THE AMERICAN MINERALOGIST, VOL. 55, SEPTEMBER–OCTOBER, 1970

SMYTHITE, $Fe_{3+x}S_4$, AND ASSOCIATED MINERALS FROM THE SILVERFIELDS MINE, COBALT, ONTARIO

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ABSTRACT

Smythite was found at the Silverfields Mine, Cobalt, Ontario, where it occurs in two distinctly different sulfide assemblages. Microprobe analyses of these smythites result in a composition of Fe_9S_{11} ($\approx Fe_{3.25}S_4$), with a measured density of 4.33 g/cm^3 (4.32 g/cm^3 calculated). Unit-cell dimensions referred to the cell described by Erd *et al.* in 1957, apparently not the true cell, at 25°C are $a = 3.4651 \pm 0.0005$ Å, $c = 34.34 \pm 0.02$ Å. X-ray powder diffraction study at elevated temperatures indicates the presence of a polymorphic transition at approximately 65°C. Precession photographs taken at room temperature reveal a cell with a doubling of the a axis; the symmetry of this larger cell is *not* $R\bar{3}m$ but possibly primitive hexagonal. Smythite from Cobalt is universally twinned (twin law: 180° rotation about [00.1]). It lacks the perfect basal cleavage typical of Indiana smythite. Its appearance is very similar to that of pyrrhotite, and only X-ray diffraction study enables one to tell them apart; smythite is, therefore, undoubtedly more common in nature than the four reported occurrences suggest.

INTRODUCTION

The mineral smythite was first described by Erd *et al.* (1957) as an iron sulfide, Fe_3S_4, which occurred in geodes at Bloomington, Indiana. This mineral is different from other iron sulfides (*e.g.* pyrite, pyrrhotite) in that it has rarely been found. Chukrov *et al.* (1965) reported an occurrence from the Kimmerian sedimentary iron ores of the Kerch Peninsula, U.S.S.R., and Morgan and Erd (1969) reported it from Boron, California. The present study is concerned with a new occurrence of this mineral, which was briefly discussed by Taylor (1969). Chemical and physical data presented below show that this smythite is distinctly different from that of the type locality at Bloomington.

GEOLOGIC SETTING

During a recent examination of the mineral assemblages at Cobalt, Ontario, Taylor (1969) discovered smythite closely associated with the silver-bearing veins at the Silverfields Mine. The geology and mineralogy at this mine are typical of the class of silver deposits in the Cobalt district and have been described by Moore (1967) and Petruk (1968).

Smythite was found in a "cross vein" within the Coleman formation along the contact of a pebble conglomerate (above) and quartzite (below). This vein, which is 6–8 inches wide and dips about 8–10°E, contains abundant sulfides, mainly pyrite, pyrrhotite, marcasite, sphalerite, galena, and chalcopyrite, as well as sparse pyrargyrite, native silver, and acanthite. High silver values, up to 20 oz/ton, have been found along this vein (H. A. Moore, personal communication, 1966). The sulfides and native Ag occur in a matrix consisting mainly of calcite with minor quartz and chlorite.

The smythite occurs in two distinct assemblages. In one it is associated with pyrite, marcasite, and sphalerite containing 9 ± 1 mole percent FeS[1] in a matrix of calcite; in the other with galena, chalcopyrite, monoclinic pyrrhotite, and sphalerite containing 13 ± 1 mole percent FeS in a matrix consisting mainly of quartz with minor amounts of calcite. If indeed these minerals represent equilibrium assemblages, the compositions of the sphalerites occurring in the univariant assemblages within the Fe–Zn–S system, *i.e.* pyrite+smythite+sphalerite and monoclinic pyrrhotite+smythite+sphalerite, are here defined at low temperatures (*i.e.* $<75°$C as discussed in a later portion of this paper). The monoclinic pyrrhotite, with 47.4 ± 0.1 atomic percent Fe composition, gave an X-ray diffractometer tracing with $I(\bar{4}08);(\bar{2}28) > I(408);(228)$ and is perhaps related to the low-temperature, iron-deficient, monoclinic pyrrhotites discussed by Clark (1966). Bladed pyrite inclusions within smythite contain 5.4 ± 0.3 weight percent Ni as determined with the electron microprobe. This is one of the highest Ni contents reported for a natural pyrite and is not consistent with the *dry* phase relations in the Fe–Ni–S system as determined at low temperatures; it may be related to the metastable pyrite compositions described by Clark and Kullerud (1963). Some smythite occurs as relatively pure masses up to 5 mm in diameter, which are free from other included sulfides. These masses occur in both calcite and quartz matrices.

