Delafossite and the system Cu–Fe–O

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Summary. An investigation of the system Cu–Fe–O has established the existence of a phase near $3Cu_2O.Fe_3O_4$ and the non-existence of $Cu_2O.Fe_2O_3$ in the system over the range of oxygen pressures investigated.

The X-ray diffraction patterns obtained from four samples of natural delafossite have been found to be similar to that obtained from a synthetic sample of the $3Cu_2O.Fe_3O_4$ phase. It has also been shown that, when heated under equilibrium conditions in the thermobalance in air, a sample of natural delafossite and the synthetic $3Cu_2O.Fe_3O_4$ behaved similarly.

FRIEDEL (1873) was the first to report the existence of a mineral delafossite to which he assigned the formula $Cu_2O.Fe_2O_3$. Subsequently, Rogers (1913, 1922) identified delafossite in copper ores from Bisbee, Arizona, and Kimberley, Nevada. He found that it was soluble in sulphuric acid and from the composition of the leachings from the former ore concluded that Cu, Fe, and O occurred in the delafossite in the proportions $1:1:2$ approximately, in agreement with the formula proposed by Friedel. Later Pabst (1946) showed that the X-ray pattern of delafossite was the same as that of a synthetic material prepared by Soller and Thompson (1935) and considered to be $Cu_2O.Fe_2O_3$. A recent investigation of the system Cu–Fe–O by two of the present authors (A.M.M.G. and J.W.), which will be published in full elsewhere, has, however, shown that a phase of the composition $Cu_2O.Fe_2O_3$ does not exist in this system. A new phase whose composition range includes the composition $3Cu_2O.Fe_3O_4$ and the X-ray pattern of which was closely similar to that reported for delafossite was, however, found to exist. A re-examination of natural delafossite, therefore, seemed desirable and requests were sent to Prof. A. Pabst and to Mr. P. G. Embrey of the British Museum (Natural History), who kindly supplied samples.

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Phase relationships in the system Cu–Fe–O *in air* (0·21 *atm oxygen*)

This system has been investigated at 0·21, 0·6, and 1·0 atm oxygen pressure. In the present paper only the results at 0·21 atm will be presented. For a full account of the experimental methods employed, see Gadalla, Ford, and White, 1963; Gadalla and White, 1964. The technique employed was based on the use of a thermobalance to follow weight changes in selected mixtures of CuO and Fe_2O_3 at equilibrium as a function of temperature at constant partial pressure of oxygen. All the mixtures were pre-reacted in the fully oxidized condition to form $CuO.Fe_2O_3$ before use, by repeated firing at low temperatures in air with intermediate grinding. Hence the weight-loss determined on the thermobalance at any temperature could be assumed to represent oxygen loss from the sample; on the ternary composition triangle, the composition reached by any mixture at any temperature was then defined uniquely by the oxygen/metal ratio at that temperature and the Cu/Fe ratio in the mixture.

The problem of finding a crucible material that would not react with the melts proved to be a serious one and was not completely solved. All the melts were extremely corrosive to oxide crucibles while platinum crucibles were found to extract copper from them the more seriously the lower the oxygen pressure (see Gadalla, Ford, and White, 1963). As a compromise, alumina crucibles lined with platinum foil were used on the principle that less copper would be dissolved by the foil than by a crucible. With most mixtures, however, it was not possible to extend the determinations much above the temperature of initial melt formation unless the quantity of liquid formed was small.

Mixtures of pre-heated CuO and Fe_2O_3 were heated to constant weight at progressively increasing temperatures on the thermobalance. From the equilibrium weight changes observed, the atomic ratio O/(Cu+Fe) was calculated and plotted against temperature to give 'dissociation curves' of the various mixtures.

From these dissociation curves an isobaric ternary diagram was constructed (fig. 1). There is some difficulty in selecting suitable components for this diagram, because the range in atomic proportions of oxygen is much greater at the copper-rich end of the series (Cu_2O 33 % O, CuO 50 % O) than at the iron-rich end (Fe_3O_4 57 % O, Fe_2O_3 60 % O); Cu_2O, Fe_3O_4, and O were finally chosen as components, although this choice leads to negative oxygen percentages for a few points.

