SHORTER COMMUNICATIONS

STRUCTURAL FORMULA AND COMPOSITION OF SKUTTERUDITE

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During part of a larger investigation of transition metal diarsenide minerals (Radcliffe 1966), the composition and stoichiometry of several skutterudite specimens were determined. Skutterudite ($CoAs_3$) is often zoned and intimately intergrown with safflorite (Holmes 1947) and its composition is best determined with a microprobe. This has been done and reported below, and these data support the opinions of some previous investigators.

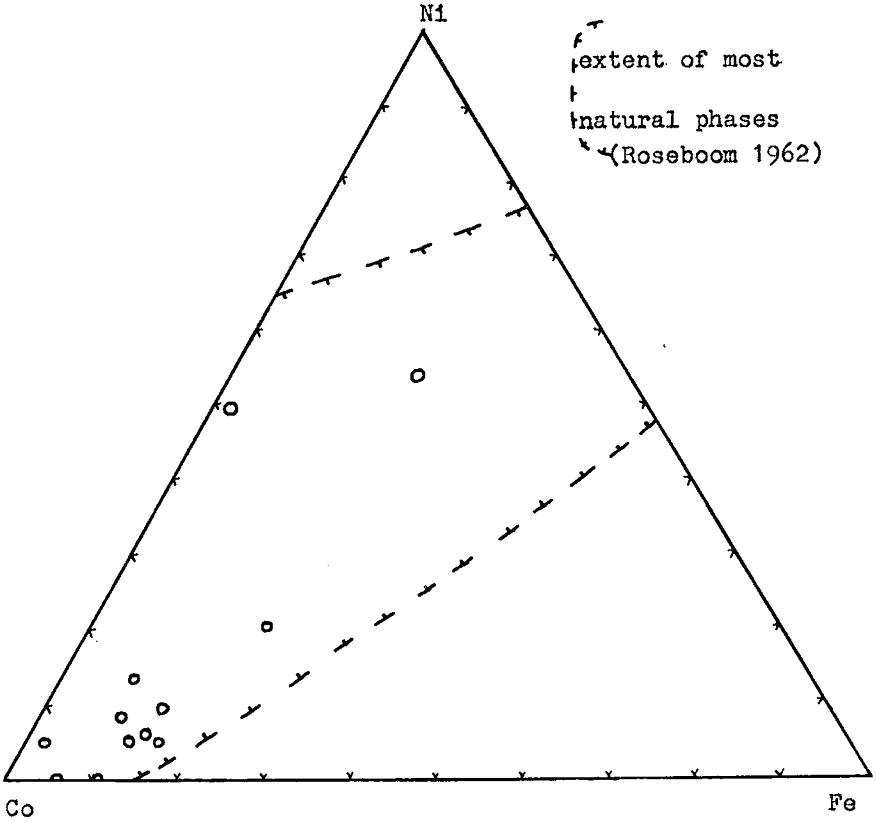

FIG. 1. Microprobe analyses (mole %) of skutterudite.

Palache *et al.* (1944) divided the isometric triarsenides with the general formula (Co,Ni) As_{3-x} into two composition series. They are the skutterudite-nickel skutterudite series with $x = 0$ to 0.5 and the smaltite-chloanthite series with $x = 0.5$ to 1.0. It was noted that Fe may substitute for (Co,Ni) up to a maximum of 12 wt. % (approx. 55 mole % $FeAs_3$).

Holmes (1947), from a study of all previous mineral analyses and of synthetic triarsenides, concluded that there is no real basis for this division as many of the apparent defects result from analyses made on impure material. He was not able to synthesize a composition with less arsenic than $CoAs_{2.95}$. This is supported by Roseboom (1962) who determined that the solubility limits of synthetic skutterudite at 800°C are $CoAs_{2.94}$-$CoAs_{2.96}$. However, in both cases the structural formulae were not determined.

The compositions of 12 skutterudite samples obtained in this study are shown in Fig. 1. The distribution of analyses is similar to that described by Holmes (1947), but the concentration maximum obtained in this study at 82% $CoAs_3$, 7% $NiAs_3$, 11% $FeAs_3$ is richer in nickel by 5% $NiAs_3$. The cell dimensions of these compositions averaged 8.21 Å.

