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# SMYTHITE, $(Fe,Ni)_9S_{11}$—A REDEFINITION

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## ABSTRACT

Smythite was originally described by Erd *et al.* in 1957 as having a rhombohedral structure, observed density of 4.06 g/cm$^3$, and $Fe_3S_4$ composition. These data are in error and smythite is hereby redefined. Specimens from the type locality of Bloomington, Indiana, as well as from numerous other localities in Australia, Canada, and the United States, have only pseudorhombohedral symmetry (possibly a hexagonal or monoclinic structure), at 25°C $a = 3.47(1)$ and $c = 34.4(1)$, calculated and observed densities of $\sim$4.32 g/cm$^3$, and $(Fe,Ni)_9S_{11}$ $(\sim(FeNi)_{3.25}S_4)$. The powder diffraction patterns are the same as reported by Erd *et al.* except for weak basal reflections from samples without preferred orientation. Smythite as redefined does *not* have a polymorphic relationship to greigite. Most smythite occurs as a low-temperature oxidation product of monoclinic pyrrhotite. Nickel is present in all smythites analyzed to date (0.4 to 7.5 wt. percent) and it is suggested that smythite is *not* a phase in the Fe–S system but possibly in the Fe–Ni–S system.

## INTRODUCTION

Minerals within the Fe–S system, especially pyrite and the various pyrrhotites, are among the most common ore minerals occurring in nature. This emphasizes the importance of an understanding of the mineralogy, compositional limits, and phase chemistry of the iron sulfide compounds. Until recently, smythite, originally described by Erd *et al.* (1957) as $Fe_3S_4$, was considered as very rare and was known from only a few deposits—Kerch Peninsula, U.S.S.R. (Chukrov *et al.*, 1965); Boron, California (Morgan and Erd, 1969); Cobalt, Ontario (Taylor, 1969). Taylor (1970a,b) discussed the apparent paucity of smythite in nature and emphasized that smythite is very similar to monoclinic pyrrhotite in its optical and magnetic properties. He stated that it should be common in nature as a low–temperature phase in association with monoclinic pyrrhotite and that it has undoubtedly been misidentified as pyrrhotite in the past.

Within the last year or so, smythite has been found in several nickel deposits in Canada (Nickel, 1972) and in many nickel ores, particularly supergene ores, in Australia (Bennett *et al.*, 1972; J. Graham, pers. comm., 1971). This smythite occurs as flamelike forms in monoclinic pyrrhotite extending inward from the margins of the pyrrhotite grains and is commonly part of an assemblage that includes magnetite (Nickel, 1972). In fact, these textures resemble those produced by secondary alteration of pyrrhotite to marcasite. In these cases, it would appear that smythite forms secondarily as an oxidation product of monoclinic pyrrhotite at conditions not far removed from room temperature and pressure. At higher temperatures, above the maximum thermal stability of smythite (*i.e.*, ~75°C; Taylor, 1970a), this oxidation could lead to the formation of "anomalous" pyrrhotite as discussed also by Taylor (1971).

Nickel and Harris (1971) reported that the smythite from Cobalt, Ontario, has reflectance values of $R_{\mathrm{max}} = 46.0$ percent, $R_{\mathrm{min}} = 42.0$ percent (at 546 nm), and a microhardness of 388 VHN. Both reflectance and microhardness are slightly greater than those of co–existing monoclinic pyrrhotite.

## Composition and Density

The $Fe_3S_4$ formula for smythite was given by Erd *et al.* (1957) and was based on 1) qualitative microchemical tests which showed major Fe and S and minor Ni; 2) a structure analysis and refinement which reached an R = 18.5 percent; and 3) density measurements of 4.06 g/cm$^3$. The first quantitative analyses of smythite were performed by Taylor (1970a) on material from Cobalt, Ontario. He reported that this smythite had a formula of $\sim(Fe,Ni)_{3.25}S_4$ ($\sim M_9S_{11}$), cell dimensions identical to the Indiana sample, but a density of 4.33 g/cm$^3$. Taylor (1970b) also attempted an analysis of the Indiana smythite, but due to the small size of the crystals, the composition was not rigorously determined and was given as approximately 57 wt. percent (43.2 at percent) Fe, 43 wt. percent (56.8 at percent) S; the statement was made that the Indiana smythite probably has a composition near $Fe_3S_4$.

