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ART. XVI. *Analysis of two Zinc Ores from the United States of America*; by M. P. BERTHIER, Engineer in the royal Corps of Mines, (translated by the Editor from the *Annales des Mines 3d Livraison Ann. 1819.**)

THESE two minerals occur together and are very abundant. They compose the principal part of a very thick and extensive metalliferous bed contained in a grauwacke formation in New-Jersey. They occur principally in Franklin, Sparta, Stirling, Rutgers, in the county of Sussex: they are accompanied by white laminated carbonate of lime, quartz, a peculiar greenish yellow garnet, and some other substances. One of these minerals (the zinc ores) is orange red, the other is of a metallic black. We will examine them successively.

1. *The Manganesian Oxid of Zinc.*

It is to Bruce that we owe the knowledge of the red mineral.† In 1814, he published a description and analysis of it in the American Journal, (vol. 1, page 96:) he found it composed of

Oxid of zinc, - - - - -	0.92
Oxid of manganese and iron, -	0.08

It was named from its composition manganesian oxid of zinc. I have subjected this ore to many trials, and have repeated the analysis in many forms; like Bruce, I have found only oxid of zinc and oxid of manganese, but in proportions a little different from his, as will appear below.

The manganesian oxid of zinc is of an orange red, approaching blood red. It is in amorphous grains irregularly disseminated in the mass of the mineral: the fracture is

* The importance of these two ores, and respect to the memory of the late Dr. Bruce, who first made these ores known, have induced me to give the memoir entire.—*Editor.*

† Mr. Maclure had already, in 1811, transmitted the New-Jersey mineral to M. Vauquelin, who extracted from it

Protoxid of iron, - - - - -	0.45
Oxid of zinc, about - - - - -	0.50
And protoxid of manganese, - - -	0.06

but it appears that this analysis was the result of a simple trial made upon the mixed mineral.

brilliant, lamellar in one direction and slightly conchoidal in the other; the thin slivers are transparent; it is fragile, easily scratched by steel; easily pulverized; the powder is of a beautiful orange red. After long exposure to the air it becomes covered with a white pearly coating, which appears to be composed of the carbonates of zinc and manganese. Its specific gravity, according to Bruce, is 6.22.

With the common blowpipe it is infusible without addition; with borax it gives a yellowish translucent glass. Under the flame of the blowpipe fed by oxygen and hydrogen it is volatilized, diffusing at the same time a brilliant white light. It loses nothing by calcination; while it is hot it appears brown, but as it cools it gradually resumes its pristine colour.

It easily dissolves in the cold in the mineral acids, and even in the acetic acid. During the solution heat is evolved, but without effervescence, and the liquor remains colourless. Still, with the muriatic acid it produces a solution of a brownish red, which, without the disengagement of any gas, gradually loses its colour: it is probable that a little chlorine is really but very gradually disengaged.* The oxids of zinc and manganese appear to have a great disposition to unite, and their complete separation is very difficult. To accomplish this object, I have employed six processes, of which I proceed to announce the results.

1. I have repeated the process of Bruce, which consists in pouring into a nitric solution of the two oxids the oxalic acid, as long as there is any precipitate, and then in washing and calcining the residuum. Bruce regarded the calcined precipitate as pure oxid of zinc[?], but I have remarked, that it always retains a very notable quantity of manganese, and that this is the reason why it always retains a foul yellow colour, more or less deep—a fact which Bruce observed without searching for the cause. The oxid of manganese is almost perfectly pure, and contains only that portion of iron, which, when the solution has not been made with the greatest caution, is accidentally present. Bruce, then, was able to obtain by this process, only an inferior quantity of manganese, to what really exists in the manganesian oxid of zinc.

* We are not told whether the *odour* of chlorine is perceptible.—*Editor*.

2. I precipitated the two oxids from their solution, by means of an alkaline sub-carbonate, having taken the precaution to boil the liquor, that it might not retain any portion: I calcined the precipitate with the contact of air, till the manganese was oxidized to a maximum, and afterwards, in one trial, I treated it with nitric, and in another with acetic acid—I evaporated it gently to dryness, and treated it again with water. Oxid of manganese remained perfectly pure, but the solution which contained the zinc, retained also a notable quantity of manganese; and when this solution was precipitated by an alkaline carbonat, the calcined precipitate was of a dirty yellow, more or less deep. By treating this precipitate anew, by means of acetic acid, a little oxid of manganese is separated, but much the greater part always remains with the oxid of zinc.

