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New data on rasvumite and djerfisherite

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Abstract

Electron microprobe analyses and X-ray diffraction studies have shown the identity of rasvumite from a new occurrence at Coyote Peak, Humboldt County, California, and holotype material from the Khibina massif, Kola Peninsula, USSR. The electron microprobe analyses have established that the correct formula is KFe_2S_3 instead of $K_3Fe_9S_{14}$, as originally proposed. We compare new electron microprobe analyses of djerfisherite from the two localities and show that these djerfisherites do not contain magnesium.

Introduction

The occurrence at Coyote Peak, Humboldt County, California, of at least five unusual iron sulfide minerals containing essential potassium or sodium has led to a thorough review of the mineral chemistry of such phases. Although three new alkali-iron sulfide phases—$K_3Fe_{10}S_{14}$, $NaFe_3S_5 \cdot 2H_2O$, and $NaFeS_2 \cdot 2H_2O$—have been found in the mafic alkalic diatreme at Coyote Peak (Czamanske *et al.*, 1977), in this report we describe the discovery there of two previously described minerals: rasvumite, KFe_2S_3, and djerfisherite, $K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$.

The occurrence of rasvumite at Coyote Peak is only the second reported, after that in the Khibina massif in the USSR (Sokolova *et al.*, 1970). Djerfisherite is a more widely known potassium-bearing sulfide that has been found in meteorites (*e.g.*, Fuchs, 1966), Talnakh ore (Genkin *et al.*, 1969), alkalic rocks and pegmatites of the Khibina massif (Sokolova *et al.*, 1971), Tazheran skarns (Konev *et al.*, 1972), Yakutian kimberlites (Dobrovol'skaya *et al.*, 1975), and South African kimberlites (Clarke *et al.*, 1977). Our report, and the progress it represents in the understanding of these unusual minerals, has been made possible by the generous exchange of specimens, data, and ideas between the Russian and American coauthors.

Rasvumite

Rasvumite was named and first described from the Khibina massif, Kola Peninsula, USSR by Sokolova *et al.* (1970). X-ray diffraction studies of the holotype rasvumite from Khibina and of the newly discovered material from Coyote Peak have established their identity. Rasvumite from Coyote Peak is orthorhombic, aspect C^*c^*; $a = 9.035(1)$, $b = 11.022(1)$, $c = 5.426(1)$A, $V = 540.4(1)A^3$; cell contents, 4 KFe_2S_3; density = 3.035 g cm^{-3} (calc); specific gravity, 3.1(1) (meas). Study of Khibina and Coyote Peak minerals by electron microprobe under identical conditions has shown that rasvumite has the most constant composition of all known potassium–iron sulfide minerals and contains the least amount of other elements. Typical analyses are presented in Table 1.

An important conclusion of our study is that the correct formula for rasvumite is KFe_2S_3. Because rasvumite alters readily in the supergene environment, we believe that the original wet-chemical analyses that led to the proposed formula $K_3Fe_9S_{14}$ were of altered material from which the potassium had been partly leached. Subsequent microprobe analyses of Khibina rasvumite (Dobrovol'skaya *et al.*, 1979) proved that the potassium content of rasvumite falls in the range of 14 to 16 weight percent K.

Table 2 presents X-ray powder-diffraction data for the Coyote Peak rasvumite; the observed pattern is essentially identical to that given by Sokolova *et al.* (1970) for the Khibina rasvumite. Note, however, that the lines reported at 2.01, 1.949, 1.857, and 1.799A for the rasvumite from Khibina do not appear in the pattern for this rasvumite from Coyote Peak. Khibina rasvumite is commonly intergrown

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Table 1. Electron microprobe analyses of rasvumite (in weight percent)*

	Khibina Grn.1	Khibina Grn.2	Coyote Peak CYP-9	Coyote Peak CYP-133	Ideal KFe_2S_3
K	16.3	16.1 $^{+0.1}_{-0.4}$**	16.1	16.0	15.8
Fe	45.2	45.0 ± 0.2	44.8	46.5	45.2
S	38.0	37.8 $^{+1.2}_{-0.2}$	37.3	38.6	38.9
Total***--	99.5	98.9	98.2	101.1	99.9

* Analyses made at 10 and 15 kV on an ARL-EMX electron microprobe; standards used were natural biotite containing 8.3 wt% K and pure synthetic FeS. Data were corrected by the theoretical scheme FRAME (Yakowitz et al., 1973). Continuing comparisons suggest that: (1) the use of a biotite and FRAME gives K contents for sulfides that are about 0.2 wt% high at the 10-wt% level, and (2) the use of pure FeS and FRAME gives S contents for K-Fe sulfides that are about 1.0 wt% low.

** Estimated limits of error for each analysis.

*** Cl, Cu, Mg, Na, and Ni have not been detected above the 0.01 wt% level, except that 0.06 wt% Na is indicated for sample CYP-9.

with djerfisherite and an unidentified copper–iron sulfide phase, so these four lines may be due to such impurities.

Djerfisherite

Typical analyses of Coyote Peak djerfisherite are compared in Table 3 to analyses obtained under identical conditions for Khibina djerfisherite and the "djerfisherite-like" compound synthesized at Argonne National Laboratory (Mrazek and Battles, 1977; Tani, 1977). The djerfisherite formula, $K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$, is based on structural studies and chemical data for djerfisherites from several known occurrences (Dmitrieva *et al.*, 1977).

