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PHILOSOPHICAL MAGAZINE,  
OR  
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OF  
CHEMISTRY, MATHEMATICS, ASTRONOMY,  
NATURAL HISTORY, AND  
GENERAL SCIENCE.

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BY  
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AND  
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"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilior quia ex alienis libamus ut apes." *Just. Lips. Monit. Polit. lib. i. cap. 1.*

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XV. *Chemical Examination of the Oxides of Manganese.* By EDWARD TURNER, M.D. F.R.S. Ed. Professor of Chemistry in the University of London, and Fellow of the Royal College of Physicians of Edinburgh.

[Concluded from p. 35.]

PART II.

*On the Composition of the Ores of Manganese described by Mr. Haidinger.*

*Method of Analysis.*—**P**URE fragments of the ores were carefully selected, reduced to fine powder in a mortar of agate, and washed with distilled water. Some of the ores yielded nothing to the action of water; but from some of them, especially from those of Ihfeld, minute quantities of the muriate and sulphate of lime, and sometimes of soda, were separated by the action of water. It is the accidental presence of the muriates which gives rise to the disengagement of chlorine when sulphuric acid is added to some of the native oxides of manganese, and which induced Mr. Macmullin to regard chloric acid as a constituent of these ores. For the correction of this error we are indebted to Mr. Richard Phillips\*, with whose observation my own experiments correspond;—none of the native oxides yield a trace of chlorine on the addition of sulphuric acid, provided the muriates have been previously removed by washing.

The ores, before being submitted to analysis, were dried at 212° F., by which means they were brought to the same degree of dryness which they possessed before being washed. The water naturally contained in them was ascertained in every instance by heating a known quantity of the ore to redness, and collecting the water in a tube filled with fragments of the chloride of calcium.

The quantity of oxygen was in most cases ascertained both by bringing the ore to the state of red oxide by exposure to a white heat, and by converting it into the protoxide by means of heat and hydrogen gas. When performed with the precautions stated in the first part of this communication, either of these methods may be relied on with confidence; but the first is more convenient in general practice, because it requires less time and a more simple apparatus. The latter is sometimes very troublesome, owing to the difficulty with which some of the ores of manganese, the native peroxide for example, are

\* Phil. Mag. and Annals, vol. i. p. 313.

reduced

reduced by hydrogen to the state of pure protoxide. I have in no instance estimated the quantity of oxygen by means of the deutoxide, the formation of this compound being in my opinion too uncertain to admit of any analytic process being founded upon it.

In searching for the presence of foreign matters I have employed the following processes. The water which was expelled from the ores by heat, was examined with test paper, but was always found quite free from alkaline or acid reaction. The absence of carbonates was ascertained by the entire want of effervescence on the addition of dilute nitric acid. Strong sulphuric acid did not cause the evolution of chlorine or any acid fumes.

On dissolving the ores in muriatic acid and evaporating the solution to perfect dryness, the residue, with the exception of a little siliceous matter and red oxide of manganese proceeding from slight decomposition of the chloride, was always completely redissolved by water. This circumstance demonstrates the absence of phosphoric and arsenic acids, which, if present, would have been left as the insoluble phosphate or arseniate of manganese. By well known methods I satisfied myself of the absence of sulphuric acid, alumina, and magnesia. In several of the ores the oxalate of ammonia detected a trace of lime. It is remarkable that every species, with one exception, contains baryta. In most of them, indeed, it is present only as an impurity; but in two of the ores, the uncleavable manganese-ore or black hematite, and the *manganese oxidé noir barytifère* of Haüy, it is an essential ingredient of the mixture. In those species in which this earth exists as an impurity, it is not united with the sulphuric or carbonic acid; but is most probably combined with the peroxide of manganese.

From the frequency with which iron has been found accompanying the ores of manganese, I was led to expect its presence, and employed the ferrocyanate of potash and hydrosulphuret of ammonia as re-agents for its detection. The muriatic solution of the different species yielded a white precipitate with the ferrocyanate of potash, and the characteristic flesh-coloured sulphuret of manganese with the hydrosulphuret of ammonia. It hence follows that all the ores submitted to analysis, even the uncleavable manganese-ore, which has been placed among the ores of iron, are perfectly free from iron, as well as from copper, lead, and similar metallic substances.