3. I precipitated the two oxids by caustic potash in excess, and allowed it to digest for some time—it was then filtered. The liquor contained nothing but oxid of zinc; but the residuum contained still a large quantity of this oxid, and it was necessary to redissolve, to precipitate anew by potash, and to repeat this operation many times, in order to complete the separation.

4. I precipitated the solution of the mineral by an alkaline carbonate, and through this solution diluted with water, I passed a stream of chlorine in excess—I obtained a violet coloured liquor and a black residuum. The liquor being evaporated in the air, became colourless, and deposited pure oxid of manganese. The black residuum having been treated by acetic acid, now contained nothing but oxid of manganese. The two liquors containing the zinc, were precipitated by a sub-carbonat. The calcined precipitate had a light yellow colour, and it was found to contain about $\frac{1}{10}$ part of its weight of oxid of manganese. It is probable, that by washing very carefully with abundance of water, the precipitate of zinc and manganese, and by agitating it for a long time with chlorine, no particle of the carbonate of manganese would escape the action of this agent, and that the two metals would be perfectly separated.

5. M. Berzelius has had the kindness to communicate to me the following method which has perfectly succeeded. I precipitated by an alkaline carbonate, washed the precipitate by decantation, digested it for sometime while still

moist, in ammonia; it became immediately brown, and the filtered liquor gave by ebullition a white deposit, which, by calcination, became perfectly white; it was the pure oxid of zinc: but I remarked that the deposit that was insoluble in ammonia, almost invariably contained oxid of zinc, sometimes in considerable quantity. To remove it entirely we may redissolve and reiterate the same operation; but it is better to calcine it, and to heat it with the acetic acid, which removes from it the greater part of the manganese, and to submit to the action of the ammonia only the deposit formed in the acetous fluid, by means of the alkaline carbonate. In this manner we separate the two oxids perfectly, and with the greatest precision.

6. Indeed, I have thought, that the zinc being very volatile, and its oxid easily reducible, we may readily separate it, in the dry way, from the oxid of manganese. This was practically verified. The oxids were mixed with a determinate weight of powdered charcoal, and the mixture placed *dans un têt étroit*, slightly hollowed, which was covered by a larger head, perforated in the upper part with little holes, a white heat was applied and a very abundant white vapour was disengaged.

As soon as it was certain that this disengagement had ceased, the head was uncovered, and the matter which it contained was roasted in order to burn out the remaining charcoal; the residuum, which was brown, was weighed, and to obtain the exact proportion of the manganese, the weight of the ashes which the charcoal would leave was subtracted, a weight which had been previously determined by experiment. The oxide of manganese proved on examination not to contain the smallest quantity of zinc.

All these trials almost exactly agree in giving for the result of the analysis of the manganesian oxid of zinc:

Oxid of zinc, - - - -	0,88
Red oxid of manganese, -	0,12
	1,00

It is difficult to say in what degree of oxidizement the manganese exists in this mineral. Its colour, and the appearances which it presents with the muriatic acid, render it probable that it is, at least, in the state of deutoxid. In order to be certain that the union so difficult to be over-

come, between the oxid of zinc and the oxid of manganese, did not depend upon the intervention of any undiscovered substances, I dissolved pure oxid of zinc with the tenth part of its weight of oxid of manganese, equally pure, and heated the solution by the process described under No. 2. I obtained, as in the case of the American mineral, an acetous solution, with which the alkaline carbonates formed a precipitate, that became, in consequence of calcination, of a dirty yellow, and contained manganese.

II. *The black zinciferous mineral, the Franklinite.*

This mineral is composed of the oxid of iron, the oxid of manganese and the oxid of zinc. The association of these three oxids has never been observed, and there is every reason to suppose that it constitutes a true species; but although it shall be discovered hereafter that these oxids are merely mixed, which appears very improbable, this mixture will appear too remarkable not to be denoted always by a name. As the chemical nomenclature cannot in every instance furnish a name, I propose to give it that of the *Franklinite*, derived from Franklin, in order to remind us that it was found, for the first time, in a place to which the Americans have given the name of a great man, whose memory is venerated equally in Europe as in the new world by all the friends of science and humanity.

