ART. IX. — *The Action of Copper Sulphate upon Iron Meteorites*; by O. C. FARRINGTON.

IN 1852 Wöhler* announced the discovery that some iron meteorites, irrespective of their nickel content or structure, are passive to neutral solutions of copper sulphate, i. e., they do not reduce copper from such a solution. This passivity he stated could be overcome by introducing a piece of ordinary iron into the solution or by adding a few drops of acid.

No data were given as to temperature, length of time allowed for deposition or the strength of the solution. The following meteorites were reported by him to be passive: Bemdego, Bohumilitz, Braunau, Cape of Good Hope, Green County (undoubtedly Babb's Mill), Obernkirchen, the Pallas Iron, Red River (probably Cross Timbers), Schwetz, Toluca, and the terrestrial iron of Greenland. A number of other meteorites which need not here be enumerated he reported at the same time as "active," i. e., they reduced copper from the copper sulphate solution; while those of a third class were designated as "intermediate," i. e., they were nearly passive, but after remaining some length of time in the solution brought about a slow reduction of copper. That the passivity was a property of the entire mass of the meteorite seemed to be proved by the fact that when the surface of the meteorite had been made active and the coating of copper was removed by filing, it would again behave passive.

Since the publication of Wöhler's article several other investigators of iron meteorites have tested their behavior toward copper sulphate with the result usually of finding them active, but the following, as listed by Cohen,† have been reported passive: Toluca by Krantz, Knoxville by Smith, Misteca by Bergemann, Octibbeha County by Taylor, Ohaba by Bukeisen (this is a stone), Charcas by Meunier and Lexington Co. by Shepard. Two of these, however, were reported by other observers to be active, viz: Toluca by Pugh, Jordan and Taylor, and Charcas by Danbrée. The observers later than Wöhler also failed to give details regarding the conditions of their experiments. Wicke and Wöhler state that the Obernkirchen meteorite, after remaining a day, reduced no copper from its salts.‡ Smith states that Knoxville is passive with reference to the action of sulphate of copper, but when immersed in a solution of the latter and allowed to remain several hours the copper deposits itself in spots on the surface

* Poggendorff's *Annalen* 1852, vol. lxxxv, pp. 448-9.

† *Meteoritenkunde*, Heft 1, p. 68.

‡ *Ann. d. Chem. u. Pharm.*, 1864, vol. cxxix., p. 123.

of the iron.* Meunier states that the section of Charcas was washed in alcohol and ether to remove grease and upon it a drop of solution of sulphate of copper was placed. At the end of some hours the drop had evaporated, leaving crystals of the salt but no copper.†

Viewed simply as a matter of reasoning, it would seem quite impossible, with our present knowledge, to account for a passive behavior of meteorites independent of their nickel content. As is probably generally known, nickel is less active to copper sulphate than iron, and it might be expected that the activity of alloys of iron and nickel would decrease in proportion as the percentage of nickel increased. But that some individuals of the same alloy (for iron meteorites are practically alloys of iron and nickel) should be entirely passive while others were normally active would be quite extraordinary. Wöhler's conclusion was that all iron meteorites were probably in their original state passive, but that through local terrestrial influences and the passage of time, some had since their arrival upon the earth become active. Mennier expressed the opinion that a peculiar molecular structure may be indicated by the passivity.‡ In view of the lack of details regarding the experiments upon which Wöhler based his conclusions and the results he obtained, it seemed to me desirable to reinvestigate the matter to some extent.

Of the meteorites listed above as passive, there are to be found in the collection of the Field Columbian Museum, specimens weighing from 10 to 1100 grams each, of the following: Babb's Mill, Bemdego, Braunau, Bohumilitz, Cape of Good Hope, Charcas, Cross Timbers, Knoxville, Lexington Co., Misteca, Pallas Iron, Toluca and the native iron of Greenland. These therefore were available for investigation. In order to test their activity each section was in turn immersed in a solution of 200 grams of Baker & Adamson's C. P. copper sulphate to a liter of distilled water. The temperature of this solution was about that of the room, or 18° C. In this test every meteorite gave an active reaction. A perceptible deposition of copper took place upon each section within one to four minutes after its immersion. The only exception to this general rule was Knoxville, which in some trials deposited in four minutes but in others required twelve or fifteen minutes. In the same solution and at the same temperature about thirty minutes was required before deposition took place upon a piece of ordinary cube nickel the surface of which had been rendered bright by filing. A specimen of josephinite, how-

* This Journal (2). xix, 155.

† Ann. Chim. et Phys., 4th ser., vol. xvii, p. 92.

‡ Loc. cit.

ever, gave no deposit at all, though left twenty-four hours in the solution. With the exception of Knoxville and josephinite the period required for deposition seemed to correspond quite closely to the percentage of nickel. Thus ordinary iron would, as it is well known to do, take on a coating of copper almost instantly upon immersion in the solution. For the native iron of Greenland, which contains 2 or 3 per cent nickel, about thirty seconds were required. Irons like Charcas, Braunau, Bemdego and Lexington Co., which contain 4 to 6 per cent of nickel, required from one to two minutes, and Cape of Good Hope and Babb's Mill, which have about 15 per cent of nickel, three to four minutes. The somewhat eccentric Knoxville is a meteorite with a high percentage of nickel and josephinite contains 72 per cent nickel. Incidentally, therefore, the experiments indicated that immersion of an iron-nickel alloy in a solution of copper sulphate will afford a rough test of the percentage of nickel contained in the alloy, and, since a meteorite must contain nickel, a quick means of distinguishing meteoric from terrestrial iron.

