

## SYNTHESIS OF THE K-Fe-Ni SULPHIDE FROM FRANK SMITH MINE

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Potassium-iron-nickel sulphide has been found in a clinopyroxene-ilmenite intergrowth from Frank Smith Mine, Cape Province, South Africa (Clarke *et al.*, 1977). The mineral occurs principally in ovoid blebs with pyrrhotite and pentlandite, and these blebs are frequently in close spatial association with the ilmenite lamellae of the host. The blebs normally consist of a core of pyrrhotite-pentlandite and a rim of K-Fe-Ni sulphide. Discrete irregular grains of K-Fe-Ni sulphide also occur in minute fractures in the clinopyroxene host. A typical chemical analysis gives (wt. %): K 8.94, Fe 41.75, Ni 13.60, Cu 1.35, S 33.49, Cl 1.36, and a structural formula of  $K_{6.1}(Fe,Ni,Cu)_{26.9}S_{28.0}Cl_{1.0}$ .

Starting materials for the experimental work consisted of: potassium thioferite ( $KFeS_2$ ), Fe sponge, powdered Ni metal, synthetic FeS, synthetic NiS and KCl. Bulk compositions lying in the plane K-(Fe,Ni)S-Cl, roughly equal to the natural compositions plus excess potassium, were prepared. Losses of both K and Fe to the capsule walls occurred. Bulk compositions A, D and F had 100 Fe/Fe+Ni = 5 (atomic), whereas  $\bar{A}$ ,  $\bar{D}$  and  $\bar{F}$  had 100 Fe/Fe+Ni = 50 (Fig. 1). The starting materials were loaded and welded in Au capsules in an Ar atmosphere, and then up to seven capsules were sealed in an evacuated silica glass tube. The tube was placed in a steel holder in a vertical resistance furnace with temperature control of  $\pm 2^\circ C$ . Care was taken not to overrun the desired run temperature during heating. All runs were at one atmosphere pressure. At the end of each run the silica tubes were lifted from the furnace and left to cool in air.

Preliminary results are given in Table 1. Bulk compositions A, D and F were contaminated with oxygen, the source of which was probably impure iron sponge, and as a result produced minor quantities of iron oxide. Nevertheless, the results on these runs are included here because of the additional information they provide on the degree of  $Fe \rightleftharpoons Ni$  substitution in the potassic sulphide phase, namely 100 Fe/Fe+Ni = 99.27-92.51. The  $\bar{A}$ ,  $\bar{D}$  and  $\bar{F}$  bulk compositions produced potassic sulphides with 100 Fe/Fe+Ni = 54.33 - 40.95. These synthetics bracket the natural compositions which have 100 Fe/Fe+Ni = 79.03 - 72.89. It is suggested that there is a continuous solid solution series from a pure iron end-member ( ${}^{100}K_6Fe_{27}S_{28}Cl_1$ ) to at least  $K_6Fe_{13}Ni_{14}S_{28}Cl_1$ , and probably extending to a pure nickel end-member ( ${}^{100}K_6Ni_{27}S_{28}Cl_1$ ). The potassic sulphide formed at temperatures from 356°C to at least 950°C, i.e. at temperatures both above and below the solidus in this sulphide system.

On the basis of textural relations in the natural sample, and phase relations in the system Fe-Ni-S, Clarke *et al.* (1977) favoured a mechanism of potassium metasomatism to generate K-Fe-Ni sulphide from the pre-existing sulphide blebs in the clinopyroxene-ilmenite nodule. The experimental work reported here demonstrates the feasibility of producing K-Fe-Ni sulphide below the solidus in the system K-Fe-Ni-S-Cl. Given that the original sulphides (pyrrhotite and pentlandite) have a well-developed flame-like exsolution texture, it seems most likely that the potassic sulphide has formed in the solid state at temperatures below 600°C., i.e.

after the diatrema had solidified. The source of the metasomatic fluid was probably the kimberlite, and the chemical constituents of the fluid included  $H_2O$  (which occurs in alteration products of the clinopyroxene host), and K, Cl and Cu (which have been added to the original Po-Pn intergrowths).

Clarke, D. B., Pe, G. G., MacKay, R. M., Gill, K. R., O'Hara, M. J. and Gard, J. A. A New Potassium-Iron-Nickel Sulphide from a Nodule in Kimberlite, *Earth Planet. Sci. Lett.* 35, 421-428, 1977.

