron and sulfur can be obtained, nevertheless, from the fact that the material identified as pyrrhotite was non-magnetic. On the basis of the work of

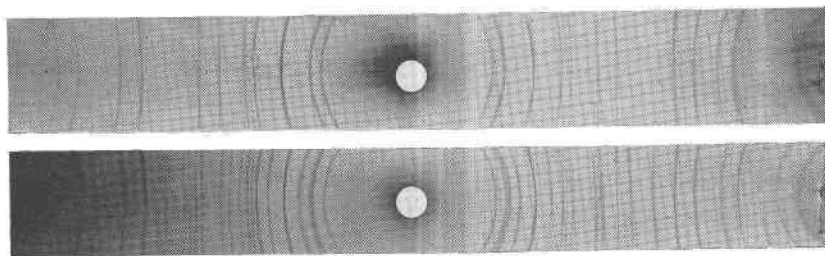


FIG. 1. (Top) Natural pyrrhotite from Cold Springs, New York. (Bottom) Undistilled residue from Saxony (?) arsenopyrite heated to 738°C.

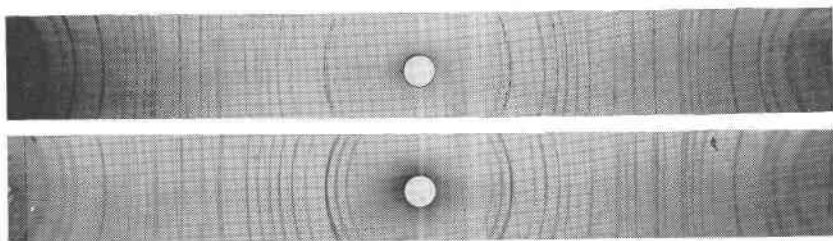


FIG. 2. (Top) Recrystallized part of Saxony (?) arsenopyrite heated to 738°C. (Bottom) Arsenic.

the Geophysical Laboratory of the Carnegie Institution,^{6,7} where it was shown that low temperature pyrrhotite containing less than about seven molecular per cent excess of sulfur is non-magnetic, it would seem that the iron and sulfur are present in about the proportions 1:1. (Hägg and Sucksdorff⁸ have shown through density considerations that actually variations in composition of pyrrhotite are due to a deficiency of iron rather than an excess of sulfur.) In the present experiments, however, the pyrrhotite was formed at relatively high temperatures. Newhouse⁹ made

⁶ Merwin, H. E., and Lombard, R. H.: *Carnegie Inst. of Wash. Yearbook*, **30**, 82-84 (1931).

⁷ Roberts, H. S.: *ibid.*, 84-85.

⁸ Hägg, G., and Sucksdorff, I.: *Zeits. physik. Chem., Abt. B*, **22**, 444-452 (1933).

⁹ Newhouse, W. H.: *Ec. Geol.*, **22**, 288-299 (1927).

synthetic pyrrhotite at high temperatures and found it to be magnetic. Merwin and Lombard¹⁰ showed that pyrrhotite produced at high temperatures with the ratio $z:x$ varying from 1.18 to 1.002 are all magnetic with, apparently, the magnetic strength decreasing as the ratio $z:x$ falls. In all probability, the material produced in the present experiments contains iron and sulfur in nearly the stoichiometric ratio for the true monosulfide of iron. There is, however, no reason to exclude the possibility of an excess of iron as some samples of arsenopyrite are known to have a ratio of iron to sulfur greater than one. Doelter and Leitmeier¹¹ cite an analysis in which the molal ratio of iron to sulfur is .652 to .480.

The non-magnetic form of the monosulfide of iron is usually called troilite. There is some question whether it is an end-member of the pyrrhotite series or a distinct species. Eakle¹² examined some natural troilite and found it to be considerably different from pyrrhotite in magnetic properties and in its reaction to sulfuric acid. Troilite was non-magnetic and dissolved easily in the acid, while pyrrhotite was magnetic and difficultly soluble in acid. He considered that these differences were too great to be accounted for on the basis of composition alone and decided that troilite was a distinct species. The chemistry of the crystals formed in the present experiment was not investigated so it is not possible to compare results. It is not possible to draw conclusions from so little evidence, but one can point out that the crystals resembled troilite in being non-magnetic and gave the same diffraction pattern as pyrrhotite.

A. Beutell¹³ first reported the decomposition of arsenopyrite, but he does not specify the temperature other than "dark red heat."

¹⁰ Merwin, H. E., and Lombard, R. H.: *Ec. Geol.*, **32**, 203-284 (1937). See especially p. 258.

¹¹ Doelter, C., and Leitmeier, H.: *Loc. cit.*

¹² Eakle, A. S.: *Am. Mineral.*, **7**, 77-80 (1922).

¹³ Beutell, A.: *Zbl. Min.*, etc., 316-320 (1911).