The appearance of this mineral is much like that of the fer oxidulé (magnetic iron.). It is of a metallic black, is magnetic but without magnetic polarity; it occurs in grains, or in amorphous masses which sometimes present crystalline faces, but they are small and of rare occurrence, and do not enable us to determine the geometrical forms to which they belong; the fracture is either uneven or conchoidal, or imperfectly lamellar; it is not very hard; the powder is of a deep red brown, which distinguishes it from the magnetic iron whose powder is black. The specific gravity is 4,87. It is scarcely affected by the muriatic acid in the cold; but, by means of this acid, we can separate the carbonate of lime and the manganesian oxid of zinc, with which it is almost always mixed, and thus we can obtain it perfectly pure. It dissolves very easily in hot muriatic acid, without effervescence but with a slight smell of chlorine. The analysis

is effected by dissolving it in muriatic acid, precipitating the solution by an alkaline carbonat, treating the wet precipitate by acetic acid to excess, evaporating to dryness by a gentle heat and removing the acetats of zinc and manganese by water; the calcined residuum is found to be the pure tri-oxid of iron. As to the zinc and manganese, they are separated by the processes pointed out above.

In a specimen from Franklin there were found :

Peroxid of iron, - - - -	0,66
Red oxid of manganese, - -	0,16
Oxid of zinc, - - - -	0,17

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As the Franklinite acts upon the magnetic needle, the iron cannot be in the state of per-oxid, but is probably oxidized in the second degree. It is evident that the manganese is at least, in the state of deutoxid, because the mineral has a brown powder, gives with muriatic acid the odour of chlorine, and its muriatic solution contains the iron entirely in the maximum state of oxidizement. It is obvious that during the solution the two oxids react upon one another, and that the oxid of iron passes to the maximum by taking away the oxigen from the oxid of manganese, which is, on the contrary, reduced to a minimum.

For the purpose of verifying the result of the humid analysis, I made the following trials:—10 gr. of the franklinite were heated in a crucible *brasqué* without addition at the temperature proper for the assay of iron. A metallic button was obtained, to which adhered a very light greenish scoria; the whole weighed 5 gr. 65; the button was of an iron grey, hard, but impressible by the file, and capable of assuming a beautiful polish; it flattened under the hammer, and was broken with difficulty; its fracture was grey and granular, the grains being crystalline; it was analysed, and found to be an alloy of iron and manganese, without a particle of zinc; the loss in the experiment then represents the oxid of zinc, and the oxigen combined in the mineral with the iron and manganese.

into another those in which the franklinite is the prevailing part—the first can be employed as ores of zinc, to afford that metal by distillation, with charcoal, or to afford brass by fusion with copper and charcoal. If we stop at the extraction of the zinc, the residuum can be advantageously melted in the high furnace to obtain the “*fonte*,” or at least it can be mixed for the same purpose, with the ores that are rich in franklinite.

As these minerals contain a considerable quantity of manganese, and their principal gangue is carbonat of lime and garnet, it is probable that they can be treated in the high furnace, without addition, and that they will prove very fusible. A “*fonte*” of excellent quality may be obtained from them, and in all probability eminently adapted for the production of the natural steel, like that which comes from the ores of spathic iron. There would be deposited in the chimnies of the high furnaces, a considerable quantity of the oxid of zinc, as is the fact in Belgium, where this substance is known under the name of *cadmie des fourneaux ou Keiss*; it is the richest and best material which can be used for the preparation of zinc and brass. It is possible that the abundance of the Keiss may somewhat impede the operation of the high furnaces, and necessitate the adoption of some particular arrangements, to extract it with facility; but the value of this substance would pay for the trouble it might occasion.

Finally, with the pure franklinite, which it will be very practicable to obtain, either by picking or washing, the trial can be made of preparing in the large way, the same alloy of iron and manganese, which I have obtained in the small way, and it can be seen whether it will not be better adapted than the common “*fonte*,” for various uses.

ART. XVII. *A new process for Nitrous Ether, by Professor ROBERT HARE, M. D.*

The making of nitrous ether is a critical process. The action of the materials will often spontaneously increase so as to produce explosion. It may be conducted with ease and safety by means of a three necked bottle represented by Fig. 7, (in the plate which exhibits the eudiometers.)