With starting mixtures containing more than 50 % Fe$_2$O$_3$, progressive loss of oxygen took place with rising temperature and in this region of the diagram the isotherms (which are also tie-lines) radiate from the Fe$_2$O$_3$ corner to the boundary CuO.Fe$_2$O$_3$–a, where a is the limiting composition of magnetite in the system Fe–O in air at 1388° C.
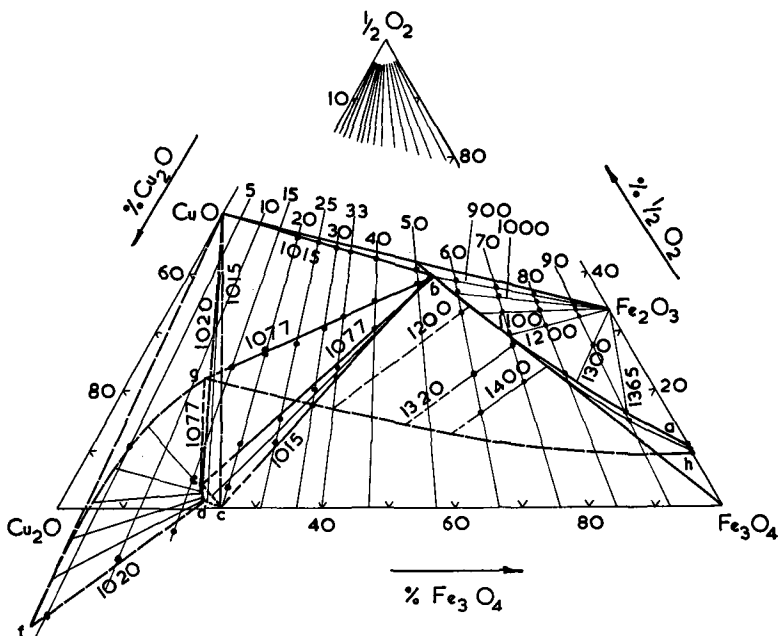
FIG. 1. Isobaric phase diagram of the region CuO–Fe$_2$O$_3$–Fe$_3$O$_4$–Cu$_2$O of the system Cu$_2$O–Fe$_3$O$_4$–$\frac{1}{2}$O$_2$ in air (molar percentage basis). The thin straight lines diverging from the oxygen corner are the dissociation paths and the numbers written above the CuO–Fe$_2$O$_3$ edge represent the initial Fe$_2$O$_3$ contents of the mixtures. Heavier straight lines are isotherms at the temperatures indicated. *fgh* is part of the isobar corresponding to 0·21 atm oxygen on the liquidus surface.

These isotherms change direction abruptly on crossing the boundary. Another abrupt change of direction occurs, as shown by the isotherms for 1300° C and 1400° C, when they cross the line CuO.Fe$_2$O$_3$–Fe$_3$O$_4$. These features show that a continuous series of solid solutions extends from CuO.Fe$_2$O$_3$ to the range occupied by the magnetite phase on the Fe–O edge of the diagram.

With mixtures containing less than 50 % Fe$_2$O$_3$, after a slight progressive oxygen loss at 1015°, an isothermal loss occurred at this temperature corresponding to the tie triangle CuO–b–c. At this

temperature CuO reacts with spinel solid solution of composition b with loss of oxygen, to form the solid phase c, which has a composition approximating to $3Cu_2O.Fe_3O_4$. It is of interest that Bergestein and Cervinka (1961) observed an endothermic arrest at 1015° C on the d.t.a. curve in air of previously prepared $CuO.Fe_2O_3$ and found that the transition involved was a reversible one.

Mixtures containing between 20 % and 50 % Fe_2O_3 then gained oxygen progressively up to 1077° C. This change was accompanied by a progressive change in the composition of the solid phase c along the boundary ce, while the composition of the spinel remained almost unchanged. At 1077° C an isothermal gain of oxygen occurred with partial melting corresponding to the tie-triangle b–e–g. At this temperature liquid of composition g coexists with the solid phases b and e.

Mixtures containing up to 17 % Fe_2O_3 lost oxygen progressively from 1015° C to 1020° C, while the composition of the solid phase c moved along the boundary cd. At 1020° C an isothermal loss occurred with partial melting forming liquid of composition f and corresponding to the tie triangle CuO–d–f. Mixtures whose dissociation paths crossed fd then gained oxygen progressively until melting was complete on liquidus isobar fg, or if their paths crossed eg up to 1077° C, when another isothermal oxygen pick-up occurred corresponding to the tie triangle b–e–g mentioned above. A progressive loss then occurred until melting was complete on the liquidus isobar gh.

