



LII. Analysis of the arseniates of copper and of iron

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To cite this article: Richard Chenevix Esq. F.R.S. M.R.I.A. (1802) LII. Analysis of the arseniates of copper and of iron , Philosophical Magazine Series 1, 12:48, 302-311, DOI: [10.1080/14786440208676067](https://doi.org/10.1080/14786440208676067)

To link to this article: <http://dx.doi.org/10.1080/14786440208676067>



Published online: 18 May 2009.



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I have now mentioned the most material circumstances which have occurred to me concerning our late respected friend. There are several of them which I have related rather because they were facts, (and every fact relative to a departed friend seems interesting to his survivors,) than because I thought them of sufficient importance to be laid before the public. I am, dear Sir,

With great esteem,
Yours very sincerely,
THOMAS ARNOLD.

LII. *Analysis of the Arseniates of Copper and of Iron.* By
RICHARD CHENEVIX, Esq. F. R. S. M. R. I. A.

[Concluded from p. 229.]

SECTION III.

Analysis of the Red Octaedral Copper Ore, in which the Metal exists in a State hitherto unknown in Nature.

IN the course of the experiments which have been stated in the preceding sections, I have had occasion to examine a great number of copper ores, and particularly of copper ores from Cornwall; but the only one which has afforded any interesting results, is the well known species called red copper ore, crystallized in regular and brilliant octaedrons. It has been so long known, and so often mentioned by mineralogists, that it may excite our wonder when we reflect, that its chemical nature has never been ascertained. For it would be an injustice to that very accurate and scrupulous analyst M. Vauquelin, to suppose that he meant to pronounce decidedly upon that point by the single experiment which he had made*, and which is mentioned by the abbé Haüy in a short extract of his crystallographical arrangement of mineral substances, published in the *Journal des Mines*.

Romé de Lisle, the baron de Born, Lametherie, the abbé Haüy, and indeed every other mineralogist, concur in calling this substance red calx of copper; but some of them assert that it contains a portion of carbonic acid. Among the many analyses which have been made of this ore by Fontana, Monnet, De Born, Renovantz, and others, I could not find one, that in the proportions, or even in the ingredients, resembled what I had found to be its contents. The

* He merely poured muriatic acid upon the ore; and, as it was entirely dissolved, without effervescence, concluded it to be an oxide, and not a carbonate, of copper.

highest

highest amount of copper (that given by Fontana) does not exceed 66 per cent., and is far short of the real quantity. The remainder, as he states, consists of water and of pure and fixed airs. The difference in the results I had obtained, together with some new facts, which I had occasion to observe during my experiments, induces me to treat the subject at some length; referring for its external characters to those mineralogists above mentioned, who have amply described the ore, and confining myself entirely to its chemical analysis, and some analogous experiments.

One hundred parts of very pure and regularly crystallized red copper ore were reduced to a fine powder, and dissolved, without the assistance of heat, in nitric acid.

During the operation, a very violent effervescence, accompanied by a disengagement of nitrous gas, unusually copious and rapid, took place. When these phenomena had subsided, the solution was blue, like every other nitrate of copper; and the ore had entirely disappeared. The liquor, perfectly limpid, was evaporated to dryness; muriatic acid was poured in, and the nitric acid was expelled by a second evaporation. Into the muriate of copper, which remained behind, a plate of polished iron was immersed, which, after the usual phenomena, gave a precipitate that was found, upon examination, to be copper, and amounted to 88.5. In order to complete the hundred parts, it would be necessary to add 11.5. But fire expelled from the ore neither water nor any other volatile substance; nor did the weight of a given quantity appear either to diminish or to increase by long exposure to a moderately elevated temperature. The only oxide of copper with which I was acquainted, as existing in nature, contains 20 per cent. of oxygen. I had therefore 8.5 of copper exceeding the quantity I should have obtained had the ore been wholly composed of black oxide of copper. And, on the other hand, as I had convinced myself that no loss of weight had been occasioned by any part of the metal remaining unprecipitated by the iron from its solution, I could not conclude the ore to be in the state of native copper. I was led, therefore, to imagine, that it might be a mixture of those two substances; and that muriatic acid, by dissolving the one, and leaving the other untouched, would be the most effectual means of producing the separation I desired, and of determining the proportion of each.

