

XXIII. *Account of a Substance found in a Clay-pit; and of the Effect of the Mere of Diss, upon various Substances immersed in it.* By Mr. Benjamin Wiseman, of Diss, in Norfolk. Communicated by John Frere, Esq. F. R. S. *With an Analysis of the Water of the said Mere.* By Charles Hatchett, Esq. F. R. S. *In a Letter to the Right Hon. Sir Joseph Banks, Bart. K. B. P. R. S.*

Read April 19, 1798.

THE substance I have inclosed was found near Diss, in a body of clay, from five to eight feet below the surface of the soil. All the pieces I observed laid nearly in a horizontal direction; and varied in size, from two or three ounces, to as many pounds. The colour of the substance, when taken fresh from the clay-pit, was like that of chocolate; it cuts easily, and has the striated appearance of rotten wood. The pieces were of no particular form; in general, they were broad and flat, but I do not recollect to have met with a piece that was more than two inches in thickness: it breaks into laminæ, between which are the remains of various kinds of shells. The specific gravity of this substance, dried in the shade, is 1.588; it burns freely, giving out a great quantity of smoke, with a strong sulphureous smell.

By a chemical analysis, which I cannot consider as very accurate, one hundred grains appear to contain,

Of inflammable matter, including the small quantity	grains.
of water contained in the substance	- - 41.3
Of mild calcareous earth	- - - 20.0
Of iron	- - - 2.0
Of earth, that appears to be silex	- - - 36.7
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	100

On the Effect of the Mere of Diss, upon various Substances.

Observing, several years ago, that flint stones taken out of the Mere of Diss were incrustated with a metallic stain, I was induced to make some experiments, in order to discover the nature or composition of this metallic substance.

Nitrous acid readily removes it, dissolving a part, and leaving a yellowish powder, which, washed and filtered, was found to be sulphur. Vegetable fixed alkali precipitated from the nitrous acid a ferruginous coloured powder, which was iron.

With a view to determine what length of time was necessary for the formation of this metallic stain upon flint stones, or other substances, I inclosed in a brass wire net the following articles: flint stones, calcareous spar, common writing slate, a piece of common white stone ware, and likewise a piece of black Wedgwood-pottery. After remaining in the water from the summer of 1792 to August, 1795, the flints and Wedgwood-ware had acquired the metallic stain in a slight degree, and the slate had assumed a rust colour; the other substances appeared not to be at all altered. I was greatly surprised to find the copper wire that held the net, surrounded with a metallic coating of a considerable thickness; it was of a deep lead colour, and of a granulated texture. When taken from the wire, and ground in a mortar, it had a black appearance, inter-

spersed with very hard shining particles. The wire was evidently eroded, and this substance deposited in the place of the copper that was decomposed, somewhat similar to the decomposition of iron in cupreous waters.

By repeated chemical analysis of this substance, one hundred grains contain, of copper, 70; of sulphur, 16.6; of iron 13.3 grains.

I have never met with an account of the decomposition of copper, in waters impregnated with iron, in any chemical work; and, as iron appears to have a greater affinity to the vitriolic acid than copper has, (as is constantly evinced in the neighbourhood of copper mines,) it appears an anomaly in chemistry, that I am not adept enough in the science to account for.

[The President and Council, thinking the effects of the water of Diss Mere deserving of further inquiry, desired Mr. WISEMAN would send some of the said water, for the purpose of examination. Mr. WISEMAN accordingly sent a quantity of the water, accompanied by the other substances described in the following letter to the President.]

SIR,

Diss, May 29, 1798.

As the Society have expressed a wish, through Mr. FRERE, to have some of the water in which the copper wire was deposited, which Mr. FRERE, at my request, laid before the Society, I have sent two gallons of the water of Diss Mere, (No. 1.) with a small quantity of copper cuttings, (No. 2.) which laid in the same water, a few feet from the side, and six feet in depth, from the 7th of February, 1797, to the 20th of the present month, May, 1798. The pieces of copper, when laid in, weighed 3051 grains; when they were taken out, and washed from the mud that lightly adhered to them, preserving and weighing the scaly matter that came off, they weighed 2944 grains, indicating a loss of 107 grains. Examining the pieces of copper, the same evening they were taken out of the water, I observed a number of small crystals formed upon some of them, in the form of pyramids joined at their bases; these crystals lost their shining appearance, by the evaporation of the water of crystallization, in the warmth of the succeeding day. Whether they will be preserved in a journey of nearly 100 miles, is perhaps doubtful. No. 3. contains two pieces of copper, on which the crystals were most abundant. No. 4. contains a small quantity of the substance formed upon the copper, that came off in washing and in weighing it.