The structural formula for two skutterudite specimens has been determined by calculating the cell content from the probe analyses, measured densities and cell dimensions. (Table 1) The calculated unit cell contents clearly indicate total Co & Fe & Ni in excess of the 8

TABLE 1. SKUTTERUDITE: STRUCTURAL FORMULA

Sample	Analysis weight %	Weight proportions	Atoms in Unit cell	Ideal cell content	
ICO2	Co 19.0	0.1889	6.83		
a=8.209 Å	Fe 2.0	0.0199	0.76	8.24	8×1.03
	Ni 1.8	0.0179	0.65		
	As 75.7	0.7525	21.49	22.88	8×2.86
V=553.2	S 2.1	0.0209	1.39		
	100.6	1.0001	31.12		8×3.89
	D_m 6.42				D_x 6.42
IB26	Co 17.7	0.1727	6.53		
a=8.205 Å	Fe 3.0	0.0293	1.17	8.41	8×1.05
	Ni 1.9	0.0185	0.71		
	As 79.3	0.7737	23.12		
V=552.4	S 0.6	0.0058	0.41	23.53	8×2.94
	102.5	1.0000	31.94		8×3.99
	D_m 6.73				D_x 6.73

Sample ICO2, Cobalt, Ontario (Queen's Univ.)
Sample IB26, Cobalt, Ontario (Queen's Univ.)
D_m. from triplicate weighings on Berman balance, sample weight about 20 mg, liquid carbon tetrachloride.