Composition and Density

No elemental chemical analysis of naturally occurring smythite has been previously reported. It would be improbable that smythite composition would be confined to stoichiometric Fe_3S_4, particularly in view of the well known nonstoichiometry of some of the other compounds in the Fe–S system (*e.g.*, various species of pyrrhotite) and because smythite consists of an atomic framework based on a stacking of pyrrhotite-like layers (Erd *et al.*, 1957).

The compositions of the smythites from the two assemblages (labeled pyrrhotite [po] and pyrite [py]) were determined by electron microprobe analyses, using as standards the synthesized compounds $Fe_{1-x}S$ of four compositions, FeS_2, and NiS. Corrections of the microprobe data were made using the computer program of Boyd *et al.* (1969). Table 1 shows the results of these analyses and the compositions of two theoretical

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[1] Sphalerite compositions were determined by electron microprobe analyses.

TABLE 1. ELECTRON-MICROPROBE ANALYSES OF SMYTHITES FROM COBALT, ONTARIO[a]

	Smythite			Theoretical Formulas	
	po assemblage	*py* assemblage	Precision	Fe_3S_4	$Fe_{3.25}S_4$
Fe	58.5	58.1	0.2	56.64	58.60
Ni	0.4	0.5	0.1	—	—
S	40.9	41.5	0.3	43.36	41.40

[a] Compositions are given in weight percent.

formulas for comparison. A spectral scan was also performed on these smythites, and no other elements in amounts greater than 0.1 weight percent were detected. The analyses show a difference in the compositions of the smythites; the one coexisting with monoclinic pyrrhotite contains 0.4 weight percent more Fe than the one coexisting with pyrite. Although this difference is near the limits of precision, direct comparison of these two samples with the microprobe showed a consistent and real compositional difference. These compositions (Table 1) indicate a metal/sulfur ratio of approximately 9/11,[1] halfway between Fe_7S_8, the formula commonly given for monoclinic pyrrhotite, and Fe_3S_4, stoichiometric smythite (see Fig. 1). If the Ni is considered to substitute for some Fe, the compositions given in Table 1 lead to the formula $Fe_{3+x}S_4$, where $x \simeq 0.25$ (see theoretical formula in Table 1), a cell content of $Fe^{3+}{}_{4.5}Fe^{2+}{}_{5.25}S_{12}$. The composition of Fe_3S_4 given for the Indiana smythite was not determined by chemical analysis but was the result of a structure determination supplemented by density measurements (Erd *et al.*, 1957). During the present study, samples of Indiana smythite (U. S. National Museum No. 112704) were also analyzed with the electron microprobe, and although not rigorously determined, the composition was 57.0 ± 0.5 weight percent Fe, 43.0 ± 0.6 weight percent S (no other elements in amounts ≥ 0.1 weight percent were found). It thus appears that the Indiana smythite does have a composition near Fe_3S_4.

Density determinations using Clerici solution were made at 25°C on a 3 mg portion of pure smythite from Cobalt and gave 4.33 ± 0.01 g/cm^3. The calculated density, using a composition of $Fe_{3.25}S_4$ and the cell parameters mentioned below, is 4.319 g/cm^3. In comparison, the Indiana specimen has a measured and calculated density of 4.06 and 4.09 g/cm^3 respectively (Erd *et al.*, 1957).

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[1] Mr. C. Taylor and Dr. R. C. Erd (personal communication, November 1969) informed me that the smythite from Boron, California, also has a composition of approximately Fe_9S_{11}.