Upon 100 parts of the ore a sufficient quantity of strong muriatic acid was poured. A total solution was effected, accompanied with disengagement of caloric. The liquor was, at first, of a very deep brown, approaching somewhat to the

tinge which water will receive when strongly impregnated with the colouring matter or dried vegetable substances; but, upon being exposed to the air, and boiled some time, it became like every other muriate of copper; and a plate of polished iron precipitated 88 of metallic copper. From this last experiment it was evident that no metallic copper was contained in the ore. But still the deficit to be supplied by oxygen amounted to no more than 12; while the copious disengagement of nitrous gas, in the first experiment, indicated that the metal was not at its maximum of oxidation; and the rapidity with which it seized upon an addition of oxygen, sufficiently showed how strong was the affinity of that principle for copper, in that particular state in which it exists in the ore.

I imagined it would be expedient to attempt some precipitations by other reagents, and make some further experiments. For this purpose, I dissolved some more of the ore in strong muriatic acid; and, when I thought that the acid had taken up as much as it could contain, and that the colour had arrived at its deepest tinge, I gently drew off the clear liquor, using all the precaution which the nature of the experiment allowed, to preserve it from the contact of the atmosphere, and proceeded to examine it. Knowing this solution of muriate of copper to be very concentrate, I attempted to dilute it; but what was my surprise, when, upon the first affusion of water, I saw the liquor become turbid and milky, and a very abundant heavy precipitate, of a white colour, fall to the bottom!

Struck with the novelty of this appearance, I proceeded to collect as much of the substance as I could, in order to give it a thorough examination. For this purpose, I decanted the supernatant liquor, and continued to wash the precipitate. Upon every subsequent addition of water, I perceived that the precipitate lost a little of its whiteness, and drew towards an orange colour, not unlike the precipitates of platina. I soon found, therefore, that by this method I had no chance of obtaining, in a permanent and constant state, this muriate of copper, fit to be subjected to experiments proper to determine its internal nature and proportions. I then attempted to make use of alcohol, as precipitant, instead of water; but I found the salt to be soluble in it, when the excess of acid necessary for its solution in water was present. Nor was I more successful, when, after having precipitated by water, I washed with alcohol; for the colour of the salt passed gradually from very white to a shade of orange; less rapidly, it is true, in this case, but still so as to convince me that I could

could not even thus procure, in a state constantly similar, the salt I wished to examine. The only conclusion which all these experiments entitled me to draw, was that, in the first instance, water precipitated the muriate of this particular oxide of copper from its solution, but in a manner very different from that in which muriate of antimony, of bismuth, and some other metallic salts are acted upon. When into either of these muriates water is poured, a precipitate ensues, but it retains a very small portion of acid, if any; whereas, in the case before us, it is a salt, and not an oxide of copper, that is thrown down. In order to effect in this salt a decomposition similar to that which takes place in muriate of bismuth, or of antimony, it is necessary to draw off the first liquor, and then proceed to wash copiously. The precipitate will by degrees assume an orange colour, which, as we shall presently see, is the real appropriate colour of this oxide of copper, prepared in the humid way.

It is evident also, from this precipitation, that this oxide of copper combines with muriatic acid by a very slender affinity.

As it did not appear to me, that I should obtain any thing very satisfactory from this combination with muriatic acid, I resolved to try some other acids. Sulphuric, phosphoric, oxalic, citric, acetic, tartareous, and acetous acids were each poured upon known quantities of the ore, and kept in bottles completely filled and well stopped, in order to prevent any absorption of atmospheric oxygen. The liquors generally became blue; and, upon trial, were found to contain the common and well known salts of copper, composed of the respective acid, and the oxide of copper containing 20 per cent. of oxygen; while a large portion of the ore appeared to remain in its original state. But, as I was certain that there could be no decomposition in most of these acids, under the above circumstances, and moreover, that no oxygen could be taken in from the atmosphere, it became a matter of no small interest to examine from what source the metal dissolved had acquired the necessary quantity of oxygen to favour its solution, and afford the usual salt of copper, in which it is oxidated in the proportion of 20 per cent.

I repeated, with all the above acids, the experiments tending to satisfy that inquiry; but, as the results from all were nearly similar, I shall mention that only which proved to be the most ample and the most conclusive.