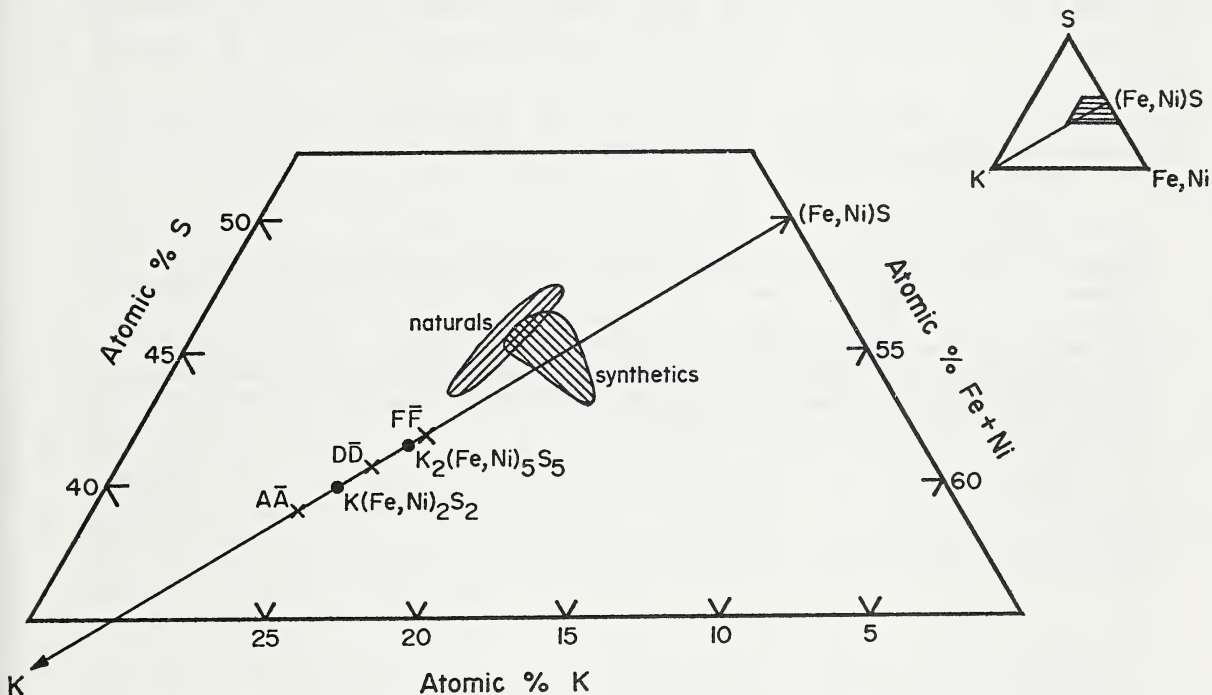


Fig. 1. Projection from chlorine into the plane K-FeNi-S showing the location of the bulk compositions ( $A, \bar{A}; D, \bar{D}; F, \bar{F}$ ), the range of composition of the naturally occurring K-Fe-Ni sulphides at Frank Smith Mine, the range of composition of synthetic K-Fe-Ni sulphides and some hypothetical compounds  $K(Fe,Ni)_2S_2$  ( $\equiv KFeS_2 + Ni$ ) and  $K_2(Fe,Ni)_5S_5$  ( $\equiv 2KFeS_2 + 2Ni + FeS$ ).

		Bulk Compositions					
Temp (°C)	Time (hrs)	<u>A</u>	<u>Ā</u>	<u>D</u>	<u>D̄</u>	<u>F</u>	<u>F̄</u>
950	10	-	4	4	1,2,4	4,5	1,2,4
850	20	4,6	1,4	2,4,5,6	1,2,4	2,4,5,6	1,2,4
750	20	-	-	2,4,6	-	2,4,6	1,2,4
650	20	-	1,4	2,3,4,6	1,2,4	2,4,6	1,2,4
550	20	-	1,4	2,3,4	1,2,4	2,3	1,2,4
450	20	2,3	2,4	2,4	1,2,4	2,4,6	1,2,4

Table 1: Run products confirmed by electron microprobe analysis; other phases may be present in some of the runs but have not yet been identified. Phases are: 1 - heazlewoodite, 2 - K-Fe-Ni sulphide, 3 - metallic Ni-Fe 4 - monosulphide solid solution, normally containing 0.1 - 5.0% K, 5 - pyrrhotite, 6 - wüstite. In addition bulk compositions F and  $\bar{F}$  were run at four lower temperatures producing K-Fe-Ni sulphide at 425°, 400°, 356°C, but not 300°C.