Reports

Djerfisherite, Alkali Copper-Iron Sulfide: A New Mineral from Enstatite Chondrites

Abstract. *A new mineral, essentially a potassium-copper-iron sulfide, occurs in accessory amounts in the enstatite chondrites Kota Kota (a find) and St. Marks (a fall), and has been identified visually in the enstatite achondrite Pena Blanca Springs (a fall). The x-ray diffraction pattern, electron-microprobe analysis, and its appearance in polished sections all serve to identify it.*

Djerfisherite was recognized as possibly a new mineral by its distinctive appearance, under the microscope, in polished sections of the Kota Kota enstatite chondrite. In color, djerfisherite is darker than cream-colored troilite and has a greenish yellow tinge; it is close to khaki olive drab. It has a submetallic luster, is isotropic in reflected polarized light, and lacks internal reflections. An x-ray powder photograph of small amounts of the material scratched from surfaces of selected grains could not be identified with any pattern published in the various x-ray determinative references.

Table 1. X-ray powder diffraction data for djerfisherite from the Kota Kota meteorite. Norelco powder camera (diameter, 11.45 cm), $CoK\alpha_1\alpha_2$, Fe filter; diamond dust used as an internal standard. Intensities are estimated.

Indices	Intensity	dÅ (calc.)	dÅ (obs.)
100	5	10.38	10.34
110	3	7.29	7.31
111	5	5.98	5.97
221, 300	1	3.43	3.45
310	4	3.259	3.269
311	5	3.113	3.118
222	7	2.983	2.985
320	1	2.852	2.868
321	1	2.765	2.764
322, 410	2	2.504	2.508
330, 411	1	2.440	2.437
331	6	2.367	2.372
420	1	2.312	2.312
332	1	2.196	2.204
510, 431	1	2.022	2.028
511, 333	2	1.985	1.990
440	10	1.824	1.828
530, 433	1	1.772	1.773
531	1	1.748	1.748
622	2	1.558	1.559
711, 551	1	1.443	1.448
731, 553	1	1.347	1.346
800	1	1.293	1.293

Grains of this mineral in Kota Kota appear to be much softer than the associated sulfide minerals and can be polished only to a matte surface; this feature probably reflects terrestrial weathering of the meteorite for an unknown period after its fall. The mineral occurs in rounded bodies, up to 0.4 mm in diameter, with iron-nickel, schreibersite, and troilite. The fact that its borders with the enclosing silicates are often irregular and jagged also suggests weathering. Other associated minerals in the meteorite are clinoenstatite, tridymite, cristobalite, daubreelite, roedderite (*1*), alabandite (not pure MnS, but probably a mixed sulfide with the rock-salt structure), and graphite. Djerfisherite probably constitutes from 0.1 to 0.5 percent of the meteorite; however, in some areas defined by the × 80 field of the microscope it is more abundant than troilite.

Unlike its incidence in Kota Kota, the mineral in St. Marks may occur as individual grains in the silicate matrix; it is slightly less hard than troilite and can be polished to a finish equivalent to that of troilite. More commonly, the grains border on practically any of the minerals present but then always have at least one border with the silicate matrix. Small dots of troilite occur as inclusions in a few grains, possibly indicating increased solubility of iron sulfide at elevated temperatures. The largest grain observed in the section studied was 0.07 mm across; most ranged between 0.02 and 0.04 mm. The straight sides and angular habit of the grains, characteristic of the troilite also, are taken from the silicates. Djerfisherite probably constitutes less than 0.1 percent of this meteorite. Perhaps 100 grains are exposed in a surface area of about 5 cm^2. In the distribution, grains are not uniform, being usually clustered in areas from 0.5 to 2 mm in diameter; only two clusters were present in another polished section 2 cm^2 in area. Associated minerals in St. Marks include enstatite, clinoenstatite, quartz, iron-nickel, plagioclase, troilite, daubreelite, and oldhamite, a cubic mineral having a cell size close to that of alabandite, schreibersite, and graphite. Minor amounts of unidentified opaque minerals were also noted by Ramdohr (*2*).

