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THE NEW MINERAL CUPROSPINEL ($CuFe_2O_4$) AND OTHER SPINELS FROM AN OXIDIZED ORE DUMP AT BAIE VERTE, NEWFOUNDLAND **

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During the course of a mineralogical examination of heavily oxidized material from an ore dump on the property of Consolidated Rambler Mines Limited near Baie Verte, Newfoundland, an assemblage of copper-bearing spinels intergrown with hematite was found in a few of the fragments. Subsequent inquiry revealed that the material on the dump had originally consisted of copper-zinc ore that had lain exposed to the environment for some years, and had ignited spontaneously and smouldered at intervals during this period.

The discovery of a spinel mineral near $CuFe_2O_4$ in composition which had not previously been reported from a natural environment, led to a new mineral name, cuprospinel, being proposed for it; this name was subsequently accepted by the I.M.A. Commission on New Minerals and Mineral Names.

The cuprospinel, and other spinels were found in several specimens from the ore dump, in close association with hematite and orthopyroxene. The spinels do not exhibit any discernible crystal forms and occur chiefly as irregular grains up to about 0.1 mm in diameter; occasionally they form lamellar intergrowths with hematite. Primary sulphides were not observed in the fragments containing the copper spinels but pyrite, chalcopyrite, sphalerite, and pyrrhotite are present in other fragments from the same dump.

Synthetic $CuFe_2O_4$

$CuFe_2O_4$ was apparently first synthesized by Weil *et al.* (1950), who obtained both the tetragonal and cubic polymorphs and suggested that

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both modifications are close to being inverse ferrites (spinels). The crystal structure of the tetragonal phase was determined by Prince & Treuting (1956), who confirmed that it is a tetragonally-distorted inverse spinel, with iron in the tetrahedral *A* sites and iron and copper in the octahedral *B* sites.

Stability relations, investigated by Yund & Kullerud (1964), Gadalla & White (1966), Buist *et al.* (1966) and Schaefer *et al.* (1970) have shown that tetragonal $CuFe_2O_4$ is a stable phase in the Cu-Fe-O system. The phase inverts to the cubic spinel at between 700°C and 800°C and this cubic phase can be quenched to room temperature. $CuFe_2O_4$ and hematite form a stable assemblage in the presence of oxygen.

Composition of cuprospinel

The cuprospinel and other spinels were analyzed with an M.A.C. electron microprobe, using synthetic oxide and metal standards, and making corrections by means of Rucklidge's computer program (Rucklidge 1967). The results of these analyses and the recalculations to atomic proportions, based on the spinel formula, are shown in Table 1. The values

TABLE 1. ANALYSES OF CUPROSPINEL AND OTHER SPINELS

	1 (Cuprospinel)	2	3	4
Fe_2O_3*	65.7	67.1	67.4	65.4
FeO	1.7	2.0	1.8	0.3
CuO	27.8	19.2	15.2	13.9
MgO	1.8	1.2	4.8	8.2
ZnO	0.7	3.0	3.4	2.5
CoO	0.6	4.4	3.4	1.4
MnO	0.2	1.7	1.0	1.6
Al_2O_3	2.6	—	1.5	4.6
	101.1	98.6	98.5	97.9
Metal atomic proportions				
Fe^{3+}	1.89	2.00	1.93	1.80
Al	0.11	—	0.07	0.20
Cu	0.80	0.57	0.44	0.38
Mg	0.10	0.07	0.27	0.45
Fe^{2+}	0.05	0.07	0.06	0.01
Co	0.02	0.14	0.10	0.04
Zn	0.02	0.09	0.10	0.07
Mn	0.01	0.06	0.03	0.05

* Iron was determined as Fe, and was recalculated into the two oxides in the proportions necessary to satisfy the spinel formula.

shown in Table 1 were obtained by recalculating the total atomic proportions to three metal atoms and by proportionating the Fe^{3+} and Fe^{2+} to give a total of two trivalent cations and one divalent cation per formula.

The analyses show that there is extensive solid solution among these spinels. The cuprospinel comes closest to $CuFe_2O_4$, but the other analyses show progressively greater substitution of Mg for Cu,, giving a formula that approximates (Mg, Cu) $(Fe,Al)_2O_4$.

