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STABLE MINERAL ASSEMBLAGES OF ANHYDROUS COPPER AND IRON OXIDES

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ABSTRACT

The equilibrium assemblages in the system Cu-Fe-O have been determined at 800° C. and below. Ternary phases are delafossite ($CuFeO_2$) and copper ferrite ($CuFe_2O_4$). Neither cuprite nor tenorite is stable with magnetite or hematite at any temperature. Copper and hematite together are stable only below 675°±25° C. Natural mineral assemblages are briefly discussed in the light of the experimental data.

The free energy of formation of delafossite has been calculated at 675° and 25° C. with the aid of the experimentally determined phase relations. The values are -83 ± 8 kcal/mole and -110 ± 6 kcal/mole, respectively.

INTRODUCTION

The subsolidus phase relations in the binary systems Cu-Fe, Cu-O, and Fe-O are characterized by phases stable from 25° to above 1000° C. Only wüstite ("FeO") and possibly cuprite (Cu_2O) are exceptions. Wüstite is not stable below about 560° C., and cuprite was reported to be unstable below about 375° C. (Vogel and Pocher, 1929). However, recent studies of copper oxidation report the formation of cuprite as low as 150° C. (Cathcart *et al.*, 1962), and it has been precipitated from aqueous solutions at 25° C. (Delhez, 1960). Some of the oxides are reported to be nonstoichiometric at high temperature, but only wüstite has a variation of more than 1 per cent in its metal/oxygen ratio below 900° C. For a more comprehensive summary of these relations see Hansen and Anderko (1958).

The ternary phases in the system Cu-Fe-O are copper ferrite ($CuFe_2O_4$) and delafossite ($CuFeO_2$). A reversible transformation in $CuFe_2O_4$ from isometric to tetragonal at 760° C. on slow cooling was reported by Weil *et al.* (1950); however, the transformation has been reported as low as 360° C. (Ohnijhi *et al.*, 1959) and as high as 970° C. (Bergstein and Cervinka, 1961). $CuFe_2O_4$ develops a defect structure above 900° C. as a result of loss of oxygen (Bergstein and Cervinka, 1961). The nonstoichiometry of $CuFe_2O_4$ may explain at least in part the reported variation in its transformation temperature. Powder *x*-ray diffraction data for tetragonal $CuFe_2O_4$ and $CuFeO_2$ (delafossite) are given by Weil *et al.* (1950) and Sollor and Thompson (1935), respectively.

In this investigation the phases CuO and Fe_2O_3 were synthesized by passing commercial grade oxygen over the metals enclosed in a silica-glass tube and heated at 900° C. for 20 to 30 hours with one or more regrindings during this period to ensure complete oxidation. The oxides Cu_2O and Fe_3O_4 were prepared by reacting the metals with CuO and Fe_2O_3, respectively, in sealed, evacuated silica-glass tubes at 900° C. All preparations were examined both by *x*-ray powder diffraction and reflected light microscopy for homogeneity and to identify the phases. Bulk compositions in the ternary were prepared from mixtures of the binary oxides and the metals, sealed in evacuated silica-glass tubes, and heated. For a discussion of this method see Kullerud and Yoder (1959). The copper and iron used for this study were each 99.99 weight per cent pure. Reported temperatures are believed to be correct to within ±5° C.

EXPERIMENTAL RESULTS

The stability of Cu_2O was investigated by heating sealed silica-glass tubes containing synthetic Cu_2O at 400°, 350° and 200° C. for 315 days. Careful microscopic examination of polished sections revealed no change in any of the samples. More positive evidence of the stability of Cu_2O at low temperature is afforded by the formation of up to 10 per cent Cu_2O from Cu and CuO at 200° C. after 315 days. These observations along with the numerous studies of copper oxidation and the thermal

TABLE 1. RESULTS OF EXPERIMENTS AT 800° C.