*Analysis of Manganite or the Prismatic Manganese-ore.*—This ore, even when selected with the greatest care, yields to distilled water traces of the muriates and sulphates of lime and soda. It dissolves without residue in muriatic acid, and

is free from siliceous earth, lime, baryta, and every other impurity. It is the purest native oxide of manganese which has fallen under my notice. Its powder has a uniform brown tint, and I have been unable to observe in it any tendency to pass into the peroxide by absorbing oxygen from the air. After exposure to the air for six months, during which it was frequently moistened with distilled water, it underwent no change of weight. Cold sulphuric acid acts very feebly on this oxide. M. Gmelin\* of Heidelberg states that it is not dissolved at all by this acid in the cold, and I was at first of the same opinion: but by employing a considerable quantity of the oxide, and agitating the mixture frequently, the acid does acquire a red tint in the course of two or three days. In this respect manganite agrees with the peroxide; but differs from all the other species, which communicate a red colour to cold sulphuric acid with much greater facility.

When manganite is heated to redness it gives out 10·10 per cent of water; and the total loss from exposure to a white heat is 13·15 per cent. Deducting from the last number the amount of water, 3·05 remain as the loss in oxygen. The result of this analysis is therefore,

Red oxide.....	86·85
Oxygen.....	3·05
Water.. .....	10·10
	100·00

According to this analysis, manganite contains an oxide of manganese, 89·9 parts of which yield 3·05 of oxygen, on being converted into the red oxide. An equal quantity of pure deut-oxide, in undergoing a similar change, should lose 2·997 of oxygen.

Exposed to a strong red heat and a current of hydrogen gas, 100 parts of manganite lost 19·09 parts in one experiment, and 19·07 in another. The mean is 19·08, and subtracting 10·10 as water, 8·98 remain as oxygen. According to this analysis the manganite is composed of

Protoxide.....	80·92
Oxygen .....	8·98
Water.....	10·10
	100·00

Now as 80·92 : 8·98 :: 36 : 3·995.

\* I regret that I have been unable to obtain a sight of that volume of the *Zeitschrift der Mineralogie*, which contains M. Gmelin's paper on the composition of the oxides of manganese. My knowledge of his labours is solely derived from M. Leonhard's *Handbuch der Oryktognosie*.

From the result of both analyses it is apparent that manganite, in relation to manganese and oxygen, is a deutoxide.

Also as 89.90 : 10.10 :: 40 : 4.494.

The fourth number is so near 4.5, half an equivalent of water, that we may safely regard manganite as a compound of 80 parts or two equivalents of the deutoxide of manganese, and 9 parts or one equivalent of water.

The material for the preceding analysis was taken from a very fine crystallized specimen from Ihlefeld. The result of Gmelin's analysis of the same variety is as follows:—Red oxide 87.1, oxygen 3.4, water 9.5. The water is here certainly underrated.

The grey oxide from Undenaes in West Gothland, analysed by Arfwedson, is a similar compound.

*Analysis of the Brachytypous Manganese-ore or Braunite.*—

The colour of this ore, both in mass and in powder, is nearly black. With sulphuric acid it yields no distinct odour of chlorine. It dissolves in muriatic acid, leaving a trace of siliceous matter. The solution gives a precipitate of sulphate of baryta with sulphuric acid, but does not contain any other impurity. Of all the native oxides this is the most easily reduced to the state of protoxide by the action of hydrogen gas. The material for analysis formed part of a specimen from Elgersburg.

As a mean of two closely corresponding experiments, this oxide contains 0.949 per cent of water.

To ascertain the quantity of oxygen, 16.634 grains were exposed for half an hour to the action of hydrogen gas at a red heat. The residue weighed 14.837 grains, and had the light green tint of the protoxide. The total loss was 1.797 grains, or 10.80 per cent; and subtracting 0.949 for water, there remains 9.851 per cent as the loss in oxygen.

The baryta was precipitated by sulphuric acid from a solution in muriatic acid of 42.09 grains of the mineral. The precipitate after being heated to redness amounted to 1.44 grains, equivalent to 0.951 of a grain or 2.26 per cent of pure baryta. According to this analysis, 100 parts of the ore contain

Protoxide .....	86.94
Oxygen .....	9.851
Water.....	0.949
Baryta .....	2.260
Silica .....	a trace.

100.000.

Now 86.94 : 9.851 :: 36 : 4.079; and as the presence of water and baryta, from the small quantity of these substances,

must be regarded rather as accidental than essential to the mixture, it follows that braunite is an anhydrous deutoxide of manganese. I apprehend the baryta must be in combination with deutoxide of manganese; since, were it united with peroxide, the loss in oxygen would exceed the quantity above stated.

I am not acquainted with any analysis of this mineral by other chemists.

