VII. *Chemical Analysis of a BLACK SAND, from the River Dee in Aberdeenshire ; and of a COPPER ORE, from Arthrey in Stirlingshire. By THOMAS THOMSON, M. D. Lecturer on Chemistry, Edinburgh.*

[Read 18th May 1807.]

THE specimen which formed the subject of the first of the following *analyses*, was brought from the banks of the river Dee, about seven years ago, by my friend Mr JAMES MILL, who at that time resided in Aberdeenshire. By him I was informed, that considerable quantities of it are found in different parts of the bed of that river,—that it is called by the inhabitants *iron-sand*,—and that they use it for sanding newly written paper. I tried some experiments in the year 1800, in order to ascertain its nature ; but was too little skilled at that time, both in mineralogy and practical chemistry, to manage an analysis of any considerable difficulty.

THE black powder is mixed with a good many small whitish, reddish, and brownish grains, which, when examined by means of a glass, prove to be pieces of quartz, felspar, and mica. From this it would appear, that the sand of the river Dee consists chiefly of the detritus of granite or gneiss.

WHEN a magnet is passed over the sand, some of the black grains adhere to it, and are by this means easily obtained separate.

rate. But after all that can be attracted by the magnet is removed, the greater part of the black powder still remains. This residue is indeed attracted by a powerful magnet, but so very feebly, that it is not possible by means of it to separate it from the grains of sand with which it is mixed. Thus we learn, that the black matter consists of two distinct substances; one of which is powerfully attracted by the magnet, the other not. As this second substance was obviously specifically heavier than the grains of sand with which it was mixed, I placed a quantity of the powder on an inclined plane, and by exposing it cautiously, and repeatedly, to a jet of water, I succeeded in washing away most of the grains of sand, and thus obtained it in a state of tolerable purity.

THE first of these minerals we may call *iron-sand*, and the second *iserine*, as they belong to mineral species which oryctognosts have distinguished by these names.

I. IRON-SAND.

THE iron-sand is much smaller in quantity than the iserine, and does not exceed one-fourth of the mixture at most. Its colour is iron-black. It is in very small angular grains, commonly pretty sharp-edged, and sometimes having the shape of imperfect octahedrons. The surface is rough; the lustre is feebly glimmering and metallic; the fracture, from the smallness of the grains, could not be accurately ascertained, but it seemed to be conchoidal. Opaque, semihard, brittle, easily reduced to powder. Powder has a greyish-black colour; powerfully attracted by the magnet; specific gravity 4.765.

1. As acids were not found to act upon this mineral, 100 grains of it were reduced to a fine powder, mixed with twice
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its weight of carbonate of potash, and exposed for two hours to a red heat, in a porcelain crucible. The mass, being softened in water, was digested in muriatic acid. By repeating this process twice, the whole was dissolved in muriatic acid, except a brownish-white matter, which being dried in the open air, weighed $19\frac{1}{2}$ grains.

2. THE muriatic acid solution, which had a deep yellowish-brown colour, was concentrated almost to dryness, and then diluted with water. It assumed a milky appearance; but nothing was precipitated. Being boiled for some time, and then set aside, a curdy-like matter fell. It was of a milk-white colour, weighed, when dry, 7 grains, and possessed the properties of oxide of titanium.

3. THE residual liquid being supersaturated with ammonia, a dark reddish-brown matter precipitated, which being separated by the filter, dried, drenched in oil, and heated to redness, assumed the appearance of a black matter, strongly attracted by the magnet. It weighed 93.7 grains, and was oxide of iron.

4. THE 19.5 grains of residual powder, being mixed with four times its weight of carbonate of soda, and exposed for two hours to a red heat, in a platinum crucible, and afterwards heated with muriatic acid, was all dissolved, except about a grain of blackish matter, which was set aside.

5. THE muriatic solution being concentrated by evaporation, a little white matter was separated. It weighed $\frac{1}{4}$ th of a grain, and possessed the characters of oxide of titanium.

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6. WHEN evaporated to dryness, and redissolved in water, a white powder remained, which proved to be filica, and which, after being heated to redness, weighed one grain.