Reactants	Composition, weight per cent[1]		Heating period, days	Condensed phases[2]
	Fe	Cu		
$Cu_2O+Fe_2O_3$	36.89	41.97	26	$CuFeO_2+Cu$ (1%)[3]
$CuO+Fe_2O_3$	46.69	26.56	26	$CuFe_2O_4+CuO$ (1%)[3]
$CuO+Fe$	50	40	13	$Cu+Fe+$"FeO"
$CuO+Fe$	29	56.7	13	$Cu+CuFeO_2+Fe_3O_4$
$CuO+Fe$	12	70.3	13	$CuO+Cu_2O+CuFeO_2$
$CuFe_2O_4+Fe$	49	25.3	13	$CuFeO_2+Fe_2O_3+CuFe_2O_4$
$Fe+Cu+$excess O_2[4]	Fe:Cu=2:3		7	$CuO+CuFe_2O_4$
Fe_3O_4+CuO	60	13.7	11	$Fe_3O_4+CuFeO_2+Fe_2O_3$
Fe_3O_4+CuO	48	26.9	11	$Fe_2O_3+CuFeO_2+CuFe_2O_4$
Fe_3O_4+CuO	38	37.9	11	$CuO+CuFeO_2+CuFe_2O_4$

[1] Remainder is oxygen.

[2] $CuFe_2O_4$ was isometric in all of these preparations.

[3] These preparations were reground after 3 days to promote reaction. Traces of Cu and CuO probably resulted from loss during regrinding.

[4] Oxygen passed over Cu and Fe in an open tube.

chemical data (Coughlin, 1954) demonstrate that cuprite is stable to well below 375° C. and presumably to room temperature. The previously reported breakdown of cuprite below 375° C. (Vogel and Pocher, 1929), which is still commonly quoted in the literature, is undoubtedly in error.

The data for the stable assemblages in the ternary system at 800° C. are listed in Table 1 and have been used to construct the phase diagram in Fig. 1. Although the possibility of nonstoichiometry in $CuFeO_2$ and $CuFe_2O_4$ was not closely investigated, the *d* values of these phases from *x*-ray powder patterns appear constant regardless of the assemblage in which the phases were synthesized, suggesting that any compositional variability is probably small (<2–3%) at 800° C.

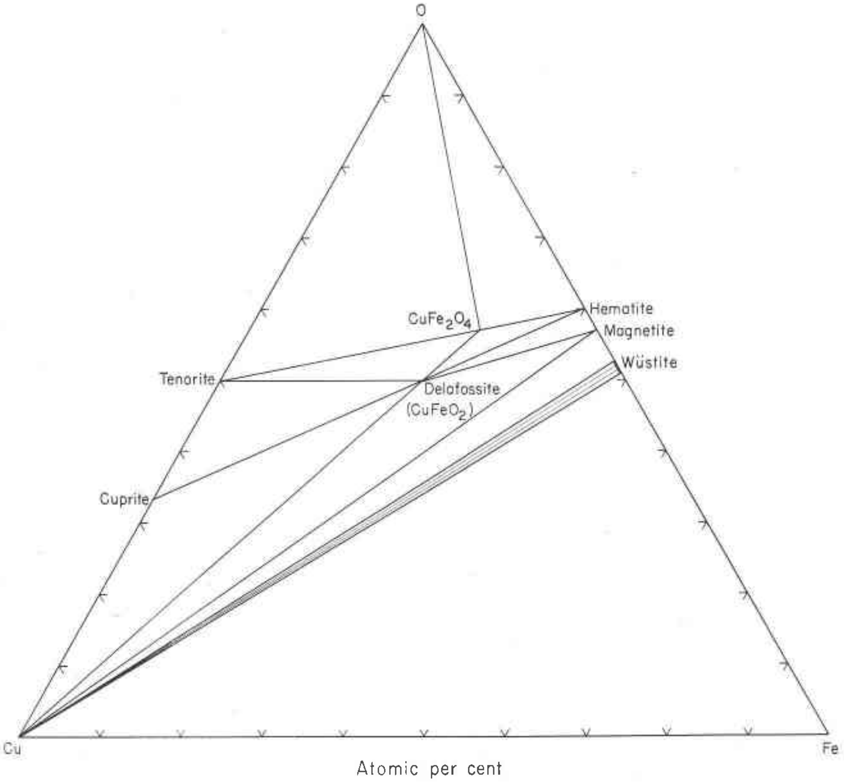

FIG. 1. Stable assemblages above 675°±25° C. This is the lowest temperature at which delafossite and magnetite are stable together.

