

ART. XXV.—*Delafossite, a Cuprous Metaferrite from Bisbee, Arizona*; by AUSTIN F. ROGERS. With an analysis by G. S. BOHART.

MR. WM. L. TOVOTE, geologist of the Old Dominion Mining Company of Globe, Arizona, kindly sent me for identification and description some specimens of what was thought to be a new mineral from Bisbee, Arizona. The mineral is hexagonal in crystallization, and on analysis proves to have the formula  $\text{CuFeO}_2$ . In 1873 Friedel\* described a Siberian mineral with the composition  $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ ; to which he gave the name *delafossite*. The Bisbee mineral must be referred to *delafossite*, and though not a new mineral the results obtained warrant the establishment of *delafossite* as a distinct mineral species.†

FIG. 1.

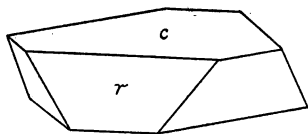
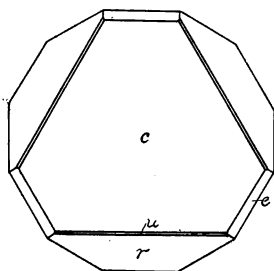


FIG. 2.



*Occurrence*.—The mineral under discussion was found by Mr. Tovote in a stope above the 14th level of the Hoatson shaft of the Calumet and Arizona property near the Copper Queen line. According to Mr. Tovote‡ it occurred in a great mass of white kaolin and ferruginous clay at about the lowest zone of oxidization. The surrounding country rock is limestone. The associated minerals include copper, cuprite, and hematite; the hand specimens contain copper and hematite.

*Crystallography*.—The mineral is found in more or less distinct crystals and subbotryoidal crystal aggregates on massive hematite. The crystals are hexagonal and greatly resemble hematite crystals, for they consist of a pinacoid  $\{0001\}$  with a rhombohedron  $\{10\bar{1}1\}$ , and are tabular to equidimensional in habit. There are also composite prismatic crystals with concave pinacoidal faces which suggest the “eisenrosen.” Fig. 1 represents a typical crystal. The hexagonal prism  $\{10\bar{1}0\}$ ,

\* Comptes Rendus, vol. lxxvii, p. 211.

† In Dana's System of Mineralogy, 6th edition (p. 259), and in Hintze's Handbuch der Mineralogie (vol. i, p. 1939) it is included in the Appendix to Oxides.

‡ Mining and Scientific Press, vol. cii, p. 206, 1911.

another positive rhombohedron  $\{h\bar{o}h\bar{l}\}$ , and a negative rhombohedron  $\{oh\bar{h}l\}$ , are also present. These are probably  $w\{10\bar{1}4\}$  and  $e\{01\bar{1}2\}$  respectively. Fig. 2 is a plan showing these doubtful forms.

Unfortunately the crystals are not suitable for goniometrical measurements. Of the various forms the basal pinacoid alone gives an image when mounted on the goniometer. The unit rhombohedral faces are composite and give no images at all. Consequently the reflections from the faces had to be relied upon, and the angles of course are only approximations. The average of five measurements of the angle  $(0001:10\bar{1}1)$  on one crystal gave  $65^\circ$ , and the average of ten measurements of the same angle on another crystal gave  $67^\circ$ . Taking the average of these two averages we have  $66^\circ$  as an approximate value. The value of the  $c$ -axis for this angle is 1.94. The angle  $(10\bar{1}1:01\bar{1}\bar{1})$  was also measured; the average of five measurements is  $76^\circ 45'$ . The calculated value, assuming the fundamental angle  $(0001:10\bar{1}1)$  to be  $66^\circ$ , for  $(10\bar{1}1:01\bar{1}\bar{1})$  is  $75^\circ 26'$ . Several contact twins with  $\{0001\}$  as the twin-plane were noted. There is an imperfect cleavage parallel to the prism  $\{10\bar{1}0\}$ .

*Physical Properties.*—The color is black; the streak, black; the luster, metallic; and the hardness, about  $5\frac{1}{2}$ . The mineral is brittle and non-magnetic, but is easily fusible and becomes magnetic when heated on charcoal. The usual pyrognostic tests for copper and iron were obtained. The mineral is easily soluble in hydrochloric and sulphuric acids, but is soluble with difficulty, if at all, in nitric acid.