Fig. 2 shows the temperature-composition diagram in air constructed by plotting the temperatures at which the dissociation curves crossed the phase boundaries in fig. 1 against the compositions of the mixtures. The horizontal lines at 1015° C, 1020° C, and 1077° C correspond to the tie triangles at these temperatures in fig. 1. The short horizontal line at 1026° C on the left of the diagram corresponds to the dissociation of solid CuO to Cu_2O, which was shown by Gadalla, Ford, and White (1963) to occur at this temperature in air.

Comparison of the phase $3Cu_2O.Fe_3O_4$ with natural delafossite

Four samples of delafossite-bearing ore were available: Spherules of delafossite from Alpha mine, Kimberley, Nevada, supplied by Prof. Pabst (M–334); massive delafossite ore containing native copper, from Bisbee, Arizona, supplied by Prof. Pabst (518–8); flaky delafossite ore from Hoatson shaft, C. & A., Bisbee, supplied by Prof. Pabst; and spherulitic delafossite from Cornwall, supplied by the British Museum (Nat. Hist.) (B.M. 89141).
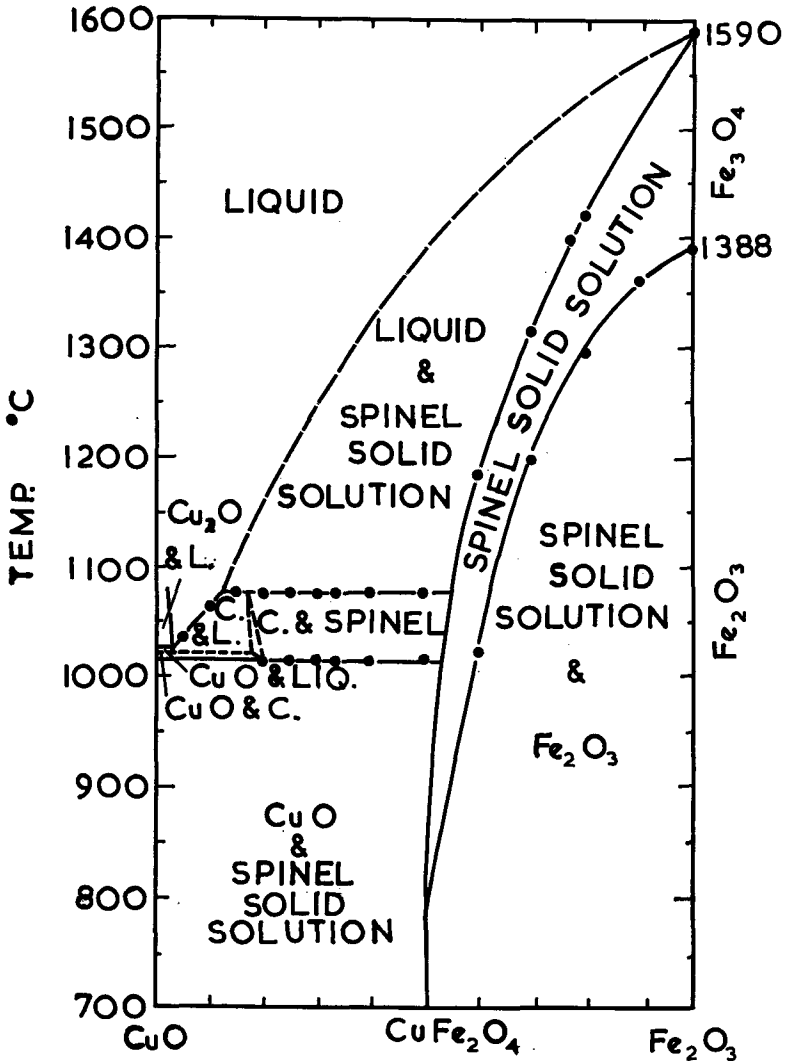
FIG. 2. Temperature–composition diagram of the partial system Cu_2O–Fe_3O_4–$\frac{1}{2}O_2$ at 0·21 atm oxygen pressure. Compositions plotted on the molar basis.

For comparison with these samples the $3Cu_2O.Fe_3O_4$ phase was prepared from a mixture containing 18 mol % Fe_2O_3 and 82 mol % CuO by repeated firing in air with intermediate grinding. This composition was chosen, rather than the stoicheiometric composition, since it would

be a single solid phase at the firing temperature (see fig. 2). After each firing the sample was cooled slowly to 1025° C, where it would still be single phase, and air quenched by withdrawing it from the furnace. The completion of reaction was checked by the microscope and by X-rays.