7. THE watery solution being supersaturated with potash, and boiled for a few minutes, was thrown upon a filter, to separate a reddish-brown matter, which had been precipitated. The clear liquid which passed through the filter, was mixed with a solution of sal ammoniac. A soft white matter slowly subsided. It was alumina, and, after being heated to redness, weighed half a grain.

8. THE brown-coloured matter which had been precipitated by the potash, when dried upon the steam-bath, weighed 20.2 grains. It dissolved with effervescence in muriatic acid. The solution had the appearance of the yolk of an egg. When boiled for some time, and then diluted with water, it became white, and let fall a curdy precipitate, which weighed, when dry, 4.6 grains, and possessed the properties of oxide of titanium.

9. THE residual liquor being mixed with an excess of ammonia, let fall a brown matter, which, after being dried, drenched in oil, and heated to redness, weighed 6 grains. It was strongly attracted by the magnet, but was of too light a colour to be pure oxide of iron. I therefore dissolved it in muriatic acid, and placed it on the sand-bath, in a porcelain capsule. When very much concentrated by evaporation, small white needles began to make their appearance in it. The addition of hot-water made them disappear; but they were again formed when the liquor became sufficiently concentrated. These crystals, when separated, weighed 1.3 grains, and proved, on examination, to be white oxide of arsenic. During the solution
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of the 6 grains in muriatic acid, a portion of black matter separated. It weighed 0.2 grains, and was totally dissipated before the blow-pipe in a white smoke. Hence, it must have been arsenic. These 1.5 gr. are equivalent to rather more than 1 grain of metallic arsenic. Thus, it appears, that the 6 grains contained 1 grain of arsenic, which explains the whiteness of their colour. The rest was iron. It can scarcely be doubted, that the proportion of arsenic present was originally greater. Some of it must have been driven off when the iron oxide was heated with oil.

10. THE insoluble residue, (No. 4.), was with great difficulty dissolved in sulphuric acid. When the solution was mixed with ammonia, a white powder fell, which weighed 0.8 grains. It was accidentally lost, before I examined its properties. But I have no doubt, from its appearance, that it was oxide of titanium.

11. THUS, from the 100 grains of iron-sand, the following constituents have been extracted by analysis :

Black oxide of iron,	-	98.70
White oxide of titanium,		12.65
Arsenic,	-	1.00
Silica and alumina,	-	1.50

Total, 113.85

Here there is an excess of nearly 14 grains, owing, without doubt, to the combination of oxygen with the iron and the titanium during the analysis.

HAD the iron in the ore been in the metallic state, the excess of weight, instead of 14, could not have been less than 30. For the black oxide is known to be a compound of 100 metal
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and 37 oxygen. Hence, I think, it follows, that the iron in our ore must have been in the state of an oxide, and that it must have contained less oxygen than black oxide of iron. A good many trials, both on iron-sand, and on some of the other magnetic ores of iron, induce me to conclude, that the iron in most of them is combined with between 17 and 18 *per cent.* of oxygen. This compound, hitherto almost overlooked by chemists, I consider as the real protoxide of iron. THENARD has lately demonstrated, the existence of an oxide intermediate between the black and the red; so that we are now acquainted with four oxides of this metal. But the protoxide, I presume, does not combine with acids like the others. Analogy leads us to presume the existence of a fifth oxide, between the green and the red.

As to the titanium, it is impossible to know what increase of weight it has sustained, because we are neither acquainted with it in the metallic state, nor know how much oxygen its different oxides contain. It is highly improbable, that, in iron-sand, the titanium is in the metallic state, if it be made out that the iron is in that of an oxide. The experiments of VAUQUELIN and HECHT, compared with those of KLAPROTH, have taught us that there are three oxides of titanium, namely, the blue, the red, and the white. From an experiment of VAUQUELIN and HECHT, and from some of my own, I am disposed to consider these oxides as composed of the following proportions of metal and oxygen:

	METAL.	OXYGEN.
1. Blue,	100	16
2. Red,	100	33
3. White,	100	49

I find, that when the white oxide of titanium is reduced to the state of red oxide, it loses one-fourth of its weight; and that
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red oxide, when raised to the state of white oxide, increases exactly one-third of its weight. It was the knowledge of these facts, that led me to the preceding numbers. And I think they may be used, till some more direct experiment lead us to precise conclusions.

