

XVII. *On the Analysis of a Mineral Substance from New South Wales. In a Letter from Josiah Wedgwood, Esq. F. R. S. and A. S. to Sir Joseph Banks, Bart. P. R. S.*

Read April 15, 1790.

DEAR SIR,

Etruria, March 12, 1790.

I HAVE the pleasure of acquainting you, that the clay from Sydney-Cove, which you did me the honour of submitting to my examination, is an excellent material for pottery, and may certainly be made the basis of a valuable manufacture for our infant colony there. Of the species of ware which may be produced from it, you will have some idea from the medallions I have sent for your inspection.

The other mineral, which you favoured me with a specimen of, seems to me to contain one substance hitherto unknown, and another not known in the state of purity in which it is here found. I shall therefore take the liberty of stating, as concisely as I can, the principal results of the experiments that have been made upon it by myself and my assistant Mr. CHISOLM; submitting it to your judgement, whether any of them be of importance enough to be laid before the Royal Society.

I have the honour to be, &c.

JOS. WEDGWOOD.

Analytical

*Analytical experiments on a Mineral from Sydney-Cove in
New South Wales.*

THIS mineral is a mixture of fine white sand, a soft white earth, some colourless micaceous particles, and a few black ones resembling black mica or black-lead; partly loose or detached from one another, and partly cohering together in little friable lumps.

None of these substances seem to be at all acted upon by the nitrous acid, concentrated or diluted; nor by oil of vitriol diluted with about equal its measure of water; in the cold, or in a boiling heat; the mineral remained unaltered in its appearance, and the acids had extracted nothing from it that could be precipitated by alkali.

Oil of vitriol boiled upon the mineral to dryness, as in the process of making alum from clay, produced no apparent change in it; but a lixivium made from this dry mass with water, on being saturated with alkali, became somewhat turbid, and deposited, exceeding slowly, a white earth in a gelatinous state, too small in quantity for any particular examination; but which, from its aspect, from the manner in which it was obtained, and from the taste of the lixivium before the addition of the alkali, was judged to be the aluminous earth.

The marine acid, during digestion, seemed to have as little action as the other two; but on pouring in some water, with a view only to dilute and wash out the remaining part of the acid, a remarkable difference presented itself; the liquor became instantly white as milk, with a fine white curdly substance intermixed; the strong acid having extracted something which the simple dilution with water precipitated.

The white matter being washed off, more spirit of salt was added to the remainder, and the digestion repeated, with a long tube inserted into the mouth of the glass, so as nearly to prevent evaporation. The acid, when cold and settled fine, was poured off clear; and on diluting it with water, the same milky appearance was produced as at first.

The digestion was repeated several times successively, with fresh quantities of the acid, till no milkiness appeared on dilution. The quantity of mineral employed was 24 grains; and the residuum, after the operations, washed and dried, weighed somewhat more than 19 grains; so that about one-fifth of it had been dissolved. In some parcels of the mineral, taken up promiscuously, the proportion of soluble matter was much less, and in none greater. It is only the white part, and only a portion of this, that the acid appears to act upon: the white sand, much of the white soft earth, and all the black particles, remain unaltered.

To try whether this tedious process of solution could be expedited by triture or calcination, some of the mineral was rubbed in a mortar; and in doing this, it appeared pretty remarkable, that though the black part bore but an inconsiderable proportion to the rest, yet the whiteness of the other was soon covered and suppressed by it, the whole becoming an uniformly black, shining, soft, unctuous mass, like black-lead rubbed in the same manner; with a few gritty particles perceptible on pressing hard with the pestle. A penny-weight of this mixt, spread thin on the bottom of a porcelain vessel, was calcined about an hour, with a fire between 30 and 40 degrees *; it became of an uniform, dull, white, or grey colour, excepting

* By degrees of *fire*, or of heat *above ignition*, I mean those of my thermometer;

excepting a very few, and very small, sparkling, black particles, suspected to be those which had eluded the action of the pestle; it lost in weight six grains, or one-fourth.

The mineral, thus ground and calcined, was found to be just as difficult of solution as in its crude state; with this additional disadvantage, that the undissolved fine particles are indisposed to settle from the liquor.

In all the experiments of dissolution, as often as the heat was at or near the boiling point of the acid, frequent, and pretty singular, bursts or explosions happened, though the matter lay very thin in a broad-bottomed glass. They were sometimes so considerable as to throw off a porcelain cup with which the glass was covered, and once to shatter the glass in pieces. In a heat a little below this, the extraction seemed to be equally complete, though more slow; but a heat a little below that in which wax melts, or below 140° of FAHRENHEIT's thermometer, appeared insufficient.

To determine the degree of dilution necessary for the precipitation of the dissolved substance, and whether the precipitation by water be total, a measure of the solution was poured into a large glass, and the same measure of water added repeatedly. The third addition of water occasioned a slight milkiness, which increased more and more to the sixth. The liquor being then filtered off, another measure of water produced a little fresh milkiness; and an eighth rather increased it; a ninth and a tenth had no effect. The liquor being now again passed through a filter, solution of salt of tartar did not in the least alter its transparency; so that, after the solution

meter; and some idea may be formed of their value, by recollecting, that they commence at visible redness; and that the extreme heat of a good air-furnace, of the common construction, is 160° , or a little more.

has been diluted with eight or nine times its measure of water, there is nothing left in it that alkali can precipitate.