*Analysis of the Pyramidal Manganese-ore or Hausmannite.*—Hausmannite, before being washed, yields a faint odour of chlorine by the action of sulphuric acid. When heated to redness it gives off 0·435 per cent of water; and at a white heat the loss is only 0·65 per cent, indicating 0·215 of oxygen. When dissolved in muriatic acid, a small quantity of silica is left, amounting to 0·337 per cent; and on adding sulphuric acid to the solution, a little sulphate of baryta subsides, indicating 0·111 per cent of the pure earth. Hausmannite is accordingly resolved by this analysis into

Red oxide . . . . .	98·098
Oxygen . . . . .	0·215
Water . . . . .	0·435
Baryta . . . . .	0·111
Silica . . . . .	0·337

---

100·000

This oxide is manifestly an anhydrous red oxide of manganese. The small quantity of oxygen lost at a white heat is probably owing to the admixture of a little deutoxide or peroxide, combined with the baryta.

From some preliminary experiments on hausmannite, M. Gmelin of Heidelberg\* inferred that it is a pretty pure red oxide, an inference which entirely agrees with the result of the preceding analysis. This is the only chemical examination of hausmannite by other chemists, which I have met with. The material for my analysis was part of a specimen from Ihlefeld, for which I am indebted to the kindness of Professor Stromeyer.

*Analysis of Pyrolusite, or the Prismatic Manganese-ore.*—The following analysis was made with a compact columnar variety from Elgersburg, which has a specific gravity of 4·94, and the individuals of which have a parallel direction. With sulphuric acid it does not yield a trace of chlorine; and the only impurities which I could discover in it are silica and baryta, the former amounting to 0·513, and the latter to 0·532 per cent.

\* Leonhard's *Handbuch der Oryktognosia*.

The quantity of water was determined as usual by means of the chloride of calcium, and amounted to 1.12 per cent.

On exposing 23.746 grains of this oxide to a white heat, the loss proved to be 3.064 grains or 12.90 per cent. Subtracting 1.12 for water, there remain 11.78 as the loss of oxygen.

Accordingly, 100 parts of the pyrolusite were resolved into

Red oxide.....	84.055
Oxygen.....	11.78
Water.....	1.12
Baryta.....	0.532
Silica.....	0.513

100.000

Now, omitting the water, baryta, and silica as accidental impurities, the remaining 97.835 parts lose 11.78 parts, or 12.04 per cent of oxygen in being converted into the red oxide. On the supposition that pyrolusite is composed of one equivalent of manganese and two equivalents of oxygen, it should lose in passing into the state of red oxide exactly 12.122 per cent of oxygen, a quantity which corresponds closely with the result of analysis. It is therefore an anhydrous peroxide of manganese.

I have analysed another columnar variety of pyrolusite, which has a density of 4.819, and of which the individuals radiate from a common centre. I brought it with me from Germany, and believed it to be from Ihlefeld, as the ticket indicated; but Mr. Haidinger, after carefully inspecting several large cabinets in Germany, has been unable to discover any similar specimen which is known to have been found in that place. Its locality therefore is doubtful.

This variety is less pure than the foregoing. Before being washed, it yields chlorine on the addition of sulphuric acid; and after the muriates have been removed by distilled water, the neutral solution in muriatic acid gives traces of lime with oxalate of potash. It contains silica and baryta nearly in the same proportion as the first variety.

The following is the result of my analysis:

Red oxide.....	85.617
Oxygen.....	11.599
Water.....	1.566
Silica.....	0.558
Baryta.....	0.665
Lime.....	a trace.

100.000

Subtracting

Subtracting 2·784 as impurities, there remain 97·214 parts, which lose 11·599, or 11·931 per cent, of oxygen in being converted into the red oxide. It is therefore an anhydrous peroxide, most probably containing an admixture of some other oxide.

*Analysis of Psilomelane, or the Uncleavable Manganese-ore.*  
 —This mineral when reduced to powder has a brownish-black colour. With sulphuric acid it does not emit any odour of chlorine. It dissolves completely in muriatic acid, excepting a small quantity of silica which amounts to 0·26 per cent; and the only substances which I could detect in the solution are baryta and the oxide of manganese. Though this ore has been placed by mineralogists among the oxides of iron, under the names of Black Hematite and Black Iron-ore, pure fragments of it do not contain a trace of that metal.

When heated to redness psilomelane gives out 6·216 per cent of water. The diminution in weight occasioned by exposure to a white heat is 13·58 per cent; and on subtracting 6·216 for water, there remains 7·364 as the loss in oxygen.

To ascertain the quantity of baryta 30·028 grains of the mineral were dissolved in muriatic acid, and the baryta precipitated by means of the sulphate of soda, a considerable excess of muriatic acid being allowed to remain in the liquid, to prevent any manganese from adhering to the precipitate. The sulphate of baryta, after exposure to a red heat, amounted to 7·434 grains, equivalent, according to the atomic numbers of Dr. Thomson, to 4·914 grains, or 16·365 per cent of pure baryta.