RED oxide being the only state in which this metal has yet occurred separate, we may conclude that it combines, in this state, with metallic oxides, and that the titanium in iron-sand, is most probably in this state. But white oxide, diminished by one-fourth, gives us the equivalent quantity of red oxide. On that supposition, the titanium present, before the analysis, in the 100 grains of ore, weighed 9.5 grains.

THE appearance of the arsenic surprised me a good deal, as it was altogether unexpected. I am disposed to ascribe it to some particles of arsenic pyrites which might have been accidentally present. This conjecture will appear the more probable, when we reflect, that arsenic pyrites very frequently accompanies iron-sand. Before the microscope, the iron-sand appears to contain some white shining particles, which, probably, are arsenic pyrites.

THE small quantity of silica and alumina, I ascribe, without hesitation, to grains of quartz and felspar, which had adhered to the iron-sand, and been analysed along with it. Some such grains were actually observed and separated. But others, probably, escaped detection.

12. IF these suppositions be admitted as well founded, the iron-sand was composed of

Protoxide of iron,	85.3
Red oxide of titanium,	9.5
Arsenic, - -	1.0
Silica and alumina, -	1.5
Loss, - -	2.7

100.0

The loss will not appear excessive, if we consider, that a portion of the arsenic must have been sublimed, before the presence of that metal was suspected.

UPON the whole, I think we may consider the specimen of iron-sand examined, as composed of 9 parts protoxide of iron, and 1 of red oxide of titanium. The presence of titanium in this ore had been already detected by LAMPADIUS, though, as I have not seen his analysis, I cannot say in what proportion.

II. ISERINE.

THE colour of this ore is iron-black, with a shade of brown. It consists of small angular grains, rather larger than those of the iron-sand, but very similar to them in their appearance. Their edges are blunt; they are smoother, and have a stronger glimmering lustre than those of the iron-sand. Lustre semi-metallic, inclining to metallic. The fracture could not be distinctly observed, but it seemed to be conchoidal; at least nothing resembling a foliated fracture could be perceived. Opaque, semi-hard, brittle, easily reduced to powder; colour of the powder unaltered; specific gravity 4.491*; scarcely attracted by the magnet.

1. A HUNDRED grains of the powdered ore were mixed with six times their weight of carbonate of soda, and exposed for two hours to a red heat, in a platinum crucible. The mass obtained being softened with water, dissolved completely in muriatic acid. When the solution was concentrated, it assumed the appearance

* If, as the following analysis would lead us to expect, the specimen examined was a mixture of four parts iserine, and one part quartz and felspar, the specific gravity of pure iserine should be 4.964.

pearance of the yolk of an egg. It was boiled, diluted with water, and set aside for some time. A white matter gradually deposited, which, when dried on the steam-bath, weighed 53 grains, and possessed the properties of oxide of titanium.

2. THE liquid thus freed from titanium, was evaporated to dryness, and the residue redissolved in water, acidulated with muriatic acid. A white powder remained, which, after being heated to redness, weighed 16.8 grains, and possessed the properties of silica.

3. THE solution was precipitated by ammonia, and the brown matter which had separated, boiled for some time in liquid potash. The whole was then thrown on a filter, to separate the undissolved part, and the liquid which came through, was mixed with a solution of sal ammoniac. A white powder fell, which, after being heated to redness, weighed 3.2 grains. It was alumina.

4. THE brown substance collected on the filter, was dried, drenched in oil, and heated to redness. It was strongly attracted by the magnet, and weighed 52 grains.

5. IT was digested in diluted sulphuric acid; but not being rapidly acted upon, a quantity of muriatic acid was added, and the digestion continued. The whole slowly dissolved, except a blackish matter, which became white when exposed to a red heat, and, as far as I could judge from its properties, was oxide of titanium, slightly contaminated with iron. It weighed 1.8 grains.

6. THE acid solution being concentrated by gentle evaporation, a number of small yellowish-coloured needles made their ap-

pearance in it. By repeated evaporations, all the crystals that would form were separated. They weighed 6 grains. I redissolved them in water, and added some ammonia to the solution. A fine yellow powder fell, which I soon recognised to be oxide of uranium. It weighed 4.2 grains.