To the experiments made in the above manner as compared with those of Wöhler, the objection may be made that Wöhler described his solution as a "*Lösung von neutralem schwefelsauren Kupferoxyd*," while a solution of copper sulphate has normally an acid reaction. In order to remove doubt on this point a solution was prepared according to the method given by Blair.* Such a solution is one of 200 grams to the liter, but to it sodium hydroxide is added until a slight precipitate appears and the latter is removed by filtration. The solution still has an acid reaction, but the possible presence of free acid is avoided.

The sections immersed in this solution gave, however, as far as could be observed, results exactly similar to those obtained with the simple solution. As no mention is made by Wöhler or other investigators of treatment to reduce the acidity of their solutions, it is highly probable that only the simple solution was used. Employment of solutions of different strengths was likewise without effect on the results obtained. Tests were made with a solution of 100 grams to the liter and some intermediate strengths, but the fact of the deposition of the copper and the period required for its deposition seemed unchanged.

Different temperatures were however of considerable influence in changing the time required for deposition. Thus the cube nickel, which required thirty minutes at 18° C., reduced copper in five minutes when the solution was heated to 63° C.

* The Chemical Analysis of Iron, 3d ed., p. 63.

The specimen of josephinite which reduced no copper at 18° C. gave a deposit in twenty minutes at 63° C. At temperatures below 18° C. the time required for the deposit is greatly increased. Thus, Cañon Diablo, which reduces copper in one minute at 18° C., required sixty minutes at 10° C. and at 0° C. was kept twelve hours without producing a deposit. Toluca, which acquires a deposit in two minutes at 18° C., required eighty minutes at 10° C. and at 6° C. was kept for four hours without receiving a deposit. It was not tried longer at this temperature.

In these tests it was found necessary to immerse the sections in water of the temperature whose effect it was desired to study, for some minutes before transferring to the copper sulphate solution. Otherwise the heat of the section would cause deposition at an earlier period. Also a fresh section which had not been exposed to copper sulphate must be used, as traces of a previous deposit of copper would hasten deposition.

The periods named as sufficient for deposition are in all cases somewhat approximate and variable, since the exact moment at which deposition begins can be determined only roughly by the eye. The general results are however sufficiently accurate for the purpose. They show nothing to support Wöhler's belief that certain meteorites are inherently passive, but on the contrary point to the conclusion that meteorites act like any other iron-nickel alloy.

Daubree considers the deposition of copper due to the fact that the different alloys in a meteorite form electric couples,* but it hardly seems necessary to appeal to this force when deposition takes place so quickly upon a piece of iron not made up of different alloys.

It is hardly essential to the purposes of this article to try to account for the results reported by Wöhler and other observers, but one or two suggestions may be made in this connection. It is possible that some of the surfaces tested by these observers may have been rendered passive by treatment with nitric acid. This was quite probably the case with Misteca as treated by Bergemann, for he reports that upon freshly dissolved (*gelöst*) pieces he could get no deposit, while pieces from the outer surface of the meteorite without luster and of dark gray color were quickly coated.† Wöhler, however, expressly states that the sections which he tested had not come in contact with nitric acid.

Again a slight film of grease or oxide may have prevented deposition of copper. A substance so active to copper sulphate even as iron will be found to have become passive,

* Comptes Rendus, 1867, vol. lxiv, p. 685.

† Pogg. Ann., 1857, vol. c, p. 246.

if heated a moment before immersion. This is probably on account of the film of oxide formed. The sections of Cape of Good Hope and Knoxville, which had an active behavior as treated ordinarily, I found to be thoroughly passive when reimmersed without rubbing after an interval of two weeks. No perceptible film of oxide could be detected, but on rubbing the surface with emery cloth deposition took place as before. There are some indications again that the molecular condition of the substance and especially of its surface may determine its degree of activity. For instance, a cube of nickel which was perfectly passive when treated in the ordinary way, no deposit being formed on it after standing 24 hours in the sulphate solution, although fresh surfaces were frequently exposed by abrasion, was made active by being heated to redness, cooled and again made bright by abrasion. A deposit of copper then formed within twenty minutes and the cube has shown active behavior since. The activity was the same both when the cube was cooled slowly and quickly. The specimen of josephinite previously mentioned as being passive at ordinary temperatures, was given a similar treatment, i. e., heated to redness, cooled and rubbed. It also became active under this treatment, reducing copper in a solution at the temperature of 18° C. at some time within a period of twelve hours, the exact time not having been noted. It was noticeable in this case, as in many others, that deposition began and was most active about capillary cracks and fissures. This would indicate that capillary tension was influential in effecting the reduction of the copper, and it is reasonable to suppose that such would be the case, since the molecules are probably brought into closer contact in such situations. It is evident that several conditions may affect the degree of activity of a meteorite or any other iron-nickel alloy, but I have found nothing to accord with Wöhler's observation that passive meteorites which had been made active by contact with iron, after the reduced copper was filed off became again passive. While several phases of the subject invite further investigation, enough evidence seems to be obtained to warrant classing all meteorites as active to copper sulphate and dropping the designation of passive meteorites.

I am indebted to my associate, Mr. H. W. Nichols, for a number of useful suggestions during the progress of the investigation.

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