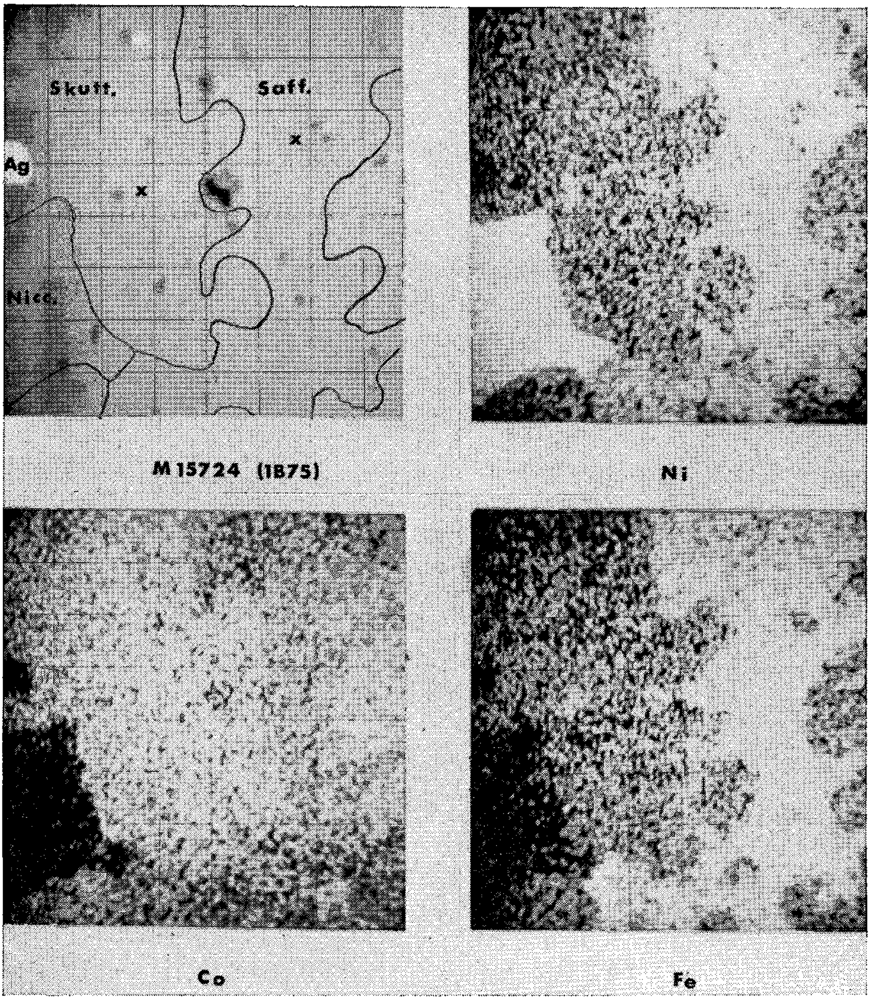

FIG. 2. *Top left.* Electron backscatter image of intergrown skutterudite and safflorite. Other photographs are x-ray scanning images of $K\alpha_1$ radiations. The area covered by these scans is the same as that of the electron backscatter. Note the relative preferential inclusion of Ni and Fe in safflorite, and Co in skutterudite. Sample from Mississagi, Ontario (ROM, M15724). Grid scale = 0.03 mm.

required for the *A* structural position and total As & S less than the 24 required for the *B* structural position. The total number of atoms is close to 32. These observations clearly indicate the presence of some metal atoms in arsenic positions in the structure as a partial explanation of the apparent deficiency of arsenic in the empirical formula. The deficiency of total atoms from the ideal 32 indicates that some arsenic sites are vacant. Both of these specimens fall within the skutterudite-nickel skutterudite series as defined by Palache *et al.* (1944).

An explanation for the grosser deficiency of As in skutterudite and smaltite as reported in previous analyses is illustrated in Fig. 2. *X*-ray scanning images distinguish safflorite and skutterudite in a fine intergrowth. They are indistinguishable under reflected light and by electron backscatter images. The intergrown lenses average 0.05 mm in length and 0.02 mm in width, and the analyses obtained at the points marked 'x' on Fig. 2 are given in Table 2.

TABLE 2. COMPOSITIONS OF POINTS 'x' ON FIG. 2

	Skutterudite	Safflorite	Skutt. (mole %)	Saff. (mole %)
Co	18.1	16.2	78.8	55.6
Fe	1.8	5.6	8.2	20.4
Ni	3.0	6.9	13.0	23.9
As	76.6	71.2		
S	0.3	0.5		
	99.8	100.4		

Sample 1B75 Mississagi, Ontario (ROM M15724)

A bulk chemical analysis obtained from such a sample would tend to indicate a highly defective triarsenide rather than a mixture of perhaps near stoichiometric di- and triarsenides. Since most skutterudite specimens are intergrown with safflorite on this fine scale it is concluded that many previous analyses were done on multiphase samples.

It may be noted that iron and nickel are preferentially absorbed by safflorite rather than by skutterudite in a cobalt-rich environment. This might appear to be a paradox because the limiting extent and abundance of most natural compositions indicate that nickel-rich skutterudite is more stable than nickel-rich safflorite. However it was found (Radcliffe 1966) that the most cobalt-rich diarsenide structure changes from a measurably orthorhombic, into a measurably monoclinic lattice and such compositions are relatively rare in nature (Radcliffe 1966). Cobalt diarsenide is essentially an advanced distortion of the marcasite structure and it is thought that cobalt-rich safflorite is probably unstable and difficult to crystallize at low temperatures.

Klemm (1965) published approximately 140 microprobe analyses of skutterudite and reported a variation of the metal-arsenic ratio from 1:1.9 to 1:3.3, which is in support of Palache's (1944) subdivision of skutterudite into two series, and therefore is in contradiction with the observations reported here. However, Klemm reports no conventional *x*-ray data on his specimens and the crystallographic symmetry of his phases may be questioned. That is, was the work done on isometric skutterudite (triarsenide) or orthorhombic safflorite (diarsenide), as microscopic examinations may not distinguish these phases due to weak anisotropy commonly exhibited by safflorite? In addition the Co-Fe-Ni ratios of Klemm's analyses are more variable than previously reported and indeed he classifies skutterudite into three types on the basis of composition: arsenic-poor, medium arsenic, and arsenic-rich. These types are characterized by low, medium, and high nickel contents, respectively. Is it more than coincidence that he shows diagrammatically a concentration of arsenic poor skutterudite in a compositional area which coincides with the most frequently occurring natural compositions of safflorite $(Co,Fe,Ni)As_2$ (Radcliffe 1966, Roseboom 1963, Holmes 1947)?

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