Microscopic examination by reflected light. Specimens were prepared for polishing by impregnating with *Araldite*; final polishing was carried out using γ-Al_2O_3 on a suede nylon cloth with water as lubricant. It was found that 1:1 HCl was a positive etchant for the mineral as well as for the synthetic phase, causing browning of the surface, while HNO_3, KCN, $FeCl_3$, KOH, and $HgCl_2$ were negative.

In section the Kimberley ore was observed to consist of concentric zones. Usually the core was dense and massive, while the outer zones were porous and consisted of elongated crystals of mainly irregular outlines (fig. 3).

The massive Bisbee ore was coated with a silicate gangue. A cut surface revealed large internal pores, consistent with the evolution of gas during crystallization (see fig. 1), and sporadic grains of metallic copper. In section two major constituents were observed, a dark grey phase identified as goethite and a yellowish-grey mineral identified as delafossite. Other minerals observed in the section were native copper, needles of an unidentified silicate, and traces of chalcocite (fig. 4). In section the flaky ore from Bisbee appeared as plates and thin laminae, the delafossite being associated with native copper, a greyish phase (identified as the spinel detected by X-rays), and traces of covelline.

The Cornish ore consisted of radiating spherules of delafossite (fig. 5).

Microhardness. The average of twelve measurements on the synthetic material gave a Vickers hardness number of 167. Reliable hardness values could not be obtained from the natural ores owing to the small crystal size and to the presence of contaminating phases.

Reflectivity measurements were made in white light using a photo-electric cell, using a clean, well-polished pyrite specimen as a standard ($R = 54.4 \%$). The average of at least twelve determinations was taken for each specimen:

Spherules from Kimberley, Nevada,	R 22·8 %
Massive delafossite from Bisbee, Arizona,	22·2
Spherules from Cornwall,	22·8
Synthetic $3Cu_2O.Fe_3O_4$,	22·8

No measurements could be made on the flaky delafossite from Bisbee, as the specimen was too small.

Folinsbee (1949) gives R 22·2 % and Schouten (1962) R 21–25 % for delafossite of unspecified origin in white light.

X-ray powder patterns were determined using Co-radiation with an iron filter (table I). No differences were observed between the delafossite in all four natural ores and the synthetic $3Cu_2O.Fe_3O_4$.
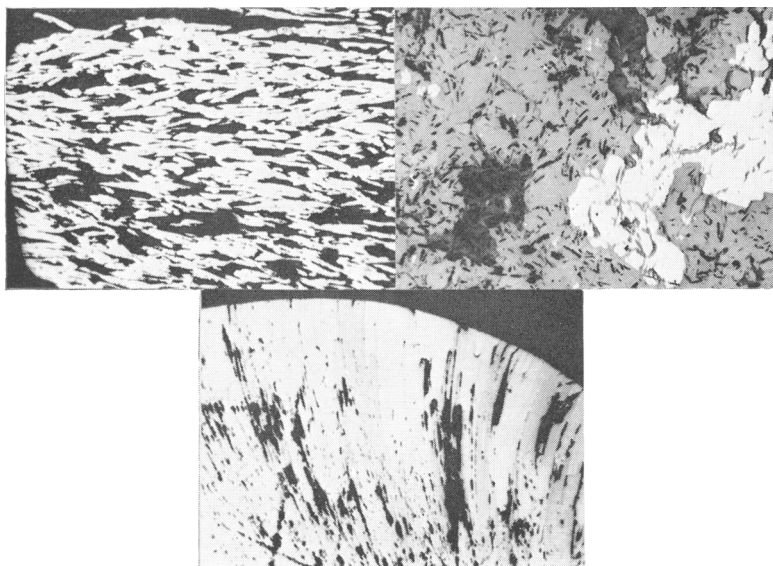
FIGS. 3–5: FIG. 3 (top left). Polished section of a spherule of delafossite, Kimberley, Nevada, showing elongate crystals of delafossite (white) and pores (black). Reflected light, ×100, unetched. FIG. 4 (top right). Polished section of the massive Bisbee ore, showing goethite (dark grey), delafossite (light grey), native copper (large bright areas), and chalcocite (small whitish areas). The black needles are an unidentified silicate. Reflected light, ×100, unetched. FIG. 5 (bottom). Polished section of part of a spherule of the Cornish ore, showing radiating intergrowths of delafossite (white and light grey) and pores (black). Reflected light, ×130, etched 1:1 HCl 15 secs.