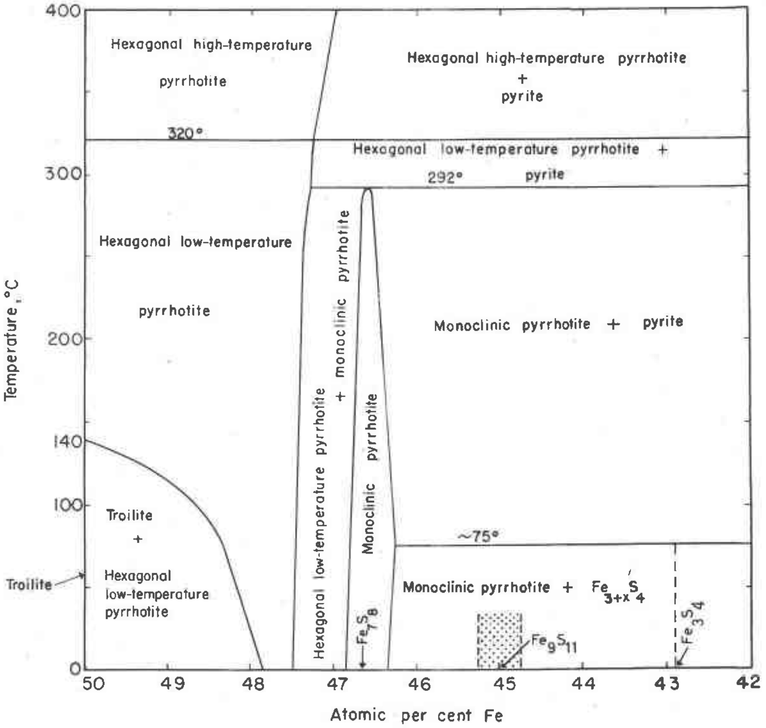

FIG. 1. A portion of the Fe—S system at low temperatures, modified after Taylor (1970). All phases and phase assemblages coexist with vapor. The shaded area represents the range in composition of the smythites from the Silverfields Mine, Cobalt, Ontario.

CRYSTALLOGRAPHY

The cell parameters at various temperatures of the smythite from Cobalt were determined. A 19-cm Debye-Scherrer camera, calibrated with Si ($a_{25°}=5.4306$ Å), on a modified Unicam unit was used to record the X-ray diffraction data. The powdered smythite was contained in sealed, evacuated silica capillaries to prevent oxidation at the elevated temperatures. A least-squares refinement (LCLSQ) based on the X-ray data of at least fifteen reflections was performed with the computer program of Burnham (1962). At 25°C, the cell parameters are $a=3.4651 \pm 0.0005$ Å, $c=34.34 \pm 0.02$ Å, $V=357.1 \pm 0.2$ Å^3, as referred to the cell used by Erd *et al.* (1957), apparently not the true cell (see below). These dimensions are close to those of the type locality samples from Indiana (*i.e.*, $a=3.47$ Å, $c=34.5$ Å).

The cell volume of smythite as a function of temperature is shown in Figure 2. These data were determined by X-ray powder diffraction ex-

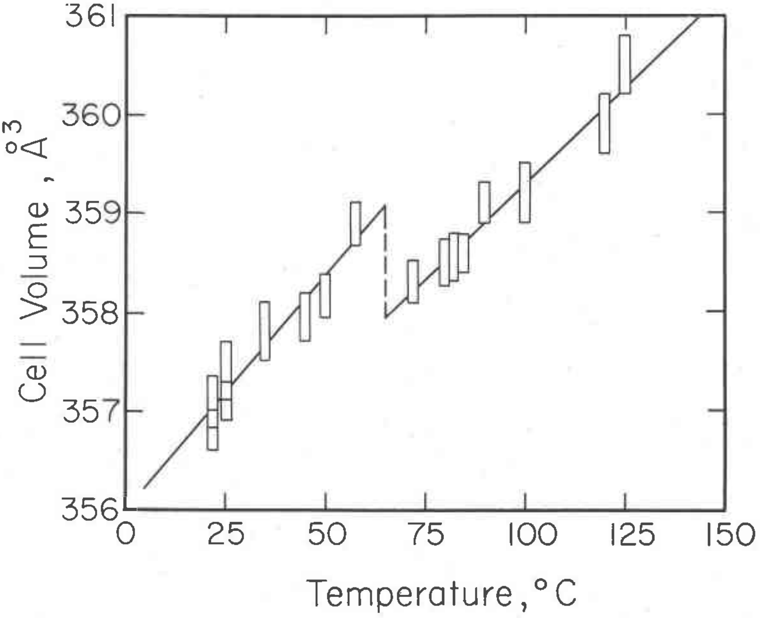

FIG. 2. Data on unit-cell volume versus temperature for smythite from Cobalt, Ontario. Volumes refer to the rhombohedral cell determined by Erd *et al.* (1957).

amination of smythite, first at 25°C and then at successively higher temperatures, followed by a reexamination at each temperature, proceeding from 152°C down to 25°C. Figure 2 shows a discontinuity in the plot of cell volume versus temperature at 65°±7°C—the result of a rapid, reversible first-order phase transition. X-ray powder patterns above and below 65°C do not show drastic changes in intensities; however, this break in slope is indicative of the presence of a high-temperature polymorph of this smythite from Cobalt.

