

## GEOCHEMISTRY

# Ferroskutterudite (Fe, Co)As<sub>3</sub>: A New Mineral Species\* from the Dolomite–Calcite Veins of the Noril'sk Ore Field

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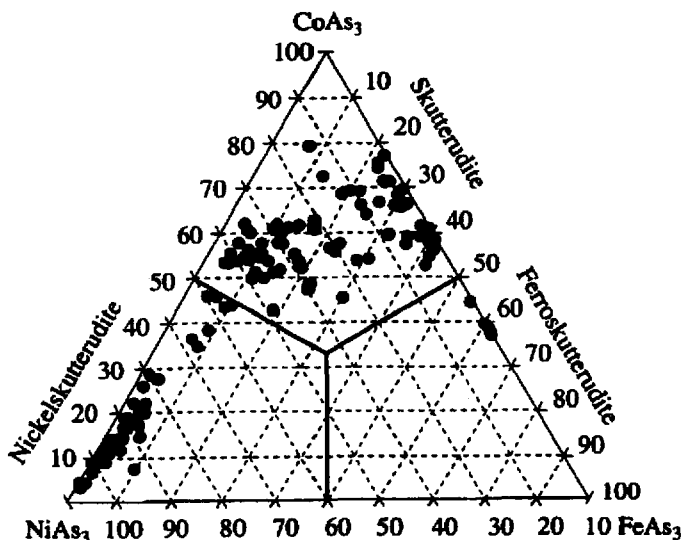
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Chalcogenides-sulfides, sulfoarsenides, arsenides, sulfoantimonides, and other compounds of Fe, Co, and Ni are characterized by a wide range of isomorphic substitution in the Fe–Co–Ni series. In some cases, these are continuous series of solid solutions: disulfides (pyrite–vaesite–cattierite), diarsenides (safflorite CoAs<sub>3</sub>–rammelsbergite NiAs<sub>2</sub>–lollingite FeAs<sub>2</sub>, and others [1–3, 6, 8, 12, 13]), and others. With the discovery of a new mineral, ferroskutterudite, this series was supplemented by triarsenides: skutterudite CoAs<sub>3</sub>–nick-

elskutterudite NiAs<sub>3</sub>–ferroskutterudite (Fe, Co)As<sub>3</sub>. Previously, only the skutterudite–nickelskutterudite series was known [1–3, 8, 10, 12–15].

The arsenide mineralization in the Noril'sk ore field was previously assigned to hydrothermal rocks—derivatives of the ~250-Ma-old (Middle Permian–Lower Triassic) trap complex, with Cu–Ni sulfide mineralization [4, 5, 9]. It was established that the antimonide–arsenide mineralization of the Noril'sk ore field is developed among the magmatic Ni–Cu ores and host



Composition of skutterudite, nickelskutterudite, and ferroskutterudite from carbonate veins of the Noril'sk ore field (filled circles).

\* Mineral (No. 2006-0210) and its name were approved by the IMA Commission on New Minerals and Mineral Names on October 24, 2006.

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Table 1. Chemical composition of ferroskutterudite

No.	wt %						Formula units calculated on the basis of 4 atoms						
	Ni	Co	Fe	As	S	Total	Ni	Co	Fe	Total	As	S	Total
1	0.05	8.70	12.95	79.43	1.31	102.44	0.002	0.398	0.626	1.026	2.864	0.110	2.974
2	0.01	7.94	12.63	77.56	1.43	99.57	0.001	0.374	0.628	1.003	2.843	0.124	2.967
3	0.05	8.04	12.38	77.09	1.39	98.95	0.002	0.381	0.619	1.002	2.877	0.121	2.998
4	0.10	8.82	10.38	77.96	1.24	98.50	0.005	0.423	0.525	0.953	2.938	0.109	3.047
Average	0.05	8.38	12.09	78.01	1.34	99.87	0.002	0.394	0.600	0.996	2.888	0.116	3.004

rocks, which experienced post-trap regional metamorphism of the zeolite and prehnite-pumpellyite facies. The hydrothermal rocks containing antimonide-arsenide mineralization are dated 164–122 Ma [6, 7, 11]. The Ni (Co, Fe) arsenides and antimonides occur mainly in the carbonate and apophyllite-anhydrite-carbonate veins with wurtzite, sphalerite, galena, chalcocopyrite, pyrrhotite, acicular cubanite, and chalcocite. The veins were precipitated from NaCl–MgCl<sub>2</sub> solutions with low salinity (0.2–1.4 wt % NaCl equiv) at  $P = 0.9–0.1$  kbar and  $T = 216–127^\circ\text{C}$ . The antimonide-arsenide mineralization was formed in two stages: (1) the arsenide-rich stage 1 trending from Ni monoarsenide through Ni–Co diarsenide and triarsenide to native arsenic; (2) stage 2 with the predominant formation of antimonide, sulfoarsenide, and sulfoantimonides of Ni.