*Chemical Analysis.*—A chemical analysis of the pure mineral (practically free from hematite) made by Mr. G. S. Bohart of the Chemistry department of Stanford University gave the following results:

	No. 1	No. 2	Average	Ratio	Theory CuFeO <sub>2</sub>
Cu	= 41.24	41.39	41.32	0.652	42.01
Fe	= 37.22	37.30	37.26	0.667	36.85
Insol. (Hematite)	= 0.25	0.17	0.21	----	----
O (by difference)	= 21.29	21.14	21.21	1.325	21.14
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> -----	<hr/> 100.00

The ratios are very closely Cu:Fe:O = 1:1:2. The slight excess of iron over copper may be explained by the fact that the analyzed sample contained a small amount of hematite, a part of which was soluble in sulphuric acid, the acid used to get the mineral in solution. The empirical formula of the

delafossite from Bisbee is  $\text{CuFeO}_2$ , which is equivalent to  $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ , obtained for the Siberian mineral by Friedel. Groth\* gives the formula  $\text{Cu}''_2\text{O}(\text{FeO}_2)_2$  on account of the supposed analogy with ludwigite,  $\text{Mg}_2\text{O}(\text{FeO}_2)(\text{BO}_2)$ .

*Chemical Constitution.*—When we attempt to establish the chemical constitution of the mineral there are serious difficulties. The delafossite, it is safe to assume, is a copper salt of an iron acid and not a mixture of copper and iron oxides. It may be cuprous metaferrite,  $\text{Cu}'\text{Fe}'''\text{O}_2$ , a salt of  $\text{HFeO}_2$ , ( $\text{H}_2\text{FeO}_3 - \text{H}_2\text{O}$ ), metaferrous acid, or a cupric salt ( $\text{Cu}''\text{Fe}''\text{O}_2$ ) of  $\text{H}_2\text{FeO}_2$ , a possible acid which we may call hypoferrous acid. A number of metaferrites are known, but there is no record of hypoferrites.

Both the hydrochloric and sulphuric acid solutions of the pure mineral give distinct tests for ferric and ferrous ions with potassium ferrocyanide and potassium ferricyanide respectively. These tests were made with coarsely crushed fragments of the pure mineral free from hematite, so that the ferric iron test was not due to oxidation by fine grinding or to admixed hematite.

These tests indicate either that both ferrous and ferric iron are originally present in the mineral or that in the act of solution a change in the valence of the iron takes place. The compound  $\text{Cu}'\text{Fe}'''\text{O}_2 \cdot \text{Cu}''\text{Fe}''\text{O}_2$  or  $\text{Cu}_2\text{O} \cdot \text{CuO} \cdot \text{FeO} \cdot \text{Fe}_2\text{O}_3$  also has the empirical formula  $\text{CuFeO}_2$  and would account for both the ferrous and ferric iron tests, but a formula of this kind is very improbable. It is more reasonable to suppose that a change of valence of iron has taken place during solution. A few rough experiments by the writer confirm this idea. A mixture of cupric sulphate and ferrous sulphate solution gives a decided test for ferric iron. This recalls the blowpipe test for ferrous iron.†

Stokes‡ gives the reaction:  $\text{Cu}'' + \text{Fe}'' \rightleftharpoons \text{Cu}' + \text{Fe}'''$ , which he established by experimental proof. The reversibility of this reaction is also confirmed by experiments made by the writer. Cuprous oxide and ferric oxide dissolve in sulphuric acid to a green solution, which gives tests for both ferrous and ferric iron. The reversibility of the reaction established by Stokes explains why tests for both ferrous and ferric iron are obtained from acid solutions of delafossite.

We are still left in doubt as to whether the formula of delafossite is  $\text{Cu}'\text{Fe}'''\text{O}_2$  or  $\text{Cu}''\text{Fe}''\text{O}_2$ . Either formula will account for the observed facts. Mr. Bohart made a quantita-

\* Tabellarische Uebersicht der Mineralien, 4th ed., p. 79, 1898.

† A borax bead made blue with  $\text{CuO}$  is changed in a neutral flame to opaque red ( $\text{Cu}_2\text{O}$ ) by ferrous iron. The equation is:  $2\text{CuO} + 2\text{FeO} = \text{Cu}_2\text{O} + \text{Fe}_2\text{O}_3$ .

‡ Bull. 186, U. S. Geological Survey, p. 44, 1906.

tive determination of ferrous iron by titrating the sulphuric acid solution of the mineral with potassium permanganate solution and obtained results which, calculated, give 34.10 and 34.62 as the percentages of ferrous iron. This might indicate that all the iron was in the ferrous state, about 2½ per cent having been oxidized by fine grinding, were it not for the fact that a solution of the coarsely crushed mineral gave distinct tests for ferric iron. Another fact to be considered in this connection is that cuprous ions will also decolorize potassium permanganate solution. The results obtained by Mr. Bohart are due to the combined effect of the ferrous and cuprous ions and there is no way of determining the effect of the ferrous ion alone. Copper, of course, should be removed when titrating an iron solution with permanganate, but it could not be done in this case without changing the condition of the iron.