The d-spacings of the spinel phase in the flakey Bisbee ore were intermediate between those of $CuO.Fe_2O_3$ and Fe_3O_4 and slightly larger than those of the spinel formed when a mixture consisting of 70 mol % Fe_2O_3 and 30 mol % CuO was heated in air at 1200° C, showing that the copper oxide content was slightly higher than in the latter.

Tests with thermobalance. To ascertain whether natural delafossite after it had been completely oxidized would give a dissociation curve similar to that of the synthetic mixture, a sample of the spherulitic

Kimberley ore was washed in a stream of water to remove the adhering clay. The finely ground material was then heated to constant weight in air at 1010° C when it picked up oxygen to form CuO and $CuO.Fe_2O_3$. The oxidized sample was then heated in the thermobalance in air to

TABLE I. Comparison of X-ray diffraction patterns of natural delafossite and synthetic $3Cu_2O.Fe_3O_4$

Spherulitic ore, Kimberley Nevada		Massive ore, Bisbee, Arizona		Flaky ore, Bisbee, Arizona		Spherulitic ore, Cornwall		Synthetic $3Cu_2O.Fe_3O_4$	
I	d	I	d	I	d	I	d	I	d
		w	4·97†Å						
		s	4·20†						
		w	3·37†						
				m	3·04‡Å				
m	2·89Å	s	2·86	vs	2·88	s	2·86Å	m	2·89Å
		m	2·69†						
		m	2·59†						
s	2·51	vs	2·51	vs	2·52‡	vs	2·55	s	2·51
		m	2·44†						
w	2·24	s	2·239†	vw	2·239			w	2·24
		vw	2·189†						
		vw	2·089*	s	2·098*				
vw	1·91	vvw	1·909	w	1·910			vw	1·91
		vvw	1·804	w	1·810				
		w	1·717†						
		vvw	1·692†						
m	1·667	m	1·660	m	1·661‡			m	1·667
		vvw	1·604†						
		w	1·562†						
m	1·520	s	1·514	s	1·517	s	1·519	m	1·520
		vvw	1·454†						
m	1·439	m	1·432	s	1·431	vvw	1·431	m	1·439
m	1·342	m	1·339	m	1·336	w	1·336	m	1·342
w	1·300	m	1·296	vvw	1·297	vvw	1·308	w	1·300
w	1·258	vvw	1·254	vvw	1·280*			w	1·258
w	1·125	vvw	1·118					w	1·125
				w	1·091*				
w	1·040	w	1·040	m	1·042	w	1·037	w	1·040
w	0·988	w	0·985	w	0·985	vvw	0·989	w	0·988
w	0·970	vvw	0·967					w	0·970
vw	0·954	vvw	0·954	vw	0·953			vw	0·954

* lines of metallic copper   † lines of goethite   ‡ lines of spinel solid solution. Other spacings attributed to $3Cu_2O.Fe_3O_4$.

constant weight at progressively increasing temperatures. The dissociation curve obtained is shown in fig. 6 where it is compared with the

curve obtained with a synthetic mixture containing 20 % Fe_2O_3 : 80 % CuO. The deviation between the two curves is to be attributed to the sluggishness of the reaction to form $3Cu_2O.Fe_3O_4$. The curve for the
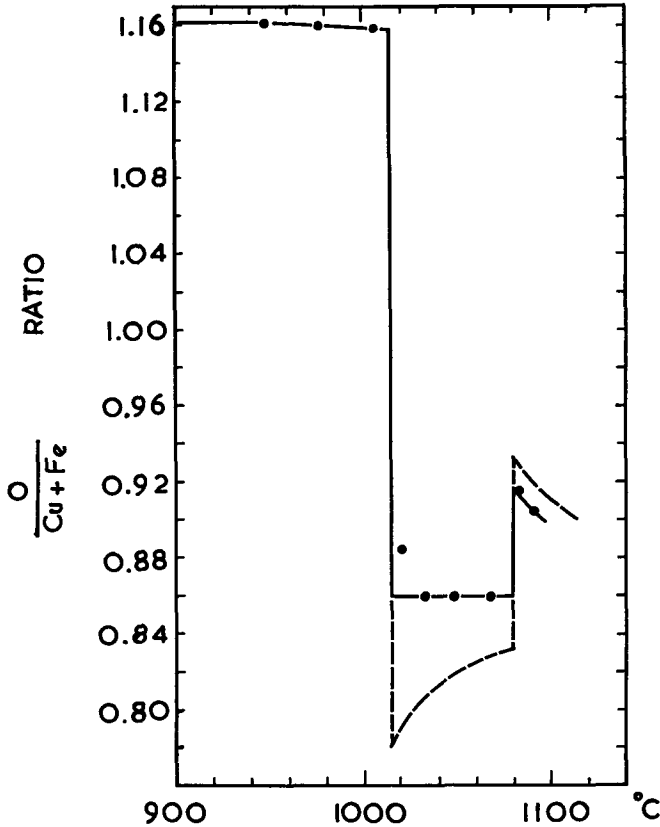

