

XI. *On a native Arseniate of Lead.* By the Rev. William Gregor. Communicated by Charles Hatchett, Esq. F. R. S.

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I.

THAT the oxide of lead and the arsenic acid, might be found in the state of natural combination, is a supposition highly probable, from the strong affinity which subsists between these two substances. But the existence of such a compound has not, as I conceive, hitherto been established by such proofs, as entitle it to be ranked amongst the *decided cases* of mineralogical science. I trust, therefore, that the observations, which I have the honour of submitting to the Society, on a new* ore of lead lately discovered in the county of Cornwall, so justly celebrated as well for the variety as for the richness of its mineral productions, will not be deemed superfluous.

This mineral was raised in the mine called Huel-Unity, a very rich copper mine, in the parish of Gwennap. According to the information with which I have been favoured by Mr. WILLIAM DAVEY, a very intelligent and experienced miner in that district, it was found in a lode south of Huel-Unity principal lode, at the depth of fifty fathoms below the surface,

* It is new at least to the miners in Cornwall; nor was there, previously to this discovery, any ore resembling it to be found in that splendid collection of minerals, which my valuable friend PHILIP RASHLEIGH, Esq. has so liberally formed, and as liberally employed in the promotion of Science.

which lode underlay about two feet in the fathom south: at the depth abovementioned; this lode fell in, or formed a junction with another small lode or vein to the south, and when the junction took place, this lead ore was found. The veins of it are, in general, from six to ten inches wide, and they diverge on going west. Some particles of this lead ore have been found in the southern part, after the separation of the lodes; but the northern lode does not contain any, until the junction takes place. This ore is intermixed with some native copper, very rich gray copper, and black copper ore, and some is mixed with quartz. The walls of both veins are killas.

II. *Description.*

This mineral is regularly crystallized. The form of its most perfect crystals is an hexaedral prism; they are of different sizes, from one tenth of an inch in diameter, to the size of a hair. The longest which I have seen, do not exceed three tenths of an inch in length: these terminate in a plane, at right angles, with the axis of the prism; but the crystals of a smaller size are frequently drawn out into a very taper acuminations, which appears to be a six-sided pyramid. A number of smaller crystals are often closely packed together in bundles, which are bent in different directions, and terminate in a point. The larger crystals, either stand alone, or adhere, on their lateral planes, to the gangue, or are confusedly matted together in a mass.

Some of them are hollow, as if an internal nucleus had been destroyed: and sometimes this internal nucleus overtops the external laminæ. The gangue is a white quartz, which fre-

quently exhibits on its surface the appearance of a partial decomposition.

The red octahedral copper ore, and the copper into which that ore passes, are often intermingled with the crystals of this lead ore and imbedded in them.

The colour of these crystals consists of a variety of tints of yellow. Some are of a beautiful wine yellow resembling the Brazilian topaz: this, in the greater number of specimens, passes into a delicate Isabella-colour: whilst, in other cases, we have the honey-yellow mingled with brown hues of different intensities: so that we meet with crystals resembling dark brown sugar-candy, or common resin.

Some of the crystals are beautifully transparent, whilst others possess this quality in part only, at their extremities, or in inferior degrees throughout their whole lengths.

The external lustre in some specimens, is vitreous; in others, resinous: but in some instances their surface is partially covered by tender and delicate filaments of a silky lustre. These filaments are sometimes found in a separate state loosely adhering to quartz; and they form a variety of this fossil.

The crystals vary as to hardness. The angular fragments of the most transparent are sufficiently hard to scratch glass.

This mineral is easily reduced to powder, which has the appearance of pounded resin; it contracts a yellower tint by long exposure to the air.

The specific gravity of the purest crystals, taken at the temp. 50° FAHRENHEIT, was 6.41.

III.

A fragment of crystal exposed to the flame of the blow-pipe in a gold spoon, melted into a brownish yellow mass, which on cooling did not assume any angular figure. It remained in a state of ignition apparently unaltered; but when a piece of it was exposed to the flame on charcoal, a rapid decomposition took place, arsenical vapours were extricated, and globules of a metal, possessing the common properties of lead, were left behind.

This mineral, in a state of fine powder, is soluble in nitric acid, even without the aid of heat. Care, however, must be taken, that it does not concrete into lumps. The vessel therefore which contains it must be frequently shaken, and the nitrat of lead produced must be, from time to time, dissolved in water, and poured off from the residuum. The process of solution is, however, accelerated by a digesting heat. Some silica remains, which, as the quantity of it is variable according to circumstances, appears not to be an essential ingredient of this fossil.