Slow rates of reaction hindered determination of the phase relations below 800° C. Although equilibrium could not be attained for many reactions at low temperature, a tie-line change at 675° ± 25° C. from $CuFeO_2$-Fe_3O_4 to Cu-Fe_2O_3 is clearly indicated by the data in Table 2 and is shown in Fig. 2.

$CuFe_2O_4$ was found to invert between 800° and 700° C. on cooling to a tetragonal modification in agreement with the previous work of Weil, Bertaut, and Bochirol (1950). The rate of the transformation from isometric to tetragonal is high, and very rapid cooling of the silica-glass tube is necessary to quench the isometric, high-temperature modification. The only other known change in the stable assemblages below 800° C. corresponds to the breakdown of wüstite below about 560° C. (Hansen and Anderko, 1958). The stable assembages below 560° C. are shown in Fig. 2.

TABLE 2. RESULTS OF EXPERIMENTS BETWEEN 300° AND 700° C.

Reactants	Composition, weight per cent[1]		T., ° C.	Heating period, days	Condensed phases[2]
	Fe	Cu			
$CuFeO_2$	36.89	41.97	300	270	$CuFeO_2$
$CuFe_2O_4$ (isometric)	46.69	26.56	700	10	$CuFe_2O_4$ (tetragonal)
$CuFe_2O_4$ (isometric)	46.69	26.56	300	270	$CuFe_2O_4$ (tetragonal)
$Cu+Fe_2O_3$	42	40	300	220	$Cu+Fe_2O_3$
$Cu+Fe_3O_4+CuFeO_2$	42	40	300	220	$Cu+Fe_3O_4+CuFeO_2+Fe_2O_3$
$Cu+Fe_2O_3$	42	40	650	50	$Cu+Fe_2O_3$
$Cu+Fe_3O_4+CuFeO_2$	42	40	650	52	$Cu+Fe_3O_4+CuFeO_2+Fe_2O_3$
$CuO+Fe$	29	56.7	650	53	$Cu+CuFeO_2+Fe_2O_3$
$Cu+Fe_2O_3$	42	40	700	50	$Cu+Fe_2O_3+Fe_3O_4$ (?)
$Cu+Fe_3O_4+CuFeO_2$	42	40	700	50	$Cu+Fe_3O_4+CuFeO_2$
$CuO+Fe$	29	56.7	700	53	$Cu+Fe_3O_4+CuFeO_2$
$CuO+Fe$	12	70.3	650	53	$CuO+Cu_2O+CuFeO_2+Fe_2O_3$ (1%)
$CuO+Fe$	12	70.3	600	72	$CuO+Cu_2O+CuFeO_2+Fe_2O_3$ (3–4%)
$CuO+Fe$	12	70.3	500	54	$CuO+Cu_2O+CuFeO_2+Fe_2O_3$ (3–4%)
$CuFe_2O_4+Fe_3O_4$	59.7	13	700	7	$Fe_2O_3+CuFeO_2+CuFe_2O_4+Fe_3O_4$
$CuFe_2O_4+Cu_2O$	28.5	51	700	7	$CuFeO_2+CuO+CuFe_2O_4$ (3–4%) $+Cu_2O$ (4–5%)

[1] Remainder is oxygen.

[2] Not all represent equilibrium assemblages.

ESTIMATION OF ΔH°, S°, AND ΔF° FOR DELAFOSSITE

The standard heats of formation (ΔH°) and entropies (S°) (25° C. and 1 atmosphere) for copper, iron, and the binary oxides of these metals have been critically evaluated by Kubaschewski and Evans (1958) and more recently by Robie (1963, in press). Standard free energies of formation (ΔF°) for Cu_2O, Fe_2O_3 and Fe_3O_4 calculated from these data can be used to obtain ΔF° for delafossite if the phase relations shown in Fig. 2 remain unchanged down to 25° C. The following relations provide limits for $\Delta F^\circ_{CuFeO_2}$.

