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THE CHEMICAL IDENTITY AND FORMULA OF ARGENTOPYRITE AND STERNBERGITE[1]

Gerald K. Czamanske, *U. S. Geological Survey, Menlo Park, California* 94025, and Richard R. Larson, *U. S. Geological Survey, Washington, D. C.* 20242.

Abstract

Sternbergite and argentopyrite have the same formula: $AgFe_2S_3$, as shown by chemical analysis and uncorrected microprobe comparisons. Previous X-ray data indicate different structures for the two minerals.

During the course of an investigation of the Ag-Fe-S system, it was considered advisable to confirm the chemical formulae of the two best-documented ternary sulfides–argentopyrite and sternbergite. These minerals, along with argyropyrite and frieseite, constitute the so-called "silberkiesgruppe," best described by Ramdohr (1955). Whereas the formula for sternbergite has generally been taken to be $AgFe_2S_3$ (after early analytical work, see Streng (1878)), several formulae have been ascribed to argentopyrite despite early suggestions of a dimorphic relationship between the two minerals and the fact that Murdoch and Berry (1954) made a strong case for the formula $AgFe_2S_3$ on the basis of structural and density considerations. Old and poor chemical analyses apparently led to Zambonini's (1916) proposal that argentopyrite is not a mineral of unique composition but has a variable formula which can be expressed as $AgFe_2S_3+n\text{FeS}+m\text{S}$ where $n+m$ are always less than one. Ramdohr (1955) and Ramdohr and Strunz (1967) still prefer to assign the formula $AgFe_3S_5$ to argentopyrite.

Distinct differences between argentopyrite and sternbergite have been noted in their physical and optical properties and are reflected in their X-ray cell data (Table 1).

Samples labelled argentopyrite and sternbergite were obtained from the U.S. National Museum (Washington, D. C.) through the courtesy of John White: USNM R9630, argentopyrite from Andreasberg, Harz, Germany; and USNM 85115, sternbergite from Jachymov, Bohemia, Czechoslovakia. X-ray powder diffraction data for these specimens were obtained using a standard 57.3 mm-diameter powder camera and a Phillips micro-focussing, Co-target X-ray tube, which facilitated the X-raying of small amounts of pure mineral powder gouged from the surfaces of polished grain mounts. Measured line spacings and intensities for these samples are in good agreement with those presented by Berry and

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[1] Publication authorized by the Director, U.S. Geological Survey.

TABLE 1. X-RAY CELL DATA FOR ARGENTOPYRITE AND STERNBERGITE[a]

Argentopyrite	Sternbergite
Orthorhombic, *Pmmn*	Orthorhombic, *Cmma*
$a = 6.64$	$a = 6.63$
$b = 11.47$	$b = 11.60$
$c = 6.45$ Å	$c = 12.68$ Å
$Z = 4$	$Z = 8$
Cell dimensions and space group from Murdoch and Berry (1954)	Cell dimensions and space group from Peacock (1942); similar cell values obtained by Buerger (1937)

[a] Based on the identical formula, $AgFe_2S_3$.

Thompson (1962). The physical and optical properties of the materials studied are in all instances comparable to those described by Ramdohr (1955).

NEW CHEMICAL DATA

Considering the chemistry and mineral associations of the "silberkies-gruppe," one may speculate that the uncertainty in ascribing compositions may be due to analysis of impure material; the ternary minerals are often found in association with other Ag- and Fe-rich phases, *e.g.*, pyrite and ruby silver. Thus, an approach which eventually involved three distinct methods of absolute and comparative analysis was applied.

As a first step, polished single grains about 1 mm in greatest dimension were examined with an electron microprobe to check their homogeneity and to get a rough measure of composition. A Materials Analysis Company Model 400 electron microprobe was operated at 20 kV with a specimen current of $1.0 \pm 0.04 \times 10^{-8}$ A. On the basis of uncorrected counting data, this phase of the study disclosed that individual grains of USNM R9630 and 85115 are homogeneous at the 10-micron level, have Ag, Fe, and S contents on the order of 30–40 weight percent each, and are identical in composition. Evidence for identical composition is summarized in Table 2, in which raw data are presented in the order taken. "Number of sites" refers to distinct specimen coordinates at which data were taken. The average number of counts corresponding to one weight percent of each element was determined by referring to standard minerals, specifically silver, argentite, pyrrhotite, pyrite, and a series of sphalerites with iron contents ranging from 0 to 45 mole percent. (As a check for the presence of major constituents other than Ag, Fe, and S, a spectrometer with a LiF crystal was slowly driven over the range corresponding to wave lengths between 0.900 and 3.100 Å; no other major constituents ($>1\%$ by weight) were detected.