In every Canadian (Nickel, 1972) and Australian (J. Graham, pers. comm., 1971; Bennett *et al.*, 1972) occurrence, without exception, as well as smythite from Boron, California, (R. C. Erd, pers. comm., 1969), the composition of smythite has been determined to be

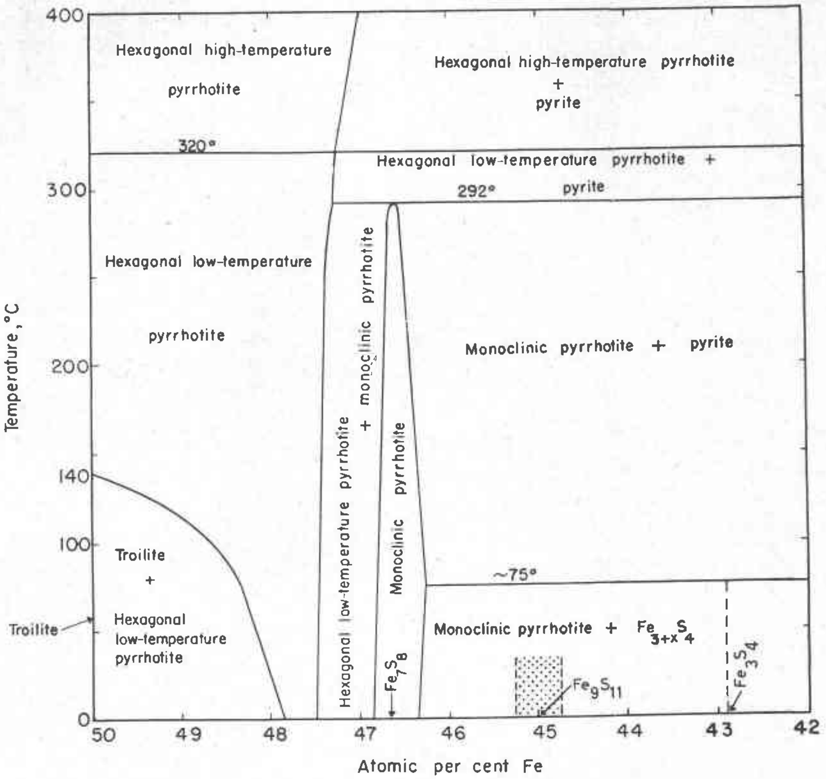

FIG. 1. A portion of the Fe–S system at low temperatures, taken after Taylor (1970a). All phases coexist with vapor. The stippled area represents the range in compositions of all smythites reported to date, including the Indiana smythites.

$\sim(\mathrm{Fe,Ni})_9\mathrm{S}_{11}$ in excellent agreement with Taylor (1970a, b), and the compositions plot within the stippled area shown in Figure 1. In light of the fact that these analyses all gave approximately the same formula, it was considered important to reanalyze the Indiana smythite, particularly for the sulfur content.

Seven smythite grains extracted by dilute HCl leaching from several calcite samples from Bloomington, Indiana, were analyzed on an Applied Research Laboratories Model EMX–SM electron microprobe. Some difficulties were encountered due to the small size of the grains, which range up to 150 μm in length and width but are only 2–3 μm thick. Initial attempts to mount them in near vertical or inclined positions within epoxy were unsuccessful because the grains are then not "infinitely wide", even for a very finely focused beam. The best results were obtained by not mounting and polishing at all, but simply setting the grains flat on a glass substrate and analyzing on carefully selected flat, smooth faces. A series of synthetic Fe–S compounds ranging in composition from 46 to 50 atom percent Fe was used as standards for the Fe and S determinations, and Ni was determined relative to a pure Ni standard. Instrumental and matrix corrections were made with a version of J. W. Colby's MAGIC computer program.