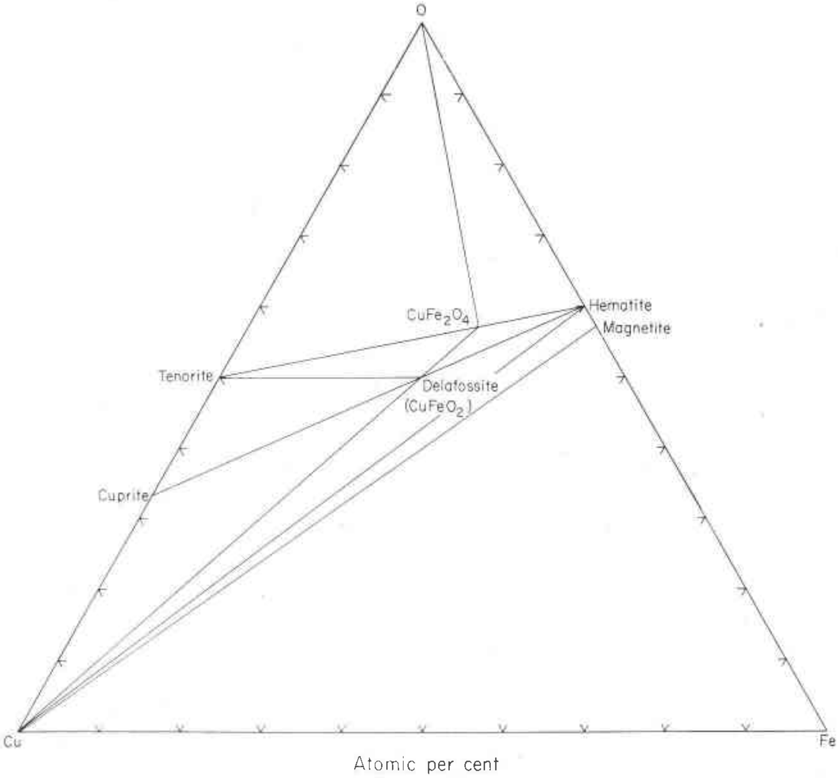

FIG. 2. Stable assemblages below 560° C., the lowest temperature at which wüstite is stable. The assemblages shown here are believed to be stable at 25° C.

$$Cu_2O + Fe_2O_3 = 2CuFeO_2 \qquad (1)$$

$$CuFeO_2 + Fe_3O_4 = Cu + 2Fe_2O_3 \qquad (2)$$

The right-hand side of each reaction represents the phases assumed to be stable at 25° C. From relation 1, $\Delta F^\circ_{CuFeO_2}$ must be more negative than half the sum of $\Delta F^\circ_{Cu_2O}+\Delta F^\circ_{Fe_2O_3}$ (-105.8 ± 1 kcal/mole) if $CuFeO_2$ is the stable phase. Similarly from relation 2, $\Delta F^\circ_{CuFeO_2}$ must be less negative than the difference of $2\Delta F^\circ_{Fe_2O_3}-\Delta F^\circ_{Fe_3O_4}$ (-111.3 ± 4 kcal/mole) if the stable assemblage is $Cu+Fe_2O_3$. The value for $\Delta F^\circ_{CuFeO_2}$ obtained from relations 1 and 2 is -110 ± 6 kcal/mole. The uncertainty of ±6 kcal/mole includes the uncertainties in the standard free energies of formation for Fe_3O_4, Fe_2O_3 and Cu_2O.[1]

Various methods for estimating the entropies of oxides and sulfides are discussed by Grønvold and Westrum (1962). Pabst (1946) concluded from a consideration of interatomic radii and coordination that the valence state of copper and iron in delafossite is probably $Cu^{+}Fe^{3+}O_2$. Because of the difficulty of estimating the expected magnetic entropy contribution to delafossite, the best estimate of $S^\circ_{CuFeO_2}$ is obtained from the observed entropies of Cu_2O and Fe_2O_3. Copper and iron have the same valences in these compounds as they do in delafossite.

$$\tfrac{1}{2}S^\circ_{Cu_2O}+\tfrac{1}{2}S^\circ_{Fe_2O_3}=S^\circ_{CuFeO_2}$$

Observed values for $S^\circ_{Cu_2O}$ and $S^\circ_{Fe_2O_3}$ taken from Grønvold and Westrum (1962) give a value of 21.6 cal/degree for $S^\circ_{CuFeO_2}$. It is unlikely that the uncertainty of $S^\circ_{CuFeO_2}$ is greater than ±2 cal/degree.

