On the composition of natural delafossite

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Summary. Two new microanalyses of delafossite from Nizhniĭ Tagil (the type locality) and Kimberly, Nevada, confirm the accepted formula $CuFeO_2$.

In September 1965, D. S. Buist, A. M. M. Gadalla, and J. White read a paper before this Society in which they described synthetic experiments on the system Cu–Fe–O, in the course of which they failed to synthesize the compound $CuFeO_2$ and presented evidence for the existence of a compound $Cu_6Fe_3O_7$; they suggested that this compound is identical with natural delafossite, and gave thermogravimetric data for material from Kimberly, Nevada, in support of this conclusion.

All three analyses of delafossite in the literature (Friedel, 1873, type material from the Ekaterinburg (= Sverdlovsk) district; Bohart in Rogers, 1913, from Bisbee, Arizona; and Schaller in Ross, 1925, from Salmon, Idaho) agree in giving a Cu:Fe ratio of 1:1, and Friedel gives full experimental detail supporting a metal:oxygen ratio of 1:1. Nevertheless it seemed possible that the Nevada material might have the composition of Buist, Gadalla, and White's synthetic phase. The X-ray powder patterns had been shown to be very similar, but there was a possibility of small differences, or perhaps a superstructure (it is difficult to get either the natural or the synthetic material quite pure); on the other hand, Soller and Thomson's unit cell (1935) can only accommodate two oxygen atoms, and the density shows that it must hold two metal atoms. Still, as natural delafossite is clearly not a high-temperature phase, often being closely associated with kaolinite, it seemed possible that the natural and synthetic phases might be different, despite similar X-ray powder patterns.

X-ray and synthetic studies, commenced in this laboratory early in 1966, were delayed by pressure of other work, but tend to confirm the results of Wiedersich *et al.* (1968); analyses of two natural specimens had just been completed when their paper was received, and these are now published (table I) as additional evidence in support of the formula $CuFeO_2$ for both natural delafossite and the synthetic phase.

TABLE I. Chemical analyses of delafossite

	1	2	1a	2a	3
Cu	25·8	34·5	42·8	42·6	41·97
Fe	21·8	29·8	36·1	36·7	36·88
O*	12·7	16·7	21·1	20·7	21·15
SiO_2	16·0	6·4‡	—	—	—
Al_2O_3	13·1	5·4	—	—	—
Loss†	[10·6]	[7·2]	—	—	—
	100·0	100·0	[100·0]	[100·0]	100·00

1. B.M. 1914, 42, from Nizhniĭ Tagil.
2. B.M. 1967, 411, from Kimberly, Nevada.

1a. }
2a. } Recalculated after deduction of kaolinite, adsorbed water, and loss.

3. Calculated for $CuFeO_2$.

* The oxygen percentages are derived by subtracting the oxygen deficiency found by titration from the oxygen necessary to form CuO and Fe_2O_3 with the Cu and Fe found.

† Including hydroxyl water of kaolinite (4·7 % in anal. 1, 1·9 % in anal. 2) and adsorbed water (over 3·6 % in anal. 1).

‡ Calculated for kaolinite from the Al_2O_3 found; an X-ray powder photograph showed that the analysed material contains an appreciable amount of clay mineral with a 7 Å basal spacing.

The specimens analysed were B.M. 1914, 42 from Nizhniĭ Tagil, Sverdlovsk, USSR,[1] and B.M. 1967, 411 from Kimberly, Nevada (kindly presented by Dr. D. S. Buist); both were so intimately intergrown with a layer-lattice mineral with a 7 Å basal spacing (definitely identified by X-rays as kaolinite in the Nizhniĭ Tagil material) that flotation in acetylene tetrabromide only effected a partial separation[2] (fig. 1).