This transition in smythite is reminiscent of the behavior of monoclinic pyrrhotite (Taylor, 1970) and may be related to the similarities of the smythite and pyrrhotite structures. Monoclinic pyrrhotite annealed above 292°C (Taylor, 1970) first inverts to a metastable hexagonal pyrrhotite of the same composition, which in turn exsolves pyrite and adjusts to a composition on the hexagonal pyrrhotite-pyrite solvus (Fig. 1). Perhaps the breakdown of smythite to monoclinic pyrrhotite+pyrite (discussed in the next section) also involves the formation of a high-temperature (*i.e.* >65°C) metastable polymorph as an intermediate step.

The space group of the Indiana smythite was given as $R\bar{3}m$ (Erd *et al.*, 1957) and did not take into account certain weak diffuse reflections.

Precession photographs of the smythite from Cobalt show more intense diffuse superstructure reflections. A lattice that takes these reflections into account requires at least a doubled *a* axis and no longer obeys the rhombohedral criteria. The photographs obtained were not of good enough quality to permit space group determination. Preliminary investigation shows that the symmetry of this larger cell is possibly monoclinic; however, Dr. H. T. Evans, Jr. (personal communication, 1969) believes that the cell is primitive hexagonal.

The $00l$ reflections with l odd are diffuse in the Cobalt patterns, whereas they are sharp in the Indiana patterns (brought to my attention by Dr. H. T. Evans, Jr.), suggesting that additional Fe atoms are present between the adjacent S layers in the Fe_3S_4 sheet structure, perhaps with accompanying vacancies in the Fe layers filled in the Indiana material. This structural change would be consistent with the higher iron content of the smythite from Cobalt and would account for the lack of cleavage observed in this material, in contrast to the perfect basal cleavage characteristic of the Indiana crystals. X-ray diffraction of powdered Indiana smythite shows abnormally intense basal reflections, which should be weak according to the proposed crystal structure. Powdered smythite from Cobalt photographed on the precession camera shows complete randomness of orientation. The very weak basal reflections in diffractometer tracings obtained from powder-smear mounts of the Cobalt samples are probably caused by this general absence of basal cleavage. If present, basal cleavage would produce some preferred orientation.

Erd *et al.* (1957) found that his material showed incipient twinning on (00.1). Precession photographs of the Cobalt crystals show that twinning by reticular merohedry (twin law: 180° rotation about [00.1]) is universal; an intensity study indicated equal volumes from the two individuals of the twin. A study was made of polished sections of smythite specimens by reflected light microscopy. Twinned individuals, identified by X-ray examination, show no optical evidence for twinning, indicating that the optical properties of smythite are controlled by a uniaxial cell, because twinning about the *c* axis does not destroy the orientation of the uniaxial indicatrix.

STABILITY

Smythite does not break down readily upon heating in sealed, evacuated silica tubes. After 194 days at $210° \pm 5°C$, only partial breakdown to monoclinic pyrrhotite and pyrite was observed, a result compatible with the phase relations shown in Figure 1. As reported in Taylor (1970), attempts to synthesize smythite in the *dry* Fe-S system using pelletized mixtures of monoclinic pyrrhotite (Fe_7S_8)+pyrite and monoclinic pyrrhotite+S were unsuccessful. A hexagonal pyrrhotite of 46.0 atomic percent Fe presynthesized at 700°C was observed to exsolve pyrite and change to the monoclinic form at temperatures down to 75°C, suggesting that smythite is stable only below this temperature, as shown in Figure 1. Several attempts at synthesizing smythite using the recipe of Rickard (1968) were also unsuccessful. Rickard claims that sulfurization of ferrous carbonate using a sodium sulfide solution produces smythite. Although he claims complete reaction in 24 hours, smythite did not result during the present investigation, even with reaction times of up to 9 months.

A second compound of Fe_3S_4 composition has been reported as the mineral greigite (Skinner *et al.*, 1964), but a polymorphic relationship between greigite and smythite, as suggested in the literature, has not been demonstrated. The 2 weight percent Fe in the Cobalt smythite in excess of that indicated by an Fe_3S_4 formula would seem to indicate that these minerals are not polymorphs. By analogy with other M_3S_4-type sulfides, Kullerud (1970) concluded that if smythite and greigite were polymorphs, smythite should be the higher temperature phase. Therefore, the equilibrium breakdown of smythite, with increasing temperature, should be to monoclinic pyrrhotite (composition near $Fe_{0.875}S$) and pyrite, as shown in Figure 1. Equations 1 and 2 give this reaction for stoichiometric smythite and iron-rich smythite, respectively.