The town of Diss is principally situated on the NNE and E sides of this piece of water. The land runs pretty steep on the W and N of it, to the height of 40 or 50 feet: on the SE, the ground comes within a few feet of the level of it. The soil of the upper part of the town is a stiff blue clay; that of the lower part, to the SE, a black sand, beneath which it is a moor.

The water in the higher parts of the town is good; in the lower parts, it is a chalybeate, of which a specimen is sent, (No. 5.)

No. 6. contains a quantity of flint stones, taken from the SE side of the Mere, where the water is shallow; many of which are strongly marked with the metallic stain, which they acquire by lying in this water a few years.

The Mere contains about eight acres, and is of various depths, to twenty-four feet: from its situation with respect to the town, it may naturally be supposed to contain a vast quantity of mud, as it has received the silt of the streets for ages. In summer, the water turns green; and the vegetable matter that swims on its surface, when exposed to the rays of the sun, affords vast quantities of oxygen gas. I cannot help considering this process as having a considerable agency in the corrosion, and in the formation of the metallic crust upon the copper deposited in this water. Some of this vegetable matter will be found in the water sent to the Society.

I intend to make some further experiments with different metallic substances, at different parts, and at various depths; but, as the process is slow, if in the mean time you, Sir, or any of the members of the Society, will have the goodness to point out any experiment you or they may wish to have made, I shall be very glad to contribute all in my power towards the illustration of the subject.

I have the honour to be, &c.

BENJ. WISEMAN.

The Right Hon. Sir JOSEPH BANKS, Bart.
K. B. P. R. S.

[The water, and other substances described in the foregoing letter, were delivered to Mr. HATCHETT, who had been previously requested, by the President and Council, to examine them. The result of his examination is related in the following letter to the President.]

Analysis of the Water of the Mere of Diss. By Charles Hatchett, Esq.

DEAR SIR,

Hammersmith, Sept. 14th, 1798.

In consequence of the request which you and the Council of the Royal Society have done me the honour to make, that I would examine the water of Diss Mere, and the other substances sent by Mr. WISEMAN, I now hasten' to acquaint you with the result of my experiments.

The substances sent by Mr. WISEMAN are as follows :

Some copper wire, with a blackish grey incrustation.

Water from Diss Mere, (marked No. 1.)

Copper cuttings, covered with a blackish crust, similar to that on the copper wire, (marked No. 2.)

Some cuttings similar to those abovementioned, (marked No. 3.)

The paper, No. 4. contained some of the black crust, detached from the cuttings.

No. 5. A quart bottle, containing some water from the lower part of the town of Diss, and called, by Mr. WISEMAN, a chalybeate water.

No. 6. Some flints, taken from the SE side of the Mere, where the water is shallow, and having (as Mr. WISEMAN terms it) a metallic stain.

My first experiments were made on the incrustation of the copper wire, mentioned in Mr. WISEMAN'S first letter.

This incrustation was easily detached from the wire, and, being reduced to powder, was digested with nitro-muriatic acid, in a gentle heat: a green solution was formed, and there remained a residuum, of a pale yellow, which proved to be sulphur.

The solution being diluted with two parts of distilled water, was supersaturated with pure ammoniac, by which, a few brown flocculi of iron were precipitated. The supernatant liquor was blue; and, being evaporated, and redissolved by sulphuric acid, the whole was precipitated by a plate of polished iron, in the state of metallic copper. The component parts of this coating were therefore copper, and a very small portion of iron combined with sulphur.

I could not extend these experiments, as the whole quantity of the coating that I was able to collect, amounted only to three grains and an half.*

The next experiments were made on the black crust of No. 2, 3, and 4.

This I found to be exactly the same as that formed on the copper wire; *viz.* it consisted of copper combined with sulphur, and a very small portion of iron.

* The copper wire, when the coating was removed, was perfectly flexible, and the surface did not appear unequal or corroded: this is commonly the case under such circumstances; for, when sulphur has combined superficially with a metal, the compound is observed to separate easily, so as to leave the metal underneath not injured in quality, and very little, if at all, affected in appearance. Those who diminish silver coin, make use of the following method.

They expose the coin to the fumes of burning sulphur, by which a black crust of sulphurated silver is soon formed, which, by a slight but quick blow, comes off like a scale, leaving the coin so little affected, that the operation may sometimes be repeated twice or thrice, without much hazard of detection, if the coin has a bold impression.

I next examined the water of Diss Mere, (No. 1.) and I was at length led on, step by step, to make a regular analysis of the fixed ingredients.

Before I made the analysis, I examined this water with certain re-agents, and remarked the following properties.