X-ray diffraction analysis

Cuprospinel gives an *x*-ray powder diffraction pattern corresponding to that of a cubic spinel with $a_0 = 8.369$Å. This is slightly smaller than the reported value of 8.383Å for the cubic-cell edge of $CuFe_2O_4$ (Prince & Treuting 1956), a difference that can be largely accounted for by the substitution of some of the Fe^{3+} by Al, and of Cu by Mg.

The *x*-ray powder diffraction data, using the indexing given by Prince & Treuting, are shown in Table 2. The data were obtained from a 57.3 mm diameter Debye-Scherrer film, corrected for shrinkage. Intensities were estimated visually. The pattern was not a good one due to the difficulty

TABLE 2. X-RAY DIFFRACTION DATA FOR CUPROSPINEL AND CUBIC $CuFe_2O_4$

hkl	Cuprospinel *I*(est.)	Cuprospinel *d*(meas.)	Cubic $CuFe_2O_4$* *d*(meas.)
111	3	4.79	4.83
220	5	2.96	2.96
—**	1	2.694	—
311	10	2.517	2.52
222	1	2.417	2.41
400	3	2.100	2.091
331	—	—	1.920
422	—	—	1.709
—**	2	1.701	—
511	4	1.613	1.612
333	—	—	—
440	6	1.479	1.481
531	—	—	1.416
?	2	1.272	—
444	1	1.204	1.210
?	3	1.087	—
?	2	0.964	—

* From Prince & Treuting (1956).
** Hematite diffraction lines.

of obtaining sufficient material relatively free of contamination by hematite and therefore the measurements were not of the highest accuracy. Nevertheless, the diffraction pattern was sufficiently good to characterize the mineral beyond doubt. Special effort was devoted to determining the presence of the low-temperature tetragonal phase but it could not be detected.

Optical and physical properties

Cuprospinel is black and opaque, with a black streak ; the high-magnesium spinels are more translucent, with a grey streak. Under the ore microscope, cuprospinel is grey, isotropic and similar to magnetite, but without the latter's pinkish tint. Its reflectance, taken at the four standard wavelengths and using a calibrated silicon carbide standard issued by the I.M.A. Commission on Ore Microscopy, is shown in Table 3. This table, which also includes data for magnesioferrite and magnetite, shows that the cuprospinel and magnesioferrite have the same kind of reflectance dispersion, *i.e.* the reflectance decreases toward the red end of the spectrum, in contrast to that of magnetite, which rises slightly toward the red end. This probably serves to explain the observed colour differences between magnetite, on the one hand, and cuprospinel and magnesioferrite on the other. The other spinels associated with the cuprospinel have lower reflectances than the cuprospinel.

The microhardness, determined by means of a Leitz Durimet microhardness apparatus using a 100 g load, is somewhat higher than that of magnesioferrite and much higher than that of magnetite (Table 3).

TABLE 3. REFLECTANCE AND MICROHARDNESS OF CUPROSPINEL

Reflectance (%)				
	Wavelength (nm)	Cuprospinel	Magnesioferrite *	Magnetite *
	470	22.7	18.9	19.7
	546	21.7	18.5	19.8
	589	21.0	18.3	20.0
	650	20.0	17.5	20.0
Microhardness (VHN_{100})		920-1081 (Av. 985)	627-910	493-607

* Taken from "International Tables for the Microscopic Determination of Crystalline Substances Absorbing in Visible Light", published by the Commission on Ore Microscopy of the International Mineralogical Association (1970).

DISCUSSION

The oxide assemblage consisting of cuprospinel, hematite, and the other Mg-Cu spinels was probably formed from previously-existing sulphides during the intense oxidation to which the ore dump was subjected during smouldering periods that roasted the sulphides. The high MgO content of some of the spinels indicates that the roasting reaction apparently also involved silicates in the ore, and this suggests that relatively high temperatures prevailed during the reactive period.

It is, perhaps, somewhat surprising that the cubic form of the spinel was retained rather than being converted to the tetragonal polymorph stable at lower temperature, particularly since cubic $CuFe_2O_4$ can only be quenched with difficulty in the laboratory (Yund & Kullerud 1964). The apparent absence of the tetragonal phase suggests that the cubic structure is probably stabilized by one or more of the other elements, particularly magnesium, present in the naturally-occurring spinels.

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