One hundred parts of the pulverized ore were introduced into a small phial, and dilute phosphoric acid was poured in, so as to fill it. A ground-stopper closed it completely; and

in that state it was suffered to remain three days, during which time the bottle was frequently shaken. The acid became at first of a light blue, and increased in colour by remaining upon the ore. At the expiration of the above term, the liquor was decanted; the residuum was well washed and dried, and weighed 42. The blue liquor contained merely common phosphate of copper, held in solution by an excess of acid. Upon the 42 parts of residuum, strong muriatic acid was poured, which did not appear to produce the smallest change or effect. It was evident, therefore, that some previous alteration had been produced; for, if it had remained in its original state, muriatic acid would have acted upon it, as in the case already mentioned. To operate more effectually, nitric acid was added, and the whole gently heated. A complete solution followed, during which much nitrous gas was disengaged. The remainder of the nitric acid was expelled by evaporation; and a plate of polished iron, immersed in this muriate of copper, afforded a precipitate of metallic copper, weighing within one part as much as the weight of the first residuum. It was evident, therefore, that a partial reduction of the ore had taken place; and, what is still more strange, had taken place by means of the presence of an acid.

In many observations which have presented themselves in the course of various analytic experiments, something similar had before occurred to me. I have known metallic oxides yield a part of their oxygen, one to the other, in favour of some particular solvent. When the metallic oxide *A*, for instance, containing 25 per cent. of oxygen, is in contact with the metallic oxide *B*, containing 10 per cent. they will each remain quiescent in their respective states. But, if the solvent *C* comes to be added, and if the substance *B*, at 10 per cent. of oxygen, has no affinity for *C*, but at 15 or 20 per cent. has a very powerful affinity for it, then may the oxide *A* lend a part of its oxygen, in order to favour the combination of *B*, at 15 or 20 per cent. with the solvent *C*. Indeed, as soon as I saw the phosphoric acid assume gradually a blue tinge, and the undissolved powder begin to wear a more brilliant appearance, I imagined I should not fail to recognize the same fact in this case. When phosphoric acid has remained long enough upon the pulverized ore to dissolve all it can, the oxygen is concentrated, as it were, to the amount of 20 per cent. in the part which is dissolved; and all that which could not be dissolved has (through the two-fold affinity of copper for oxygen, to the amount of 20 per cent. and of phosphoric acid for that oxide of copper, at that degree

degree of oxidation,) yielded up its entire share of oxygen, to favour the combinations which take place in a new order, the only one which can exist among the substances now present. It is, therefore, to the disposing affinity *, caused by the presence of the phosphoric acid, which seeks to combine with black oxide of copper, that the reduction of 42 per cent. of this ore is entirely to be attributed. All the acids above mentioned are capable of producing the same change, but in a manner, perhaps, not quite so distinct or satisfactory.

From the foregoing experiments it appears, that copper exists in this ore in a state hitherto unknown in nature; and that it contains much less oxygen than has ever been suspected in any oxide of copper; for, from the quantity which was precipitated in the metallic state by iron, it appears to be combined in the proportion of about 11,5 per cent. To confirm this idea, and ascertain, as nearly as I could, the precise quantity, I dissolved 100 parts in nitric acid; then boiled with potash, and filtered. One hundred and eleven remained upon the filter, which, as they had combined with a new portion of oxygen from the nitric acid, were in the state of black oxide, and correspond exactly to 88,75; so that I believe I shall be within one per cent. of the truth, in asserting the proportions to be,

Copper	-	-	88,5
Oxygen	-	-	11,5
			<hr/>
			100,0

When, into a solution of muriate of suboxide of copper, liquid potash or soda is poured, a bright yellow precipitate, not unlike the precipitate of platina, takes place. This precipitate differs only in colour from the original ore; for it is soluble in muriatic acid, and affords the same solution and precipitation by water, and the same appearance with alcohol. It is likewise soluble in nitric acid, but with disengagement of nitrous gas, and gives the same appearances with the other acids above enumerated. The difference of colour seems to arise merely from the tenuity of its molecules, compared to the mechanical pulverization of the natural oxide. When alone and dry, it is much more permanent in its nature than when combined with muriatic acid; but any part

* As the term *predisposing affinity* has been objected to, I have used the term *disposing*, which, I trust, will not be thought improper. When in two bodies which, while together, remain in their original state, the equilibrium of their principles comes to be broken by the presence of a third, we cannot but allow that it is this third which has disposed them to the rupture of that equilibrium; and, most certainly, be the fact explained as it may, whatever disposes may be called disposing.

of it that happens to be in contact with a filter, becomes green, and then blackish, leaving a mark of the same shade upon the paper. Were it not for this property of changing, it might be of use in the art of painting; for the colour is extremely beautiful, and would be highly valuable if durable.