According to this analysis, 100 parts of psilomelane have yielded of

Red oxide .....	69·795
Oxygen .....	7·364
Baryta .....	16·365
Silica .....	0·260
Water .....	6·216

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100·000

The precise atomic constitution of psilomelane is not made apparent by this analysis; and, indeed, the result is of such a nature as to leave no doubt of this mineral containing more than one oxide of manganese. For it follows, from the quantity of oxygen expelled by heat, that a considerable part of the manganese must be in the form of peroxide; but it is equally clear that the whole of it cannot be in that state, because 69·795 parts of red oxide require 9·627 instead of 7·364 parts of oxygen to constitute the peroxide. On perceiving this



this deficiency of oxygen, I at first suspected that the baryta might prevent the usual quantity of oxygen from being expelled from the peroxide by heat. Accordingly I ascertained the quantity of pure red oxide by the way of precipitation; but its amount corresponded closely with the number already stated. Psilomelane must therefore, I conceive, be a mixed mineral. I was at first disposed to regard it as a compound of baryta and peroxide of manganese, accidentally containing an admixture of some other oxide in a lower stage of oxidation; but the fact noticed by Mr. Haidinger of psilomelane being frequently and intimately associated with pyrolusite in the mineral kingdom, appears to justify the inference, that the un-cleavable manganese-ore consists essentially of some compound, in proportions not yet ascertained, of baryta and the deutoxide of manganese, and that pyrolusite is the accidental ingredient. The propriety of this view is further shown by an analysis of the following ore from Romanèche, a mineral which is analogous to psilomelane in the proportion of its ingredients, and in which an admixture of pyrolusite may be detected by the eye.

*Analysis of the Manganèse oxidé noir Barytifère from Romanèche.*—The observations of Mr. Haidinger leave no doubt of this ore being a mixed mineral; and according to my analysis it is very analogous to psilomelane. The specific gravity of some of the purest fragments which I could select, is 4.365; and the density of psilomelane, according to Mr. Haidinger, is 4.145. The colour of both minerals is similar.

The black oxide of Romanèche yields a very faint odour of chlorine with sulphuric acid. When heated to redness it gives out 4.13 per cent of water. At a white heat it loses 11.39 per cent; and after subtracting 4.13 for water, there remain 7.26 as the loss in oxygen.

In order to ascertain the quantity of baryta, 32.13 grains were dissolved in muriatic acid; and after separating a small portion of silica, which amounted to 0.953 per cent, I precipitated the baryta by means of the sulphate of soda. The insoluble sulphate, after exposure to a red heat, weighed 8.113 grains, equivalent to 5.363 grains, or 16.69 per cent of pure baryta. 100 parts of the oxide are accordingly resolved into

Red oxide . . . . .	70.967
Oxygen . . . . .	7.260
Baryta . . . . .	16.690
Silica . . . . .	0.953
Water . . . . .	4.130

100.000

This

This mineral was analysed some years ago by Vauquelin and Dolomieu; but the numbers which they have mentioned, owing to the insufficient mode of analysis employed at that time, are not entitled to any confidence.—(*Journal des Mines* ix. 778.)

**XVI. General Solution of the Problem: to represent the Parts of a given Surface on another given Surface, so that the smallest Parts of the Representation shall be similar to the corresponding Parts of the Surface represented. By C. F. GAUSS. Answer to the Prize Question proposed by the Royal Society of Sciences at Copenhagen\*.**

Ab his via sternitur ad majora.

THE author of this paper believes that he must consider the repeated selection by the Royal Society of the question which forms the subjects of it, as a proof of the importance which the Royal Society attaches to it; and has thereby been induced to submit a solution found by him some considerable time since, as the lateness of the time at which he was informed of the prize question would otherwise have prevented him from sending an answer. He regrets that the latter circumstance has obliged him to limit his inquiry to the essential part only, besides hinting some obvious applications to the projection of maps and the higher branches of geodetics. Had it not been for the near approach of the term fixed by the Society, he would have followed up several inquiries, and have detailed numerous applications of the subject to geodetical operations; all which he must now reserve to himself for another moment and another place.

December 1822.

1. The nature of a curve surface is determined by an equation between the coordinates belonging to every point of the same  $x, y, z$ . In consequence of this equation, every one of these three variable quantities may be considered as a function of the two others. It is still more general to introduce two new variable quantities  $t, u$ , and to represent each of the quantities  $x, y, z$  as a function of  $t$  and  $u$ , by which at least generally speaking, determinate values of  $t$  and  $u$  always belong to every determinate point of the surface, and *vice versa*.

2. Let  $X, Y, Z, T, U$  have the same signification for a second surface, which  $x, y, z, t, u$  had in reference to the first.

3. To represent the former surface on the second means to

\* From Prof. Schumacher's *Astronomische Abhandlungen*, No. 3.