1. The water of Diss Mere has a yellowish tinge, and the flavour is rather saline; but it has not any perceptible odour.
2. Prussiate of potash did not produce any effect.
3. Acetite of lead produced a slight white precipitate.
4. Nitrate of silver formed one, very copious.
5. Tincture of galls had not any effect.
6. Muriate of barytes caused a slight precipitate.
7. Ammoniac, potash, and oxalic acid, severally produced precipitates, when added to different portions of this water.

ANALYSIS.

A. Three hundred cubic inches of the water, by a gentle evaporation, left a pale brown scaly substance, which weighed 58 grains.

B. These 58 grains were digested in alcohol, without heat, during 24 hours, and afforded a solution, which, by evaporation, yielded muriate of lime, slightly tinged by marshy extract, 18 grains.

C. Six ounces of distilled water were then poured on the residuum, and, with repeated stirring, remained during 24 hours. By evaporation, this afforded muriate of soda, with a very small portion of sulphate of soda; in all, 10 grains.

D. What remained was boiled in 800 parts of distilled water, and the solution, being evaporated, left of selenite 1.70 gr.

E. The undissolved portion now weighed 25 grains, and was digested with diluted muriatic acid: a great part was dissolved, with much effervescence, and, being filtrated, afforded, by ammoniac, of alumine 1.50 gr. From this, I afterwards separated a very minute quantity of iron, by means of prussiate of potash.

F. Carbonate of soda was then added to the liquor, and precipitated carbonate of lime 21 grains.

G. The insoluble residuum weighed 3.50 gr.; and proved to be principally carbon, (produced by decomposed vegetable matter,) with a very small quantity of siliceous earth.

The result of this analysis was, therefore,

	grains.
B. Muriate of lime - - - -	18
C. Muriate of soda, with a very small portion of sulphate of soda - - - -	10
D. Selenite - - - -	1 70
E. Alumine, with a portion of iron too small to be estimated - - - -	1 50
F. Carbonate of lime - - - -	21
G. Carbon, with a little siliceous earth -	3 50
	55 70
Loss	2 30
	58 0

It is worthy of notice, that the iron present was in so very small a quantity as not to be detected by any test, till it had been separated in conjunction with the alumine.

The water No. 5, from Mr. WISEMAN'S account, does not appear to have been concerned in producing the effects which he has observed, and the quantity was too small to be subjected to a regular analysis, I noted, however, what follows.

1. It has a very strong hepatic flavour and smell.
2. A plate of polished silver, put into it, became black in a few hours.
3. It became faintly bluish with prussiate of potash, after standing five or six hours.
4. Tincture of galls produced a faint purple cloud.
5. Solution of acetite of lead afforded a brown precipitate.
6. Nitrate of silver produced the same.
7. Potash, and ammoniac, caused a precipitate; but that of the former was the most copious.
8. Oxalic acid produced a precipitate.
9. Muriate of barytes had also a slight effect.

The water No. 5. cannot, therefore, be considered as a chalybeate, (the quantity of iron contained in it being scarcely perceptible;) but it appears to be a water containing some hepatic gas, together with substances similar to those contained in No. 1.

From the above experiments it is evident, that the water No. 1. does not contain any of the component parts of the crust formed on the copper wire and cuttings, although it is certain that the incrustation took place during the immersion of those bodies; but, before I mention my ideas on this subject, I shall give an account of some experiments made on the flints, No. 6. These were coated with a yellowish shining substance, which appeared to me to be pyrites; and, as the flints could not have contributed any metallic substance to form this coating, I was enabled by their means to ascertain, whether the copper of the crust, formed on the wire and cuttings, had been furnished by the pieces of copper, or by any thing in the vicinity of the water.

1. I poured nitro-muriatic acid on some of the flints, in a matrass, so as completely to cover them.

The coating was rapidly dissolved, with much effervescence; and, when the flints appeared perfectly uncoated, and in their usual state, I decanted the liquor.

2. A yellow matter subsided, which proved to be sulphur.

3. Prussiate of potash produced Prussian blue; and the remaining part of the solution, being supersaturated with ammoniac, afforded an ochraceous precipitate of iron.

The supernatant liquor did not become blue, as when copper is present, nor was the smallest trace of it afforded by evaporation.

Martial pyrites is, therefore, the only substance deposited on bodies immersed in the water of Diss Mere; and the copper of the crust, formed on the wire and cuttings, was furnished by those bodies.

It is proved by the analysis, that the water of Diss Mere does not hold in solution any sulphur, and scarcely any iron; it has not, therefore, been concerned in forming the pyrites; but it appears to me, that the pyritical matter is formed in the mud and filth of the Mere; for Mr. WISEMAN says in his letter, that "the Mere has received the silt of the streets for ages." Now it is a well known fact, that sulphur is continually formed, or rather liberated, from putrefying animal and vegetable matter, in common sewers, public ditches, houses of office, &c. &c.; and this most probably has been the case at Diss. Moreover, if sulphur, thus formed, should meet with silver, copper, or iron, it will combine with them, unless the latter should be previously oxidated.