7. Thus it appears, that the 52 grains (No. 4.), attracted by the magnet, contained 46 grains of iron, and 6 grains of uranium and titanium.

8. THE following are the substances separated from 100 grains of iserine, by the preceding analysis :

Oxide of titanium,	54.8
Oxide of iron, -	46.0
Oxide of uranium,	4.2
Silica, - -	16.8
Alumina, -	3.2
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Total,	125.0

Here is an excess of no less than 25 grains, to be accounted for by oxygen, which must have united to the three metals during the process. As to the silica and alumina, there can be little hesitation in ascribing them to grains of sand, which had been mixed with the ore. The pure iserine, in all probability, was composed of iron, titanium, and uranium. If we suppose that each of these metals existed in the state of protoxide, we must diminish the titanium by one-fourth, the iron by one-seventh nearly, and the uranium, according to BUCHOLZ's experiments, by one-fifth. This would give us,

Titanium,

Titanium,	-	41.1
Iron,	-	39.4
Uranium,	-	3.4
Silica and alumina,		20.0
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		103.9

Here, then, is still an excess of nearly 4 *per cent*. But this I am disposed to ascribe to the oxides of titanium and uranium, having been only dried upon the steam-bath. Upon the whole, it appears, that, in the specimens of iserine analysed, the proportions of titanium and iron were nearly equal, and that the uranium did not exceed 4 *per cent*. The appearance of uranium surprised me a good deal. I perceive, however, that it has already been detected in this ore, from an analysis published by Professor JAMESON, in the second volume of his Mineralogy, which, I understand, was made by LAMPADIUS. The specimen examined by LAMPADIUS yielded very nearly 60 parts of titanium, 30 of iron, and 10 of uranium. Whereas, in mine, if the foreign matter be removed, there was obtained, very nearly,

	-	48 titanium,
		48 iron,
		4 uranium,
		<hr/>
		100

But, there can be no doubt, that the iserine which I analysed was still contaminated with a good deal of iron-sand; for it was impossible to remove the whole.

Analysis of the GREY COPPER ORE, from Airthrey.

THE copper mine of Airthrey, near Stirling, consists of a thin vein, which runs through the west corner of the Ochils. It has been twice wrought, by two different companies. But, in both cases, was abandoned, after a few years trial. I went to it some years ago, and examined the ore, at the request of one of the proprietors. The specimens which were employed for the subsequent analysis, were the purest that I could select, out of a considerable quantity. I was told, however, that from the lower level, which was at that time full of water, much richer ore had been extracted. But, afterwards, when the lower level was freed from its water, I went down to it myself, and found the ore precisely of the same kind as in the upper, with this difference, that it was more mixed with calcareous spar, and perhaps, on that account, more easily smelted.

THE veinstones in the Airthrey mine are sulphate of barytes, and carbonate of lime, and with these the ore is almost always more or less mixed.

THE colour is at first light steel-grey ; but the surface soon tarnishes, and becomes of a dark dull leaden-grey, and in some places assumes a beautiful tempered steel tarnish. Massive and disseminated. In some specimens, it exhibits the appearance of imperfect crystals. Internal surface shining and metallic ; but, by exposure, it soon becomes dull. Fracture small-grained, inclining to even. Fragments indeterminate, and rather blunt-edged. Semihard, the degree being almost the same as that of calcareous spar ; for these two minerals reciprocally scratch each

each other. Streak similar, opaque, brittle, easily frangible; specific gravity 4.878.

1. To free the ore as completely as possible from foreign matter, it was reduced to a coarse powder, and carefully picked. It was then digested in diluted muriatic acid, which dissolved a quantity of carbonate of lime, amounting to 13 per cent. of the original weight of the ore.

2. Thus purified, it was dried on the steam-bath, and 100 grains of it were reduced to a fine powder, and digested in diluted nitric acid, till every thing soluble in that menstruum was taken up. The residue was digested in the same manner, in muriatic acid; and when that acid ceased to act, the residue was treated with nitro-muriatic acid till no farther solution could be produced. The insoluble matter was of a white colour; it weighed 6.9 grains, and was almost entirely sulphate of barytes. No traces of sulphate of lead, nor of oxide of antimony, could be detected in it by the blow-pipe.