The nitric solution is colourless; its transparency is not disturbed by nitrat of barytes. Nitrat of silver renders it turbid, and a small quantity of white curdly matter is deposited. Sulphuric acid and the liquid sulphats, produce copious precipitates of a white heavy matter. If the fluid be poured off from this subsided matter, and it be freed from the superfluous sulphuric acid, by the means of nitrat of barytes, it will yield, on the affusion of liquid nitrat of lead, an abundant white precipitate, which urged by the flame of the blow-pipe on a support of charcoal, resolves itself into reduced lead and arsenical vapours.

These preliminary experiments led me to the probable conclusion, that this fossil chiefly consisted of oxide of lead, arsenic acid, and a small quantity of the muriatic acid.

IV. *Analysis.*

A.

1. Fifty grains, carefully selected from crystals of a pale Isabella-colour, were reduced to a fine powder and exposed to a low red heat for about an hour. Their weight was diminished by 0.15 of a grain.

2. The yellowish powder was now transferred to a vessel of pure silver, and mixed with a lixivium containing fifty grains of potash, prepared by the means of alcohol; a quantity, which I had previously ascertained to be sufficient to effect a complete decomposition of this mineral. The ley was gradually evaporated to dryness in a sand-bath. The soluble part was extracted by distilled water, and poured off from a yellowish white matter, which was sufficientlyedulcorated (*a*).

3. Liquid nitrat of ammonia was now dropped into the alkaline fluid, as long as it produced any cloudiness: the clear fluid was now decanted from a small quantity of white matter, which had subsided, and rendered acid by nitric acid; ammonia, added to excess, produced a slight turbidness. These precipitates, after sufficientedulcoration, were added to the yellowish white residuum (*a*).

4. The liquid was now rendered slightly acid by nitric acid, and a solution of nitrat* of lead in distilled water was dropped

* If the colourless liquid *oxynitrat* of lead be dropped into a dilute solution of arsenic acid, or of arseniat of potash acidulated by nitric acid, no immediate precipita-

into it, as long as it separated any precipitate. The clear fluid was poured off, and evaporated nearly to dryness, and a small quantity of white matter, thus obtained, was added to the former precipitate, which dried, and exposed to a low red heat weighed, whilst still warm, 40.8, which, according to the proportion of 33:100, established by Mr. CHENEVIX, implies 13.46 of arsenic acid.

5. The superfluous lead was now separated from the fluid by sulphat of soda, and filtered off. Ammonia precipitated a minute portion of flaky matter; it weighed, after ignition, 0.2 of a grain; it consisted of silica and oxide of lead, and must be attributed to the nitrat of lead employed.

B.

1. The yellowish white residuum (*a*) (A, § 2.) was dissolved without effervescence in nitric acid, except a minute portion of silica, which, after ignition, = 0.28. A white heavy matter was thrown down from this solution, by liquid sulphat of soda. The clear decanted fluid was evaporated to a small volume, and sulphat of soda produced a further separation of white matter; It was sulphat of lead, which after exposure to a low red heat, and weighed, whilst warm, = 47.5, which, upon the supposition that one hundred parts of sulphat of lead contain 69.74 of lead + 3.48 of oxygen, is equivalent to 34.77 of oxide of lead.

2. The fluid, now freed from lead, deposited, on the affusion of an arseniat of lead is produced; but crystalline grains are, after a time, gradually deposited at the bottom of the vessel. But liquid *nitrat* of lead causes an immediate and abundant precipitate from these same dilute solutions. These two combinations therefore must be different.

sion of ammonia, a greenish matter, which, after ignition, became red, and = 0.033 of a grain. It was oxide of iron.

C.

1. One hundred grains of larger crystals, some of which were hollow, and the surfaces of which were slightly and partially covered with silky filaments, treated in the same way yielded 95.28g of sulphat of lead equivalent to 69.76 of oxide, and 80 of arseniat of lead, which indicates 26.40 of arsenic acid. The oxide of iron, in this case, amounted to only .05 of a grain, and the residuary silica was in too small a quantity to be weighed.

2. I have endeavoured to decompose this fossil by boiling it to dryness in a solution of four times its weight of the purest subcarbonat of potash, and exposing the dry mass, for a very short time, to a low red heat; but I found, that only a part of the arsenic acid had united to the alkali; the larger portion of it was detected in the nitric solution of the residuum; but the relative proportions of the oxide and the acid, were found to correspond almost exactly with the foregoing statement of them.

3. I found also, that carbonat of ammonia precipitated this mineral, *in an unaltered state*, from its solution in nitric acid: as no arsenic acid had united with the precipitant. The solution of the nitrat of ammonia was evaporated to dryness, and exposed to a red heat in a platina crucible; but nothing was left, except a slight trace of oxide of lead. We may infer from hence, the absence of both the fixed alkalies.