FIG. 6. Dissociation curves in air of a fully oxidized sample of purified spherules of delafossite from Kimberley, Nevada (solid line), and of a synthetic mixture of CuO and $CuO.Fe_2O_3$ containing 20 % Fe_2O_3 and 80 % CuO (dashed line).

synthetic mixture in the range 1015–1040° C was determined by repeatedly quenching the specimen, grinding, and reheating rapidly to the same temperature. The quantity of natural ore available was too small to permit this to be done.

A sample of the massive Bisbee ore was also tested by heating in the thermobalance after separation of the native copper and was found to

lose weight due to dehydration of the goethite. No further work was, therefore, carried out on it. The samples of the flaky Bisbee ore and the Cornish ore were too small to be examined by means of the thermo-balance.

Conclusions

An investigation of the system Cu–Fe–O in air and in 0·6 and 1·0 atm oxygen pressure[1] has established the existence of the compound $3Cu_2O.Fe_3O_4$ and the non-existence of $Cu_2O.Fe_2O_3$ in the system, and has shown that $CuO.Fe_2O_3$ and magnetite form a continuous series of spinel solid solutions. The non-existence of $Cu_2O.Fe_2O_3$ at low oxygen pressures has also been demonstrated by heating a mixture of CuO and Fe_2O_3 in the molecular proportions 2:1 at 1000° C in high-purity argon, when X-ray examination showed the presence of a spinel phase and $3Cu_2O.Fe_3O_4$, and not a single phase as would have been expected if $Cu_2O.Fe_2O_3$ had existed.

The solid phases compatible with $3Cu_2O.Fe_3O_4$ in the system at appropriate temperatures and oxygen pressures are cuprite, tenorite, the spinel solid solutions, and (probably) metallic copper. These conclusions are at variance with the solid state phase diagram proposed by Yund and Kullerud (1961), which attributes the composition $Cu_2O.Fe_2O_3$ to delafossite and shows that it is compatible with hematite, no solid solubility between $CuO.Fe_2O_3$ and magnetite being indicated.

The stability relationships established also show that when $CuO.Fe_2O_3$ is heated in air above 1077° C the products will be a spinel solid solution and a liquid phase, which on cooling will precipitate $3Cu_2O.Fe_3O_4$ with loss of oxygen, before complete re-oxidation to $CuO.Fe_2O_3$ can occur below 1015° C. This finding suggests that the phase identified by Soller and Thompson (1935), Kushima and Amanuma (1955), and Bergestein and Cervinka (1961), in mixtures of $CuO.Fe_2O_3$ and CuO that had been heated above 1100° C in air, was $3Cu_2O.Fe_3O_4$ and not $Cu_2O.Fe_2O_3$ as reported by them.

The X-ray diffraction patterns obtained from four samples of natural delafossite have been shown to be identical with that obtained from a synthetic sample of the $3Cu_2O.Fe_3O_4$ phase. It has also been shown that, when heated under equilibrium conditions in the thermobalance in air, a sample of natural delafossite and the synthetic $3Cu_2O.Fe_3O_4$ behaved similarly. The narrow temperature range of stability of

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[1] At 1·0 atm. oxygen pressure melting intervened before dissociation to $3Cu_2O.Fe_3O_4$ had occurred.

$3Cu_2O.Fe_3O_4$ in air (and also at the other oxygen pressures investigated) may account for the relative rarity of delafossite in oxidized copper ores.

In view of the discrepancy between the present results and the composition proposed for delafossite on the basis of chemical analyses of the natural mineral, further investigation of the constitution of this mineral would appear to be desirable.

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