My colleague, Professor G. H. Clevenger, suggested that the original condition of the copper in the mineral under discussion might be determined by using as a reagent silver sulphate solution. In the Ziervogel process (a metallurgical process of silver extraction) the presence of cuprous oxide, an undesirable constituent, is indicated by testing the product with silver sulphate solution, in which case thin flakes of metallic silver appear. This is known as the "spangle reaction."\*

The powdered delafossite when heated with a slightly acidulated silver sulphate solution gave a beautiful spangle reaction after standing about two days. Ferrous iron also gives this reaction, as the writer proved with siderite. In fact, almost any reducing agent may give it. But in delafossite the only possibilities to consider are cuprous copper and ferrous iron. Now, in delafossite the iron is, in all probability, combined with the oxygen as a radical and it probably does not act as iron, but only as a radical. The composition of delafossite, then, is probably cuprous metaferrite,  $\text{Cu}'\text{Fe}'''\text{O}_2$ .

Chalcopyrite,  $\text{CuFeS}_2$ , and magnetite,  $\text{FeFe}_2\text{O}_4$ , also give the spangle reaction with silver sulphate. With chalcopyrite it is the cuprous copper, and with magnetite it is the ferrous iron that acts as a reducing agent. This would indicate that these minerals are, respectively, cuprous metasulfoferrite,  $\text{Cu}'\text{Fe}'''\text{S}_2$ , and ferrous metaferrite,  $\text{Fe}'\text{Fe}_2'''\text{O}_4$ . Some mineralogists have considered these as the most probable formulæ; the spangle reaction, perhaps, makes it more certain.

*Similar Compounds.*—Magnetite,  $\text{FeFe}_2\text{O}_4$ , franklinite,  $(\text{Zn}, \text{Fe})\text{Fe}_2\text{O}_4$ , magnesioferrite,  $\text{MgFe}_2\text{O}_4$ , and jacobsite,  $\text{MnFe}_2\text{O}_4$ , are well-known metaferrites, all isometric in crystallization.

\* Egleston, *The Metallurgy of Silver, Gold and Mercury in the United States*, vol. i, p. 134, 1887.

Cupric metaferriite,  $\text{CuFe}_3\text{O}_4$ , is known\* but not its crystal form. One would expect it to be isometric.

Not many cuprous compounds are known, but they seem to be related to alkali compounds rather than to the dyad metal compounds.  $\text{CuCl}$ ,  $\text{CuBr}$ , and  $\text{CuI}$  are isometric like the sodium and potassium haloids. Sodium metaferriite,  $\text{NaFeO}_2$ , crystallizes in hexagonal plates and rhombohedral plates according to van Bemmelen and Klobbie.† This compound and delafossite are perhaps isomorphous. Chalcopyrite,  $\text{CuFeS}_2$ , analogous to  $\text{CuFeO}_2$ , is tetragonal, but the sulpho-salts are not usually isomorphous with the corresponding oxy-salts.

*Identity with Delafossite.*—As the Bisbee mineral is a pure, well-crystallized compound of definite chemical composition, it is entitled to recognition as a distinct mineral species. It is hexagonal-rhomboidal in crystallization and has the empirical composition  $\text{CuFeO}_2$ . It agrees with a Siberian mineral described by Friedel under the name of delafossite except in cleavage and hardness. As these properties are not fundamental the Bisbee mineral is referred to delafossite and the evidence, it is believed, is complete enough to establish delafossite as a definite independent mineral species. It is probably cuprous metaferriite,  $\text{Cu}'\text{Fe}'''\text{O}_2$ .

NOTE.—Since writing the above Mr. Tovote has sent me several additional specimens of delafossite from Bisbee. One of them is a soft, black, graphite-like mineral which marks paper and has a lamellar structure. It gives the same chemical tests as the crystallized delafossite and agrees with the description of the Siberian mineral. The lamellar structure may account for the apparent cleavage and also for the inferior hardness. Hematite presents an analogous case, for some varieties are very soft and have an apparent cleavage in one direction which is due to lamellar structure.

Stanford University in California,  
November, 1912.

\* List, Berichte d. Deutsch. Chem. Ges., vol. xi, p. 1512, 1878.

† Jour. prakt. Chemie, vol. cliv, p. 509, 1892.