The precipitate caused in the muriate of copper by the carbonates of potash and soda, is of a brighter yellow, and is a real carbonate of suboxide of copper. But, if ammonia is poured, at first in a small quantity, into the above solution, the precipitate is blue; and, upon adding an excess of the precipitant, the whole is redissolved, and the liquor is like any other ammoniacal solution of copper.

In order, however, to determine in what state the copper was dissolved by that alkali, I poured some ammonia upon 100 parts of this suboxide in a well-closed phial. The liquor became blue; and I expected to find that part of the ore had been reduced, as with phosphoric acid; but the residuum was entirely soluble in muriatic acid, with the usual phenomena.

A spirituous tincture of galls, poured into muriate of suboxide of copper, afforded no precipitate, owing, I suppose, to the excess of acid; but sulphurated hydrogen gas threw down a black, and prussiate of ammonia a lightish brown, precipitate.

I endeavoured to obtain muriate of suboxide of copper by evaporation, and by distillation in a retort; but, as I could perceive the liquor constantly assume a blueish tinge, I could not reckon upon the purity of the salt, sufficiently to submit it to analysis.

Such were the principal experiments, which the fleeting and precarious existence of the salt allowed me to make upon it. But, from some properties which I had remarked, I could perceive that this ore was a natural oxide of copper, nearly in the same state as that artificial oxide which Mr. Proust had found in the white muriate of copper, obtained by pouring a recent solution of muriate of tin into a solution of muriate of copper.

If, however, by the very nature of the substance, (which, as I saw it ever changing, I thought it would be loss of time to examine further,) I have been turned aside from more certain results, I have been more successful in imitating by art the state of this natural product.

By exposing oxide, hydrate, or carbonate of copper, without addition, to a violent heat, in an open crucible, I frequently obtained the suboxide, which then presented all the properties already recognized in the above species of copper ore. In one instance, I so far succeeded, that, upon the very first inspection,

inspection, the well-experienced eye of the Count de Bournon recognized a lump of it to be a mass of semi-fused, artificial, red copper ore.

But I have found a method of producing at pleasure, in the humid way, all the new salts, and the oxide above described. As I had found about 11,5 per cent. of oxygen to be the quantity contained in the ore, I took that quantity of black oxide of copper which corresponded to 1,5 of oxygen; (57,5 of black oxide was the proportion thus indicated;) on the other hand, I took 50 parts of metallic copper, which had been precipitated by iron from muriate of copper, and which was in a state of tenuity not inferior to the finest powder. These were well mixed, by trituration in a mortar, and put, with muriatic acid, into a well stopped phial. A violent disengagement of caloric took place; the liquor became of the same colour as with the ore, and contained a salt in every respect similar to that afforded by the ore; while a portion of metallic copper remained, with all its lustre, at the bottom of the phial. The solution was decanted, and the residuum of metallic copper weighed 7,5. Consequently, 42,5 had been dissolved, which, with 57,5 of black oxide, complete the hundred parts.

No experiment could prove, in a manner more satisfactory, the quantity of oxygen contained in 100 parts of this suboxide; nor could any afford results more important, or more conclusive. The passage of a portion of oxygen from one part of the metal to another, to favour its solution, as already stated, is proved beyond the possibility of doubt; and is doubly interesting, as it is the inverse of what happens to the ore when treated by phosphoric acid.

In the experiments of Mr. Proust, he has estimated the quantity of oxygen, contained in 100 parts of this oxide, to be 17. This proportion was calculated upon the deficit of a single analytic experiment, made upon the salt of muriate of suboxide of copper, after having determined the quantity of acid, of water, and of metallic copper. But, first, the salt cannot easily be obtained (as I have before observed) in a state sufficiently certain to be relied on, in an experiment of this nature; and, in the next place, it is probable, as happens in almost every analysis, that the deficit was greater than the real quantity of oxygen. For, the agreement between the analytic and synthetic experiments I have just stated, seems to confirm 11,5 to be more exactly the proportion.