3. THE three acid solutions being mixed together, no cloudiness appeared, nor was any change produced; a proof that the ore contained no silver.

4. THE solution being evaporated nearly to dryness, was diluted with water, and precipitated by muriate of barytes. By this means, the sulphuric and arsenic acids, which had been formed during the long-continued action of the nitric acid on the ore, and the presence of which had been indicated by reagents, were thrown down; for nitrate of lead, added to the residual liquid, occasioned no precipitate; a proof that no arsenic acid was present.

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5. THE liquid, thus freed from arsenic acid, was mixed with an excess of ammonia. It assumed a deep blue colour, while a brown matter precipitated. It was separated by the filter, and being dried, drenched in oil, and heated to redness, it was totally attracted by the magnet. It weighed 45.5 grains, and was iron.

6. THE ammoniacal liquid was neutralised by sulphuric acid, and the copper thrown down by means of an iron plate. It weighed 17.2 grains.

7. To ascertain the quantity of sulphur and arsenic, 100 grains of the purified ore, in the state of a fine powder, were put into the bottom of a coated glass-tube, and exposed for two hours to a red heat. When the whole was cold, and the bottom of the tube cut off, the ore was found in a round solid mass, having the metallic lustre, a conchoidal fracture, and the colour and appearance of *variegated copper-ore*. It had lost 16 grains of its weight.

8. The upper part of the tube was coated with a yellowish-brown substance, like melted sulphur. It weighed 12.6 grains. Thus, there was a loss of 3.4 grains. As the tube was long, this loss can scarcely be ascribed to sulphur driven off. I rather consider it as water. For towards the beginning of the process, drops of water were very perceptible in the tube. Whether this water was a constituent of the ore, or derived from the previous digestion in muriatic acid, cannot be determined.

9. WHEN the 12.6 grains of yellowish brown matter detached from the tube, were digested in hot potash-ley, the whole was dissolved, except a fine blackish powder, which weighed

weighed 1 grain, and was arsenic. The dissolved portion I considered as sulphur.

10. THE potash solution, being mixed with nitric acid, 4 grains of sulphur fell. The remaining 7.6 grains must have been converted into sulphuric acid, by the action of the nitric acid. Accordingly, muriate of barytes occasioned a copious precipitate.

11. THE 84 grains of roasted ore being reduced to a fine powder, mixed with half their weight of pounded charcoal, and roasted a second time in a glass-tube, one grain of sulphur sublimed. But the tube breaking before the roasting had been continued long enough, the process was completed in a crucible. The roasted ore weighed 70 grains.

12. FROM the preceding analysis, we learn that the constituents of the Airthrey ore, are as follows :

Iron,	-	45.5
Copper,	-	17.2
Arsenic,	-	14.0
Sulphur,	-	12.6
Water,	-	3.4
Foreign bodies,		6.9
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		99.6
Loss,	-	.4
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		100.0

If we suppose the water and the earthy residue to be only accidentally present, then the only essential constituents are the first four, and the ore would be a compound of

Iron,	51.0
Copper,	19.2
Arsenic,	15.7
Sulphur,	14.1
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	100.0

If we compare this analysis with several analyses of grey copper ore, lately published by KLAPROTH, we shall find, that the constituents are the same in both ; but the proportions of the two first ingredients are very nearly reversed. KLAPROTH obtained from 0.4 to 0.5 of copper, and from 0.22 to 0.27 of iron. This renders it obvious, that the two ores were not in the same state. I have little doubt, that the difference, however, is merely apparent, and that it arose, altogether, from a quantity of iron pyrites, and perhaps also of arsenic pyrites, which I could not separate from the grey copper ore which I examined. Both of these minerals could be distinctly seen in many of the specimens, intimately mixed with the grey copper ; and I have no doubt that the same mixture existed, even in those specimens which were selected as purest. The difference in the proportions of copper and arsenic, obtained by KLAPROTH * in his various analyses, is so considerable, as to lead to a suspicion, that even his specimens, in all probability, contained a mixture of foreign matter.

* GEHLEN'S Jour. vol. v. p. 9. 11. 13.