The sulphur has therefore, in the present case, met with iron, in, or approaching, the metallic state, and has formed pyrites; which (whilst in a minutely divided state, or progres-

sively during formation,) has been deposited on bodies, such as the flints, when in contact with the mud.

But an excess of sulphur appears to be present; for, when copper is put into the Mere, the sulphur readily combines with it; and, at the same time, a small portion of iron appears to unite with the compound of copper and sulphur, possibly by the mere mechanical act of precipitation.

The incrustation on the copper wire and cuttings is, in every property, similar to that rare species of copper ore, called by the Germans *Kupfer schwärtze*, (*Cuprum ochraceum nigrum*;) and I consider it as absolutely the same. In respect to the martial pyrites on the flints, there can be no hesitation; and, as in these two instances, there were evident proofs of the recent formation of ores in the humid way, I was desirous to ascertain the effect on silver. I therefore wrote to Mr. WISEMAN, to request that he would take the trouble to make the experiment; and received from him the following answer, accompanied by the specimens.

“ SIR,

Diss, 8th September, 1798.

“ Immediately upon the receipt of your letter, (27th July,) I laid some silver plate, and silver wire, into the Mere; the whole weighed 235.6 gr. I took it out on Thursday last, (Sept. 6th) and, after cleaning it carefully from mud and weeds, I find it weighs 242.8 gr. ; an increase of 7.2 gr.

“ The silver plate you will find much tarnished, in some parts almost black; the wire is in many places fairly incrustated, which crust, upon the pressure of the fingers, comes off in thin scales. The whole appearance of the silver strongly indicates

the presence of sulphur, which I have no doubt abounds in every part of the Mere.

“ The peculiar smell of the mud gives me reason to suppose, that a great deal of hepatic air is produced ; which, probably, uniting with the iron held in solution in the water of the Mere, may account for the martial pyrites found on the flints.

“ By what affinity the copper wire, laid in this water, is attacked, I am not chemist enough to determine.

“ I have begun a set of experiments, with the view of producing the same effects upon copper wire by artificial means ; but whether I shall succeed, I am not able at present to say.

“ I am, &c.

“ BENJ. WISEMAN.”

P. S. By experiments I have lately made, I find hepatic gas precipitates carbonate of iron in the form of a black flocculent matter ; 71 parts of which are iron, and 29 sulphur.

The silver plate I found (as Mr. WISEMAN has mentioned) much tarnished, and in many places almost black, but I could not detach any part of it. I succeeded better with the wire, and collected a small portion of a black scaly substance, which, as far as the smallness of the quantity would allow it to be ascertained, was sulphuret of silver ; and was similar, in every respect, to the sulphurated or vitreous ore of silver, called by the Germans *Glaseritz*.

This effect on the silver was to be expected; and I recollect to have read, not many months ago, in one of the foreign journals, that Mr. PROUST had examined an incrustation, of a dark grey colour, formed in the course of a very long time, on some silver images, in a church at (I believe) Seville. This incrustation he found to be a compound of silver with sulphur, or, in other words, vitreous silver ore.

The same principle is the cause of the tarnish which silver plate contracts with so much ease, particularly in great cities; for this tarnish is principally a commencement of mineralization on the surface, produced by the sulphureous and hepatic vapours dispersed throughout the atmosphere, in such places.

To Mr. WISEMAN'S observations we are much indebted, as they make known the recent and daily formation of martial pyrites, and other ores, under certain circumstances. It is not to be supposed that such effects are local, or peculiar to Diss Mere; on the contrary, there is reason to believe that similar effects, on a larger scale, have been, and are now, daily produced in many places.

The pyrites in coal mines have, probably, in great measure thus originated.

The pyritical wood also may thus have been produced; and, by the subsequent loss of sulphur, and oxidation of the iron, this pyritical wood appears to have formed the wood-like iron ore which is found in many parts, and particularly in the mines on the river Jenisei, in Siberia.

In short, when the extensive influence of pyrites in the mineral kingdom, caused by the numerous modifications of it, in

the way of composition and decomposition, is considered, every thing which reflects light on its formation becomes interesting; and I cannot but regard as such, the effects which Mr. WISEMAN has observed in the Mere of Diss.

With great respect, I remain, &c.

CHARLES HATCHETT.

The Right Hon. Sir JOSEPH BANKS, Bart.

K. B. P. R. S. &c.