When, in the dry way, the above proportions of metallic copper and of black oxide of copper, or, when metallic copper with a corresponding proportion of hydrate or of carbon-

ate of copper, were intimately mixed, and heated at a low red heat, the oxygen seemed to be equally distributed through all the mass; and every particle seemed perfectly homogeneous.

In the ore here spoken of, it is by no means rare to find large pieces of real native copper; and, whether we consider it mineralogically or chemically, it certainly is an interesting substance. But, how much more will it be esteemed, if it is regarded with a view to public utility!

The Baron de Born has mentioned a gray cupreous pyrites, which, he says, contains 90 per cent. of copper. I have analysed a similar one from Cornwall, (gray vitreous copper ore, p. 212,) which I found to contain 86 of the same metal. But if we reflect, not so much on the quantity as upon the extreme purity of this copper, and the wonderful facility with which this useful metal may be extracted, it will be found much superior to every copper ore hitherto discovered. It would be well worth the attention of miners, to keep a constant look-out for this substance, which, I am informed, is not rare in Cornwall. It contains no iron, and no sulphur; the absence of which latter is a peculiar advantage. It is a fact not generally known, I believe, that there is hardly such a thing in commerce, as copper which does not contain a little sulphur; at least, I have rarely met with any such; and it requires but a very minute portion of sulphur to increase the fusibility of copper. The advantage of obtaining copper free from sulphur, is too obvious to require to be pointed out; and that advantage does this ore possess.

To work it separately, if ever it should be found in sufficient quantity, would well repay the labour it would cost; and a very small mixture of any disoxidating substance would, in a short time, reduce immense quantities.

From the foregoing experiments we may perceive into how many errors we may be drawn, if, in arguing from the results which we obtain, we pronounce too hastily upon the state in which a substance exists, in the subject of any analysis. After what has been shown, with regard to the action of muriatic acid upon a mixture of metallic copper and black oxide of copper, both reduced to powder, and of the action of phosphoric acid upon the ore itself, it may be still a doubt whether this ore is really a suboxide, or a mixture of metallic copper and oxide of copper, at 20 per cent. of oxygen. But, as similar proportions of both, after having been made red-hot, presented all the properties and appearances of the ore much more strongly than when simply mixed, it is fair to conclude that it is a real suboxide. Had not muriatic acid been

been used, the natural conclusion would have been, that the ore was a mixture, or at most a combination, of these two substances; for such did it appear to be by the testimony of the other acids. The truth is, we are but little acquainted with the exact state in which substances exist in many natural combinations. However, in the mineral kingdom, such fallacious conclusions are less frequently to be dreaded than in the vegetable and animal kingdoms. But, in every research, it is important to leave as little room for them as possible; and he who would indicate a sure and constant method of ascertaining whether, in many cases, what we deem a component part, is not, in fact, a product of the operation, would render to science a service, the real value of which is, perhaps, not now entirely foreseen.

LIII. *Communications on the Subject of Navigation, from*
JOHN COOKE, *Esq. M. R. I. A.*

SIR,

Dublin, April 25, 1802.

I REQUEST permission to communicate to the public, through your Magazine, the inclosed attempts to advance the art of navigation; they consist of methods of measuring distance at sea, and of discovering currents, with the plan of a new sea chart. My object in publishing them is to offer them to the consideration of others who are more capable of detecting their imperfections and of suggesting remedies than myself, for which I shall be thankful; but, as I intend to make experiments, and to follow up these inventions, I do not wish to have it understood that I relinquish my exclusive right to them by this step, or that any person may make use of them without my consent. I am, Sir,

Your most obedient servant,

To Mr. Tilloch.

JOHN COOKE.

THE distance through which a ship sails is the product of the time and velocity of its progress: the time is easily ascertained by well-known methods, and the log-line exhibits the degree of motion during the experiment with tolerable certainty: but, since the motion is perpetually varying, this method would require an uninterrupted succession of experiments to afford an accurate measure; therefore it is a desideratum in navigation to obtain some easy method of registering the several changes of velocity which take place in sailing, with the intervals of time between each; which objects,