Of special importance is the fact that the Khibina djerfisherite discussed by Sokolova *et al.* (1971) and Dmitrieva and Ilyukhin (1975) is now shown to be free of magnesium. Russian microprobe analyses have also failed to confirm the presence of magnesium in the Khibina djerfisherite, and it is presumed that the original wet-chemical analysis was on material contaminated with a magnesium-bearing silicate. Therefore, no natural djerfisherite analyzed to date contains magnesium.

Knowing that magnesium is not a constituent of djerfisherite, the senior author questioned the presence of 0.23 to 0.29 weight percent Li in the djerfisherite-like compound synthesized at Argonne National Laboratory. Evidence for lithium within the compound was considered desirable because: (1) the compound was synthesized in a LiCl–KCl melt, (2) Li_2FeS_2 and Li_2S are known products of the cell reaction, and (3) the compound was analyzed in bulk. Ion microprobe analysis for lithium by I. M. Steele (written communication, 1978) has proved that lithium at about the reported level is, indeed, uniformly distributed within grains of djerfisherite-like phase.

The original structural determination for djerfisherite (Dmitrieva and Ilyukhin, 1975) was based on chemical data presented with the initial description of material from the Khibina occurrence (Sokolova *et al.*, 1971). According to these data, location of an

Table 2. X-ray powder-diffraction data for rasvumite from Coyote Park, Humboldt County, California

hkℓ	Calculated* $d_{hk\ell}$ (A)	Observed** $d_{hk\ell}$ (A)	Observed** I_a	Observed** I_b
110	6.988	6.98	62	60
020	5.511	5.513	100	60
200	4.518	4.521	2	---
111	4.286	---	---	---
021	3.867	---	---	---
220	3.494	3.492	17	15
130	3.403	3.403	43	30
221	2.938	2.935	12	100
310	2.905	2.905	12	5
131	2.883	2.882	3	---
040	2.756	---	---	---
002	2.713	2.707	2	---
311	2.561	2.560	1	---
112	2.529	2.529	5	10
041	2.457	---	---	---
022	2.434	2.435	1	15
240	2.352	2.352	2	---
330	2.329	2.329	12	20
202	2.326	---	---	---
150	2.142	2.141	1	---
331	2.140			
420	2.090	2.091	6	10
151	1.992	---	---	---
312	1.983	1.983	2	30
060	1.837	1.837	6	5
350	1.779	1.778	14	30
440	1.747	1.747	12	30
530	1.622	1.622	1	---
170	1.551	1.552	2	---
600	1.506	1.506	1	---
080	1.378	1.378	3	---
710	1.282	1.282	2	---

* All calculated hkℓ's listed for $d_{hk\ell}$ ≥2.300A; all $d_{hk\ell}$'s are indexed. Indices are from least-squares analysis of X-ray powder diffraction data, using the digital computer program of Appleman and Evans (1973).

** Sample 77-CYP-9. X-ray diffractometer conditions are: chart X-4292; Cu/Ni radiation, λCuK_{α_1} = 1.540598A; Si internal standard; scanned at 1/8°min^{-1} from 12 to 80°(2θ). I_a = intensities in diffractometer trace; I_b = visual estimate of intensities in Film 861 (Debye-Scherrer photograph).

Table 3. Electron microprobe analyses of djerfisherite (in weight percent)*

	Khibina		Coyote Peak		Argonne
			CYP-133	CYP-134	DS-11 & RD21-22
K	9.60	±0.15**	9.45	9.00	9.90
Na	0.70	±0.05	0.10	0.76	0.00
Mg	0.00		<0.05	<0.05	0.00
Cu	14.0	±0.2	9.69	8.37	0.00
Ni	0.04	±0.05	0.76	1.41	0.00
Fe	41.5	±0.2	44.2	45.4	54.2
S	33.2	±0.6	33.8	33.8	34.5
Cl	1.20	±0.03	1.13	1.26	1.49
Total---100.24			99.18	100.05	100.09***

* Analyses and corrections as in Table 1 except that K and S values are averages between: (1) values obtained by using biotite and pure FeS as standards, and (2) values obtained using natural rasvumite as a presumed stoichiometric standard. As suggested in footnotes to Table 1, these values differ by about 0.2 and 1.0 wt%, respectively. Fe values typically differ by less than 0.1 wt% regardless of use of FeS or rasvumite as standard. Additional standards used were: (1) synthetic $CuFeS_2$ for Cu, (2) crocidolite containing 4.63 wt% Na, (3) sodalite containing 6.82 wt% Cl, and (4) synthetic monosulfide solid solution containing 9.89 wt% Ni.

** Estimated limits of error for each analysis.

*** Also reported to contain 0.23 to 0.29 wt% Li and nine trace elements totaling 0.51 wt%. (Mrazek and Battles, 1977; L. H. Fuchs, personal communication, 1978).

Mg atom in position 1*a* of space group *Pm3m* (*i.e.*, at the origin) seemed quite reasonable because of the appropriate bond distance (Mg–S, 2.626A) and low *R* factor (0.073).

Electron microprobe analyses have shown that, although djerfisherite contains no magnesium, the sodium content approaches 0.8 Na atoms per unit cell in djerfisherites from the Khibina massif and Coyote Peak. Accordingly Na should be placed at the origin position instead of Mg. This replacement should not change the *R* factor significantly because of the close similarity between the X-ray scattering factors for Mg and Na, although the Na–S distance may be somewhat short.

The origin position 1*a* or, by a shift in origin, the body-centered position 1*b* could be occupied by still other atoms. For example, Tani (1977) assigned Li to position 1*b* in a djerfisherite-like compound, $K_6LiFe_{24}S_{26}Cl$. For iron-rich djerfisherite, the presence of octahedrally coordinated Fe at position 1*a* or 1*b* seems a reasonable hypothesis.

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