The results of the analyses are shown in Table 1. They were obtained with an accelerating potential of 12 kV, and are significantly better than a set obtained at 15 kV; even so the totals are slightly low, indicating that the samples were not quite "infinitely thick" under these conditions. However, no improvement was obtained at 10 kV, the lowest practical potential which permits the simultaneous determination of Fe, Ni, and S using the *Kα* emission in each case. With low accelerating voltages and samples of less than infinite thickness, differences in the depth function of X–ray generation between samples and standards, particularly in terms of continuum excitation, are more pronounced for the higher energy X–rays. The sulfur results are therefore considered to be more accurate than those for iron and nickel. No elements other than Fe, Ni, and S were detected in concentrations of ≥ 0.1 weight percent.

Table 1. Electron microprobe analyses of smythite from Bloomington, Indiana The atomic per cent compositions have been recalculated to 100%.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| | wt.% | wt.% | wt.% | wt.% | wt.% | wt.% | wt.% |
| Fe | 56.72 | 56.87 | 57.06 | 57.08 | 56.69 | 57.26 | 57.15 |
| Ni | 1.28 | 0.63 | 0.96 | 0.99 | 1.47 | 0.99 | 0.94 |
| S | 40.84 | 40.91 | 41.00 | 40.91 | 40.80 | 41.00 | 40.95 |
| TOTAL | 98.84 | 98.41 | 99.02 | 98.98 | 98.96 | 99.25 | 99.04 |
| | At% | At% | At% | At% | At% | At% | At% |
| Fe | 43.95 | 44.18 | 44.10 | 44.16 | 43.89 | 44.18 | 44.17 |
| Ni | 0.94 | 0.46 | 0.70 | 0.73 | 1.09 | 0.73 | 0.69 |
| S | 55.11 | 55.36 | 55.20 | 55.12 | 55.02 | 55.09 | 55.13 |

| | Mean Composition and two sigma limits | | Formulas based on 4 S atoms | | |
|---|---|---|---|---|---|
| | wt.% | At% | Indiana | Cobalt, Ontario | $Fe_3S_4$ (At.%) |
| Fe | 56.98 ± 0.17 | 44.09 ± 0.09 | 3.20 | 3.23 | 42.86 |
| Ni | 1.04 ± 0.20 | 0.76 ± 0.15 | 0.05 | 0.02 | --- |
| S | 40.92 ± 0.05 | 55.15 ± 0.09 | 4.00 | 4.00 | 57.14 |

Smythite from the type locality at Bloomington, Indiana, *does not* have metal/sulfur ratio of 3:4 as reported by Erd *et al.* (1957). Indeed, it has a composition, as do all smythites analyzed to date, approximately halfway between $Fe_3S_4$ and monoclinic pyrrhotite ($Fe_7S_8$); all smythites have the general formula $(Fe,Ni)_{3+x}S_4$ where $x = 0.25$–$0.30$, an approximate $(Fe,Ni)_9S_{11}$ formula.

All smythite analyses reported to date (this study; Taylor, 1970a,b; Nickel, 1972; Bennett *et al.*, 1972) show nickel present in small amounts (0.4 up to a maximum of 7.5 wt. percent Ni). The associated monoclinic pyrrhotite also contains minor amounts of nickel (up to 1.2 percent, Nickel, 1972). Smythite has not been synthesized in the Fe–S system; these compositional data suggest that it is possibly a ternary phase in the Fe–Ni–S system. In any case, because of the low thermal stability of smythite (*i.e.*, ~ 75°C), it will be difficult to synthesize in the laboratory.