$$Fe_3S_4 \rightleftarrows 2.667Fe_{0.875}S + 0.667FeS_2 \qquad (1)$$

$$Fe_{3.25}S_4 \rightleftarrows 3.333Fe_{0.875}S + 0.333FeS_2 \qquad (2)$$

At ~75°C, using the cell volumes calculated from the thermal expansion data given by Taylor (1969), and assuming that the thermal expansion coefficient for Fe_3S_4 is approximately the same as for $Fe_{3.25}S_4$, equations 1 and 2 show:

$$72.78\ \text{cm}^3 = 46.86\ \text{cm}^3 + 16.02\ \text{cm}^3 \qquad \Delta V = -9.90\ \text{cm}^3 \qquad (1)$$

$$72.25\ \text{cm}^3 = 58.54\ \text{cm}^3 + 8.01\ \text{cm}^3 \qquad \Delta V = -5.70\ \text{cm}^3 \qquad (2)$$

The ΔV values are the largest calculated to date for any sulfide reaction and indicate that the upper stability curve for smythite should have a decided negative slope—*i.e.*, increased pressure lowers the maximum thermal stability—a factor perhaps responsible for the scarcity of smythite in nature.

The calculations above also suggest that pressure tends to favor the formation of the iron-rich variety of smythite, a suggestion compatible with the occurrence of near-stoichiometric smythite in geodes at Bloomington, Indiana (pressure <30 bars; Erd *et al.*, 1957), and the formation of iron-rich smythite in the silver-bearing veins at Cobalt, Ontario (pressure$\gg$30 bars). The composition of smythite may be indicative of the pressures existing during its formation, provided reequilibration did not take place.

FLUID INCLUSION DATA

The fluid inclusions in the calcite and quartz that contain the smythite consist of various combinations of the phases liquid, solid, and vapor. The majority of the inclusions contain large crystals of NaCl (verified by cooling the inclusion and observing the formation of birefringent $NaCl \cdot 2H_2O$) and are indicative of highly saline mineral-forming solutions.

Many of the inclusions contain only small vapor bubbles, and the majority contain no observable vapor phase. In several instances, induced freezing of the inclusions containing no vapor phase produced, upon melting, a small bubble, showing that the liquid, at least in some of the inclusions, is metastable. This procedure of freezing and melting obviously aids the nucleation of the vapor phase from these metastable liquids.

A limited number of filling temperatures were determined for inclusions containing a vapor phase. A range of filling temperatures was found from 40° to 120°C, with the majority being near the middle of this range. The general impression obtained from inspection of these fluid inclusions is that they formed under conditions of low temperature and high pressure (E. Roedder, personal communication, 1969). These conditions are compatible with the previous discussion concerning the stability of smythite.

GENESIS

The paucity of smythite in nature is a problem. The low temperature (*i.e.*, $<75°C$) for the maximum stability of smythite, coupled with the possibility that pressure would tend to lower the stability of smythite even more, may account for the rarity of this mineral. Actually, smythite is undoubtedly much more common in nature than the few reported occurrences would lead one to believe. Monoclinic pyrrhotite and smythite are practically indistinguishable in hand specimen—possessing similar hardness, color, ferromagnetism, tarnish, fracture, etc.—or in polished section, and can be identified with certainty only by X-ray diffraction analysis. Possibly a significant percentage of the pyrrhotites observed in natural assemblages is, in reality, actually smythite.

Rickard (1968) stated that the presence of siderite is prerequisite to the formation of smythite in nature. At Cobalt, however, evidence of siderite was not found anywhere in the vein in which the smythite occurs. Even if all the siderite had been transformed to smythite or replaced by calcite, it would not explain the occurrence of smythite as relatively pure masses in quartz completely devoid of any carbonate.

Some of the smythite at Cobalt is present as single pure masses. The occurrence of monoclinic pyrrhotite and pyrite in the correct proportions to react upon cooling to form smythite without excess pyrrhotite or pyrite seems exceedingly unlikely. The chemical inertness of pyrite at these low temperatures, well known to the experimentalist, is also not favorable to such a reaction. It therefore appears probable that this smythite was deposited directly from solution at a low temperature not far removed from room temperature.

ACKNOWLEDGMENTS

I wish to acknowledge the many helpful suggestions and critical comments of Drs. G. Donnay, H. T. Evans, Jr., G. Kullerud, and G. Roland. The helpful assistance with the crystallographic observations by Drs. G. Donnay, H. T. Evans, Jr., and M. Rieder, and the discussions with Dr. E. Roedder, concerning the interpretations of the fluid inclusions, are also recognized. Thanks are due to Silverfields Mines, Ltd., and especially to Mr. H. Moore for the cooperation during my visit in June, 1966.

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Manuscript received, February 13, 1970; accepted for publication, March 7, 1970.