Ferroskutterudite was identified in the dolomite-calcite veins, which contain triarsenides and crosscut calcite veins with arsenides and diarsenides (Komsol'skii Mine). Ferroskutterudite is a scarce mineral formed in dolomite-calcite veins, where zoned aggregates of Co–Ni and Ni skutterudite are replaced by granular intergrowths of low-Co nickelskutterudite, Fe-skutterudite, and ferroskutterudite. The ferroskutterudite varies in size from  $n$  to 30–100  $\mu\text{m}$ . This mineral has a tin white color and metallic luster. It is practically indistinguishable from skutterudite and is characterized by high relief, which is close to that of skutterudite and safflorite but higher than that of nickelskutterudite. Microindentation hardness  $VHN_{30} = 700–1050$  kg/mm<sup>2</sup> ( $n = 4$ ). In reflected light, ferroskutterudite has a high reflectance (58–54%). The mineral is white, isotropic, and pinkish creamy in the intergrowths with nickelskutterudite. Its reflectance spectrum is similar to that of skutterudite, but the reflectance is slightly higher than that of skutterudite. The reflectance ( $R$ ) was measured in air (based on the certified standard WTiC): 57.2 (400 nm), 57.6 (420 nm), 58.0 (440 nm), 58.2 (460 nm), 58.2 (470 nm), 58.2 (480 nm), 58.0 (500 nm), 57.6 (520 nm), 57.3 (540 nm), 57.2 (546 nm), 56.9 (560 nm), 56.4 (580 nm), 56.2 (589), 56.0 (600 nm), 55.5 (620 nm), 55.2 (640 nm), 54.9 (650 nm), 54.7 (660 nm), 54.3 (680 nm), and 53.8 (700 nm).

The chemical composition of the skutterudite-group minerals was determined using a Camebax-microbeam microprobe (accelerating voltage 20 kV, beam current 20 nA; standards: pure Ni, Co, and Fe; synthetic GaAs, and cobaltite CoAsS as standards of As and S, respectively; I.M. Kulikova, analyst). Data points of the skutterudite-group minerals from the Noril'sk ore field are shown by filled circles in the figure. As is seen, the minerals of the continuous skutterudite–nickelskutterudite series are the most abundant, while Fe–Ni skutterudite and minerals of the skutterudite–nickelskutterudite series are less abundant. The composition of the scarce mineral ferroskutterudite is shown in Table 1. Its average composition corresponds to the formula  $(\text{Fe}_{0.600}\text{Co}_{0.394}\text{Ni}_{0.002})_{0.996}(\text{As}_{2.888}\text{S}_{0.116})_{3.004}$ , which is close to  $(\text{Fe}_{0.6}\text{Co}_{0.4})_1(\text{As}_{2.9}\text{S}_{0.1})_3$ .

Cubic triarsenides skutterudite, nickelskutterudite, and ferroskutterudite have similar diffraction parameters. The X-ray pattern of ferroskutterudite (Debye-Scherrer camera,  $D = 57.3$  mm,  $\text{CuK}\alpha$ ) is given in Table 2. The mineral was indexed by analogy with skutterudite. The major lines in the XRD powder pattern are as follows ( $d/n$ , intensity  $I$ , and  $hkl$ ): 2.585 Å (10) (310); 2.182 (9) (321); 1.829 (7) (420); 1.667 (5) (422); 1.602

Table 2. X-ray pattern of ferroskutterudite

$hkl$	$d_{\text{meas}}$ , Å	$d_{\text{calc}}$ , Å	$hkl$
3	5.8	5.77	110
3	4.10	4.085	200
4	3.34	3.335	211
10	2.585	2.584	310
9	2.182	2.184	321
4	1.928	1.926	411
7	1.829	1.827	420
3	1.744	1.742	332
5	1.667	1.6677	422
7	1.602	1.6023	510
6	1.402	1.4011	530
3	1.364	1.3617	600
2	1.291	1.2918	620

(7) (510); 1.402 (6) (530). Ferroskutterudite is a cubic mineral (space group  $Im\bar{3}m$ ,  $a = 8.17(1) \text{ \AA}$ ,  $V = 545.34(3) \text{ \AA}^3$ ,  $Z = 8$ ).

The specimen with ferroskutterudite (no. 3440/1) is stored in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

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