The cell dimensions of three grains of Indiana smythite were measured from single crystal precession photos and determined to be $a = 3.47(1)$Å, $c = 34.4(1)$Å, as referred to the $R\bar{3}m$ cell[1] used by Erd *et al.* (1957), and these values are the same as they determined. The powder diffraction patterns of all smythites are the same as reported by Erd *et al.* except for weak basal reflections from samples without preferred orientation.

The Indiana smythite with a composition of $(Fe,Ni)_9S_{11}$ and the above cell dimensions calculates to a density of 4.32 g/cm$^3$. Erd *et al.* (1957) determined a density of 4.06 g/cm$^3$, reinforcing their hypothesized $Fe_3S_4$ composition (calculated density = 4.09 g/cm$^3$). Because of the apparent discrepancy between their observed density and the calculated density based on the actual composition determined during this study, a redetermination of the Indiana smythite value was conducted. The procedure as described by Jahns (1939) was followed, and Clerici solution was employed. Single grains of smythite were immersed in the solution, and their behavior was observed with a petrographic microscope (40X). If necessary, water was added and the solution stirred, until the density of the solution allowed the smythite to sink. The density of the Clerici was then estimated from its refractive index using the data of Jahns (1939) and a Leitz–Jelley microrefractometer. The highest density of Clerici used was 4.28 g/cm$^3$ (because of solidification of higher density solutions at 22°C). The

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[1] The structure of smythite was shown by Taylor (1970a) to be based *not* on the $R\bar{3}m$ space group as originally determined by Erd *et al.* (1957) but on some other symmetry, possibly primitive hexagonal or monoclinic.

sink–float centrifuge method used by Taylor (1970b) for Cobalt, Ontario, smythite was not successful because the 3–4 μm platelets of smythite disintegrated and remained as a cloudy suspension regardless of the Clerici solution density.

Although the Jahn's method did not allow us to determine an absolute density, it verified our suspicions that the original density by Erd *et al.* (1957) was in error. Of eleven density determinations, the grains all sank at densities between 4.15 and 4.28 g/cm$^3$, and it can be stated that the Indiana smythite has a density greater than 4.22 (7) g/cm$^3$. It was fortuitous that Erd *et al.* (1957) found a density so near their calculated value. It seems probable that Indiana smythite has a density of approximately 4.32 g/cm$^3$.

Greigite was originally described by Skinner *et al.* (1964) as $Fe_3S_4$ and a polymorph of smythite. All greigite analyses which we are aware of (*e.g.*, Williams, 1968) show that this composition is essentially correct. However, because smythite as redefined has a composition of $(Fe,Ni)_9S_{11}$—*i.e.*, > 2 wt. percent more metal than $Fe_3S_4$—greigite and smythite *do not possess any polymorphic* relationship.

## SUMMARY

1) Smythites from numerous occurrences in Australia, Canada, and the United States including specimens from the type locality at Bloomington, Indiana, have compositions of $(Fe,Ni)_9S_{11}$ ($\sim(Fe,Ni)_{3.25}S_4$), *not* $Fe_3S_4$.
2) The density of smythite is approximately 4.32 g/cm$^3$, *not* 4.09 g/cm$^3$.
3) Smythite is *pseudorhombohedral* and the true cell is possibly hexagonal or monoclinic. Dimensions using the pseudorhombohedral cell are $a = 3.47(1)$ Å, $c = 34.4(1)$ Å.
4) The powder diffraction pattern is the same as that reported by Erd *et al.* (1957) except for weak basal reflections with specimens not having preferred orientations.
5) Smythite and greigite ($Fe_3S_4$) are *not* polymorphs. In fact, smythite may not be a mineral in the Fe–S system but a phase in the Fe–Ni–S system as suggested by the presence of Ni in the smythite analyses.
6) Most smythites occurring in nature are probably products of low-temperature oxidation of monoclinic pyrrhotite.

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