The standard heat of formation for delafossite calculated from $\Delta F^\circ_{CuFeO_2}$ and S° is -122 ± 7 kcal/mole.

The free energy of formation for $CuFeO_2$ at 675° ± 25° C. can be obtained from the relation

$$CuFeO_2+Fe_3O_4\overset{675^\circ\text{ C.}}{=}2Fe_2O_3+Cu$$

which corresponds to the tie-line change observed experimentally. The heat capacities of Fe_3O_4, Fe_2O_3, and Cu which were used in this calculation are from Kelley (1960). The calculated value of -83 ± 8 kcal/mole for ΔF_{CuFeO_2} at 675° C. is not based on any assumptions about the phase relations as was the standard free energy at 25° C. Therefore, the difference in free energy of $CuFeO_2$ between 675° and 25° C., which requires a normal heat capacity for delafossite, supports—although it does not prove—the assumption that the assemblage Cu-Fe_2O_3-$CuFeO_2$ remains stable down to 25° C.

GEOLOGICAL CONSIDERATIONS

This study was undertaken as part of an investigation of the stable mineral assemblages in the geologically important system Cu-Fe-O-S

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[1] Similarly, limits for $\Delta F^\circ_{CuFe_2O_4}$ can be obtained although the uncertainty is larger because $\Delta F^\circ_{CuFeO_2}$ is included in the calculation. The value obtained by this method is -217 ± 13 kcal/mole.

and the principal significance of this study is its contribution to the phase relations in that quaternary. However, several geological considerations pertaining to assemblages of native copper and the oxides of copper and iron may be mentioned here.

The formation of cuprite in the oxidized zone of mineral deposits was irreconcilable with the often cited instability of Cu_2O below 375° C. Recent investigations of copper oxidation and additional evidence presented in this paper demonstrate that Cu_2O is stable down to 200° C. and presumably lower, which is in accord with the geological evidence. Furthermore, the identity of the powder patterns of natural cuprite and synthetic Cu_2O indicates that the phases are structurally identical, and the possibility of two distinct phases with different limits of thermal stability is eliminated.

Oxides of copper and iron are commonly reported to occur together in the oxidized zone, although a careful examination often reveals that the iron oxides are in fact goethite or lepidocrocite (see also McKinstry, 1959). Thus the incompatibilities of cuprite and tenorite with magnetite or hematite as determined in this study are not in disagreement with many natural assemblages. For example, specimens of delafossite from Bisbee, Arizona, were examined and found to consist of delafossite, native copper, cuprite, and goethite or lepidocrocite. Magnetite or hematite was not present. Undoubtedly equilibrium is not attained in the low-temperature oxidized zone of all deposits. It is surprising, perhaps, that stable assemblages ever form in this environment.

The apparent absence of $CuFe_2O_4$ in the oxidized zone is probably best explained by the partial pressure of oxygen and water in the oxidizing environment favoring the formation of other phases (*i.e.*, cuprite, tenorite, goethite, etc.) rather than by the instability of $CuFe_2O_4$ at low temperature (Table 2). It is impossible to calculate useful limits of the partial pressure of oxygen in equilibrium with assemblages containing $CuFe_2O_4$ because of the relatively large uncertainty of $\Delta F^{\circ}_{CuFe_2O_4}$.

Coexistence of hematite and native copper is common and perhaps best exemplified by the deposits in the Keweenaw Peninsula of Michigan. The copper mineralization in this area is generally believed to have taken place at low temperature. Results of the present study indicate that copper and hematite are stable together below 675° C. and probably as low as 25° C.

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