4. I found in one specimen only of this fossil any notable difference in the relative proportions of the oxide of lead and

of the acid, to which it is united. It consisted of crystals confusedly matted together in a more compact mass, than this fossil generally assumes. One hundred grains were dissolved in nitric acid; the marine acid was separated by nitrat of silver, and any redundant silver by muriat of ammonia. The lead was separated by sulphuric acid, and the superfluous portion of that acid by nitrat of barytes, and the arsenic acid was combined with the oxide of lead by the affusion of nitrat of lead. The muriat of silver = 9.8; the sulphat of lead = 97.6, and the arseniat of lead = 72, equivalent to 1.63 of muriatic acid, 71.46 of oxide of lead, and 23.88 of arsenic acid, respectively. The quartz = 0.35, and the oxide of iron .02, nearly,

Another portion taken from the same specimen treated with an alkali, gave very nearly a similar result.

D.

It will now be necessary for me to speak concerning an ingredient of this fossil, which I may have seemed to overlook. I mean the muriatic acid: I have found some difficulty in ascertaining the proportion which it bears to the other constituent parts, and from a cause, which I did not suspect. I considered that the only sure mode of determining this point, was to have recourse to nitrat of silver, which might effect a direct separation of the marine acid from the nitric solution of this fossil. But I found, in many experiments upon given quantities of this mineral, that the results, which I derived from this most valuable chemical test, were variable and uncertain.

At last, I was enabled to trace the error and uncertainty up to two sources. In the first place, I found that the muriat of

silver was more abundant in the cases, where I employed a vessel with a long neck for the solution, and *did not expose it to heat*.

I concluded therefore, that when the process was conducted under different circumstances, the predominating *mass* of nitric acid produced its effect, and volatilized a portion of the muriatic.

Another source of error I found in the following anomalous circumstance, *viz.* a simultaneous precipitation of a portion of arseniat of lead takes place with that of the muriat of silver. Whatever combination this may be, it is a weak one, and may be severed by nitric acid, which dissolves the arseniat and leaves the muriat; or by ammonia, which takes up the muriat, to the exclusion of the arseniat.

The conclusion, to which many experiments have led me, is this, that the muriat of silver produced in the nitric solution of one hundred grains of arseniat of lead by nitrat of silver, amounts to about 9.5.

E.

In order to prove that the acid, which is combined with the oxide of lead in this mineral, *is the arsenic acid*, and that it is not combined with phosphoric, I decomposed some of its acid, which had been combined with lead in the foregoing experiments, by means of sulphuric acid, and filtered off the sulphat of lead. The fluid which passed through the filter was evaporated nearly to dryness, and it assumed the appearance of crystalline grains. Some of it was exposed to the flame of the blow-pipe in a gold spoon; at first it became like a white dry powder, which melted before an increased heat: placed

on *charcoal* and ignited, it was totally dissipated in arsenical fumes.

Some of it was dissolved in water, and dropped into liquid sulphat of titanium, a white precipitate was produced: combined with soda, it precipitated silver from the nitrat of silver, of a brick colour. It precipitated mercury from its nitrat, of a yellowish colour, which afterwards became reddish. This precipitate exposed to the flame of the blow-pipe on charcoal, exhibited the same phenomena as arseniat of mercury.

I precipitated magnesia from its muriat, and redissolved it by carbonat of ammonia, perfectly saturated with carbonic acid. I divided this liquid into two portions, and dropped into *both* a solution of the combination of the acid of this mineral and soda. No precipitate was produced. I dropped into *one* of the vessels some liquid phosphat of soda, and a separation of saline matter was instantly produced. I soon, however, found, that this mode of distinguishing the phosphoric from the arsenic acid could not be depended upon. For in the other vessel, in which no phosphat of soda had been dropped, in a short time, saline tufts made their appearance, and an abundant deposition of saline matter was formed. I found also, that if the solution had been more concentrated, the precipitation would have immediately taken place.

On making a comparative experiment with arsenic acid, I found that it forms a triple salt with ammonia and magnesia, analogous to the phosphoric salt described by Dr. WOLLASTON. The figure of the arsenical salt, as far as I could determine it from a confused crystallization, is a triedral prism.

We are therefore, I think, authorized from the experiments herein detailed, to conclude, that the fossil which is the subject

of this paper, is an arseniat of lead, and that if we state that the relative proportion of the constituent parts of it are in one hundred, as follows, we shall not be far from the truth :

Oxide of lead	-	69.76
Arsenic acid	-	26.40
Muriatic acid	- -	1.58

The silica and the oxide of iron, which account for a portion of the loss, and the alumina and copper which are sometimes found in an analysis of this fossil, I do not conceive to be essential to it.

The existence of a minute portion of muriatic acid as a constant ingredient of it, is a curious fact: and it is still more curious, when we consider it in connexion with the analogy, that in this particular it maintains with the natural phosphats of lead.

Creed, March 1, 1809.