Ramdohr pointed out to me that he had observed a mineral, undoubtedly identical with djerfisherite, in both St. Marks and the enstatite achondrite Pena Blanca Springs; he had correctly recognized it as a new mineral on the basis of its appearance under the microscope and referred to it as mineral C (*2*). The largest of a few scattered grains in the section of Pena Blanca Springs available to me had a mean distance across of about 0.02 mm —it was too small to yield x-ray data; on the basis of appearance alone, this meteorite probably represents the third occurrence of the mineral. The following enstatite chondrites were unsuccessfully examined for the presence of djerfisherite: Hvittis, Indarch, Adhi Kot, St. Sauveur, Atlanta, and Abee.

X-ray powder data on djerfisherite from both enstatite chondrites are comparable in pattern; because of the greater amount of material available, the pattern of djerfisherite from Kota Kota contained more lines (Table 1). I should point out that the techniques employed to obtain results from small amounts of material yield powder photographs considerably weaker than those normally obtained from an x-ray capillary; the lines can be indexed in a primitive cubic cell with an edge of 10.34 ± 0.01 Å.

The unaltered appearance of grains in the polished section of St. Marks led to their selection for analyses by electron-microprobe methods; the averaged results from 12 grains appear in Table 2. The composition, after subtraction of the chlorine content as $FeCl_2$ (*3*), is $K_{2.93}(Na_{0.17}\ Cu_{0.87})_{1.04}(Fe_{11.82}\ Ni_{0.18})_{12.00}\ S_{13.93}$; or, within the errors (about 1 percent) of the analyses, $K_3(Na, Cu)(Fe, Ni)_{12}S_{14}$. The calculated density, if one assigns two molecules per unit cell, is 3.9 g/cm^3; I could not measure density or hardness.

Synthetic alkali copper sulfides, as

Table 2. Chemical composition of djerfisherite in the St. Marks meteorite. Electron-microprobe data averaged for 12 grains and corrected for background and dead time, fluorescence (*11*), absorption (*12*), and atomic number (*13*).

Element	Percentage (weight)
Fe	50.7
S	33.8
K	8.7
Cu	4.2
Cl	1.0
Ni	0.8
Na	0.3
	99.5

well as some alkali iron sulfides, have been reported, but the only alkali copper-iron sulfides found in the literature are: $K_3Fe_2Cu_4S_7$, $K_3Fe_2Cu_5S_7$, or $K_5Fe_3Cu_{12}S_{14}$ (*4*); none resembles djerfisherite in composition.

I have tried in preliminary experiments to synthesize the mineral, but it has been impossible to obtain a single phase by heating a mixture of appropriate chemicals, proportioned according to the formula, in sealed, evacuated, silica tubes. Three phases are usually obtained: troilite; a phase of unidentified composition, yielding an x-ray pattern identical with that of natural djerfisherite; and one unidentified. Temperatures of about 650°C appear to be necessary. A preparation containing the desired phase, heated to 750°C in evacuated and sealed tubes, undergoes a transition that is not reversed by heating at 600°C for 3 weeks. The difficulties encountered in these experiments suggest a narrow field of stability, the successful determination of which would be of considerable importance to the problem of origin of those djerfisherite-bearing meteorites.

Existence of the mineral is notable in several respects. It is the only sulfide mineral known that contains potassium as a major constituent—or even as a minor element (*5*). The only other alkali sulfide-bearing mineral reported is gerstleyite, a sodium sulfantimonite-sulfarsenite from the borate mines of California (*6*). Thus, the chalcophilic nature of potassium is established in addition to its hitherto lithophilic nature; in meteorites it is the third mineral, in addition to the two recently discovered silicates, merrihueite (*7*) and roedderite, known to contain essential potassium. The presence of native copper in Hvittis (*8*) contrasts with its chalcophilic behavior in these two enstatite chondrites and marks another dissimilarity that many investigations have shown to exist between Hvittis and other meteorites in its class.

Using the abundances of elements in various enstatite chondrites (*9*), I could not correlate the incidence of djerfisherite wth potassium content. Thus, the 1000-ppm K content of St. Marks is less than the 2700-ppm K content of Hvittis, which fact implies the existence of a potassium-containing mineral, perhaps djerfisherite, in Hvittis; however, the 3.3 (weight) percent S in Hvittis is less than the 5.5 percent S in St. Marks. If all of the potassium content of St. Marks were present as djerfisherite, the mineral would constitute about 1 percent of the meteorite—far more than the content observed. Even if one allows for the nonuniform distribution of djerfisherite, it appears that the bulk of the potassium is contained in another mineral phase in the meteorite. No chemical data exist on Kota Kota, but it is interesting to note that this meteorite contains the potassium-magnesium silicate mineral, roedderite, as well as djerfisherite. A possible reaction that could provide potassium sulfide to account for the coexistence of these two minerals is

$$\underset{\text{troilite}}{FeS} + \underset{\text{roedderite}}{K_2Mg_5Si_{12}O_{30}} \rightleftharpoons K_2S + \underset{\text{enstatite}}{5MgSiO_3}$$
$$+ \underset{\text{metal}}{Fe} + \underset{\text{silica}}{7SiO_2} + 1/2O_2$$

The removal of oxygen from the system favors the formation of K_2S.