A portion of about 20 mg of each concentrate was taken for analysis; it was dissolved in a mixture of 5 ml $M/5$ ICl (in 1:1 HCl) and 5 ml conc.HCl in a stoppered flask; after two days for solution in the cold, the state of oxidation was determined

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[1] This is almost certainly the type locality. Friedel's type specimen (1873) was labelled: Graphite sur une lithomarge blanche de Catherinebourg [Ekaterinburg], Sibérie. Abbé Grandidier, Saint-Pétersbourg, 1820. This could refer to any of the mines in the Sverdlovsk region, but it is clear from Rose (1837) that the Nizhniĭ Tagil mine, opened for copper working in 1812, is the only mine in the region where copper minerals occur associated with a white clay: Die Erze liegen auch in Nischne-Tagilsk nesterweise beisammen in einem Thon, der meistens weiss . . . ist. The specimen 1914, 42, purchased from F. Krantz, was labelled: Dokotschajewit. Nischne Tagilsk, Ural. Dokotschajewit was, according to Dr. Busz (priv. comm. to Dr. L. J. Spencer, 1926), an unpublished name of Fersman's for a supposed new mineral.

[2] This separation, kindly undertaken by Mr. R. F. Symes, removed a great deal of clay, but after several repetitions the Nizhniĭ Tagil material still contained 40 % of kaolinite.

by titration of the liberated iodine with $M/200$ KIO_3 using a globule of carbon tetrachloride as indicator. After titration, the solution was evaporated with HF and HCl to expel silica, then twice with HCl, and made up to 200 ml; copper was determined on 5 ml colorimetrically with sodium diethyldithiocarbonate, extracting the complex into carbon tetrachloride, and iron on 5 ml with sulphosalicylic acid, adding an appropriate amount of copper to the standard iron solution;[1] aluminium was determined on 100 ml of the solution, which was evaporated, the bulk of the iron removed by isopropyl ether extraction from $7M$ HCl, and copper and any remaining iron complexed by addition of cyanide and hydroxylamine hydrochloride to the ammoniacal solution, to which citrate had been added to keep the aluminium in solution; the aluminium was then precipitated as 8-hydroxyquinolate. For the Kimberly material, silica was calculated from the Al_2O_3 found, and water taken by difference. More of the Nizhniĭ Tagil material was available, and a second portion, also about 20 mg, was gently ignited in the hope of determining water, but the result was gravely low and it appears that oxidation of the delafossite sets in before the kaolinite is wholly dehydrated. The ignited material was dissolved in conc. HCl and the silica dehydrated by evaporation with $HClO_4$ to fumes, filtered off with a King microfilter and weighed. In the filtrate, copper was determined with salicylaldoxime.

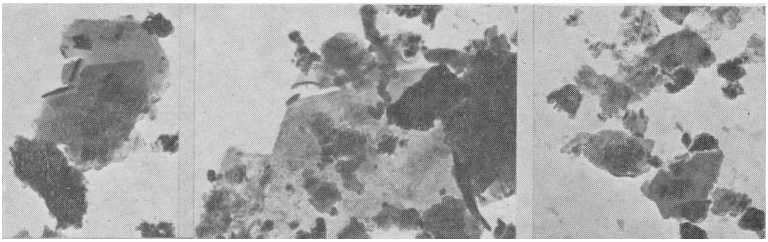

FIG. 1. Electron micrographs showing the close association of delafossite and kaolinite in a specimen from Nizhniĭ Tagil (B.M. 1914, 42); left and centre micrographs, ×12 000, right ×9 000.

References

BUIST (D. S.), GADALLA (A. M. M.), and WHITE (J.), 1966. Min. Mag., vol. 35, p. 731.
FRIEDEL (C.), 1873. Compt. Rend. Acad. Sci. Paris, vol. 77, p. 211.
ROGERS (A. F.), 1913. (G. S. Bohart, anal.). Amer. Journ. Sci., ser. 4, vol. 35, p. 290.
ROSE (G.), 1837. Reise nach dem Ural . . ., vol. 1, pp. 262–274, 307–318, 400–419.
ROSS (C. S.), 1925. Bull. U.S. Geol. Surv., no. 774, p. 23.
SOLLER (W.) and THOMPSON (A. J.), 1935. Phys. Rev., vol. 47, p. 644.
WIEDERSICH (H.), SAVAGE (J. W.), MUIR (A. H., *Jr.*), and SWARTHOUT (D. G.), 1968 Min. Mag., vol. 36, p. 643.

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[1] This precaution was later found unnecessary; although an amount of copper equal to the iron changes the tint of the sulphosalicylic complex noticeably, there is no measurable change in the absorption at λ 425 mμ; it was also noted that citrate does not interfere with the determination of iron by sulphosalicylic acid.