Thus, chemical identity between USNM R9630 and 85115 was established. However, a direct analysis of argentopyrite seemed desirable. While the microprobe data could be refined, the problem of standards presents a serious limitation, and it was concluded that a more sensitive technique, subject to fewer corrections, should be employed. Such a technique is that developed by Rose *et al.* (1965) involving X-ray fluorescence analysis of solutions absorbed on cellulose powder. As applied to the present study, this technique dictated the following procedure (see also Rose and Cuttitta, 1968).

Argentopyrite sample aliquots of 3.24 and 9.74 mg were taken into solution with 2 ml of

TABLE 2. UNCORRECTED ELECTRON PROBE DATA IN SUPPORT OF THE CHEMICAL IDENTITY (AND UNIFORMITY) OF STERNBERGITE AND ARGENTOPYRITE

Element	Mineral	Grain	Number of sites	Average counts per 20 sec	Background counts per 20 sec
Ag	Argentopyrite	I	4	792	26
	Sternbergite	I	3	807	
	Argentopyrite	II	1	809	
	Sternbergite	II	1	794	
	Argentopyrite	II	1	780	
Fe	Argentopyrite	I	2	5011	47
		II	4	5047	
	Sternbergite	I	2	5022	
		II	2	5023	
S	Argentopyrite	I	2	1360	14
		II	2	1351	
	Sternbergite	I	3	1369	
	Argentopyrite	II	3	1381	

fuming nitric acid in a closed 10 ml volumetric flask. The dissolution was carried out slowly at room temperature over several days, with addition of several drops of 30 percent hydrogen peroxide to promote the complete oxidation of sulfur to the sulfate form. After making the solutions up to volume, two aliquots of each were taken to dryness in 10 ml beakers on a steam bath. The residues were then taken into solution in 1 ml of 5 percent HNO_3 and absorbed on 500 mg of chromatographic-grade cellulose powder. Thourough mixing of the moist powder mush and hand grinding of the cellulose powder after drying at about 80°C normally assure a powder on which the solution residue is evenly distributed. The homogeneous, dry powders were pressed at 70,000 psi into 1 in. diameter pellets with a strengthening cellulose backing. Five standards, each containing Ag, Fe, and S in varying porportions, were made from suitable reagents and prepared in a manner identical to that employed for the unknown.

The results obtained for Fe and S are listed in Table 3. The data were gathered with a General Electric XRD-6 X-ray fluorescence unit with a proportional flow counter and the following operating conditions: Fe—Pt target tube, 50 kV, 40 mA, air path, LiF crystal; S—Cr target tube, 50 kV, 40 mA, vacuum path, PET crystal. Linear calibrations were obtained with backgrounds on a blank pellet of 17 and 162 counts per second for Fe and S respectively; counting rates of about 1200 counts per second were obtained for standards containing one milligram of the element sought. The Ag determination was made by an even more sensitive atomic absorption technique using a Perkin Elmer Model 303 instrument with a standard burner. Analyses were made on an aliquot of the same

TABLE 3. COMPOSITION OF ARGENTOPYRITE (USNM R9630) BASED ON X-RAY FLUORESCENCE AND ATOMIC ABSORPTION TECHNIQUES (IN WEIGHT PERCENT)

Element	Determined 9.74 mg sample	Determined 3.24 mg sample	Theoretical $AgFe_2S_3$	Theoretical $AgFe_3S_5$
Ag	33.0 ± 0.3[a]	Not attempted	34.17	24.76
Fe	35.5 ± 0.6	36.3 ± 1.0	35.37	38.46
S	30.7 ± 0.6	30.96 ± 1.0	30.46	36.78
Total	99.2 ± 1.5		100.00	100.00

[a] Determination by atomic absorption by Frederick Simon, U.S. Geological Survey.

sample dissolution used for the X-ray fluorescence analysis. The unknown was bracketed between Ag standards containing Fe and S.

Consideration of the X-ray cell data (Table 1), uncorrected electron probe results (Table 2), and chemical analysis (Table 3) indicates that sternbergite and argentopyrite have the same formula, $AgFe_2S_3$, but differ crystallographically; they are therefore dimorphs.

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