For all classes of meteorites considered, calculations, based on reactions concerning selected minerals present, show that the enstatite chondrites have the lowest oxygen fugacities governing subsolidus equilibration (10). At 1000°K (the upper limit for formation of djerfisherite, as deduced from the synthesis experiments), $\log_{10}f(O_2)$ (atm) is -30 and reduces to -55 at survival temperatures of 600°K. An equilibrium expression that includes actual phases in the meteorite would be more meaningful than the above reaction in which potassium sulfide is not an observed phase. However, such an expression cannot be written until another copper-bearing mineral is found to coexist with djerfisherite; this association is in fact predicted by the presence of the latter.

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References and Notes

1. For the properties of roedderite see L. Fuchs, C. Frondel, C. Klein, Jr., *Amer. Mineralogist*, in press. The occurrence of roedderite in Kota Kota was communicated to me by R. A. Binns on the basis of work performed with R. Davis at the British Museum.
2. P. Ramdohr, *J. Geophys. Res.* **68**, 2011 (1963).
3. It was thought by some members of the Commission on New Minerals and Mineral Names of the International Mineralogical Association that the chlorine has no place in the structure of a sulfide mineral and that, therefore, its detection here may have resulted from unobserved traces of lawrencite. All grains examined averaged 1 percent chlorine; such consistency suggests the absence of random contamination. Future work on the synthesis of djerfisherite may resolve this objection. In accordance with the recommendation, the chlorine has been tentatively removed from the composition.
4. L. Cambi and L. Szego, *Atti Accad. Lincei* **15**, 599 (1932).
5. M. Fleischer, in *Econ. Geol. 50th Anniv. Vol.* (1955), p. 970.
6. C. Frondel and V. Morgan, *Amer. Mineralogist* **41**, 839 (1956).
7. R. Dodd, R. van Schmus, U. Marvin, *Science* **149**, 972 (1965).
8. See *2*; this observation was confirmed by me on another section of Hvittis.
9. B. Mason, *Geochim. Cosmochim. Acta* **30**, 30 (1966).
10. E. Olsen and L. Fuchs, in preparation.
11. S. J. B. Reed and J. V. P. Long, *Mineral Mag.*, in press. Method outlined by J. V. Smith, Department of Geophysical Sciences, Univ. of Chicago, in prepared notes for users of the microprobe.
12. J. Philibert, in *X-Ray Optics and X-Ray Microanalysis*, H. Pattee, V. Cosslett, A. Engstrom, Eds. (Academic Press, New York, 1963), p. 379.
13. J. V. Smith, *Amer. Mineralogist* **51**, 273 (1966).
14. Work supported by the AEC. The new mineral is named after D. Jerome Fisher, professor emeritus of mineralogy, Univ. of Chicago, and past president of the Mineralogical Society of America and the International Mineralogical Association; the name is approved by the I.M.A. I thank Brian Masan, Edward Henderson, Roy Clarke, Jr. (U.S. National Museum), and Edward Olsen (Field Museum of Natural History) for supplying the meteorites. The electron-probe analyses were made independently by Norbert Stalica of this laboratory and Charles Knowles of the Department of Geophysical Sciences, Univ. of Chicago. Edward Olsen assisted in correcting the data. I thank also Elizabeth Gebert for measuring the x-ray film and George Montet for a critical review.

7 April 1966

Mummified Pleistocene Ostracods in Alaska

Abstract. *Preserved soft parts of ostracod specimens were recovered from beach and lagoon sediments from the Gubik Formation, of Quaternary age, at Barrow, Alaska.*

During study of microfossils obtained from the perennially frozen sediments of the Gubik Formation at Barrow, Alaska, chitinous parts of several ostracods were found preserved inside closed valves. When a closed specimen of *Paracyprideis pseudopunctillata* was pried open, remains of soft parts were found still attached to the dorsal hinge