From the manner in which the solution is necessarily prepared, it cannot but contain a great redundance of acid; for the small quantity of acid, sufficient for holding the soluble part suspended, would be soaked up or entangled by the undissolved part, so as scarcely to admit of any being poured off; and it cannot be diluted, or washed out, but by the strong acid itself. The solution with which the above experiment was made was reckoned to have only about six grains of the soluble matter to three ounces of spirit of salt, having been prepared by digesting that quantity of the spirit by half an ounce at a time on thirty grains of the crude mineral.

A *saturated* solution was obtained by digesting, in a small portion of the solutions thus prepared, the precipitate thrown down by water from the larger portions till the acid would take up no more. A solution, thus saturated, cannot bear the smallest quantity of water, a single drop, on the first contact, producing a milky circle round it.

Examination of the above substance, extracted from the mineral by marine acid, and precipitated by water.

This substance, washed and dried, is indissoluble in water, as indeed might be expected from the manner of its preparation.

Nor is it acted upon by the nitrous or vitriolic acids, concentrated or diluted, cold or hot; nor by alkaline solutions, mild or caustic, of the volatile or fixed kind.

It is dissolved by strong marine acid, but not without the assistance of nearly the same degree of heat that is necessary for its extraction from the mineral. From this solution it is

precipitated by water; and, after repeated dissolutions and precipitations, it appears to have suffered no decomposition or change.

Spirit of nitre, added to the saturated solution, makes no precipitation; and if the quantity of nitrous acid exceeds, or at least does not fall much short of, that of marine acid in the solution, the mixture suffers no precipitation from water. Nor does any precipitation happen, though the nitrous spirit be *previously* mixed with even a large quantity of water; provided the quantity of solution added to it does not exceed that of the nitrous spirit in the mixture. The appropriate menstruum for this substance (that is, for keeping it in a state of dilute solution) appears therefore to be aqua regia; and the due proportions of the two acids, of any given strength, might be determined, if necessary, with greater accuracy and facility for this than for any other body I know of; because, if there be even a very minute surplus of marine acid in the solution, that surplus will instantly betray itself on dropping a little into water, all that was dissolved by *it*, and no more, being precipitated by the water. It may be observed, however, that where an addition of nitrous acid is used, a *saturated* solution cannot be obtained (unless by subsequent evaporation), the same quantity of marine acid being necessary with as without that addition: the change, or modification, which the nitrous acid produces in the marine, serves, in the present instance, not for effecting the solution, as in the case of gold and some other metals, but merely for enabling it to bear water without depositing its contents.

Oil of vitriol, dropped into the saturated marine solution, occasions no change till its quantity comes to be about equal to that of the solution; a considerable effervescence and heat are then

then produced, the liquor becomes milky, and the marine acid is extricated in its usual white fumes. The mixture, heated nearly to boiling, becomes transparent, and afterwards continues so in the cold. This vitriolic solution is precipitated by water, and the precipitate is re-dissolved by marine acid.

The saturated marine solution is indisposed to crystallize. By continued evaporation in gentle heat, it becomes thick and butyraceous, and in this state it soon liquefies again on exposure to the air. The butyraceous mass, in colour whitish or pale yellow, is not corrosive, like the similar preparations made from some metallic bodies; nor is it more pungent in taste, but rather less so than the combination of the same acid with calcareous earth. In a heat increased nearly to ignition, the acid is disengaged, and rises in white fumes, which, received in a cold phial, condense into colourless drops, without any appearance of sublimate. From the remaining white mass, spirit of nitre extracts so little as to exhibit only a slight milkiness on adding alkali; a proof that nearly all the marine acid had been expelled; for, while that acid remains, the whole is dissoluble by the nitrous.

The substance in question is not precipitated by Prussian lixivium. A drop or two of the lixivium do indeed occasion a little white or bluish-white precipitation in the *saturated* marine solution; but in the more dilute no turbidness appears till the quantity of lixivium is such as to produce that effect by its mere water; and when the precipitate has at length been formed, it re-dissolves in marine acid as easily as that made by water; whereas the precipitates resulting from the union of the Prussian matter are not acted upon by acids, till that matter has been extracted from them by an alkali. For further satisfaction in this important point, the experiment was

repeated with a solution in aqua regia. Here the Prussian lixivium, in whatever quantity it was added, occasioned no precipitation at all (only the usual bluishness, arising from the iron always found in the common acids); and pure alkali, added afterwards, precipitated the original white substance unchanged.

The following experiments of precipitation by alkalies were made with the marine solution, before the effect of an addition of nitrous acid had been discovered; and they were made with so much care and attention, that it was not thought necessary to repeat them afterwards. To obviate, as much as possible, the equivocal results that might arise from *water* contained in the precipitants, the different alkalies were applied in the dryest state I could reduce them to; *viz.* pure *salt of tartar*, kept for some time in a heat just below redness; crystals of *marine alkali*, melted and dried in the same manner; *volatile alkali* in crystals, a little surplus acid being, in this instance, previously added to the solution, to counteract the water of crystallization in the alkali; *salt of tartar causticated* by quicklime, and hastily evaporated to dryness; the *marine alkali causticated* in like manner; and the vapour of *caustic volatile alkali* arising, with a very gentle heat, from a retort into a phial containing the solution. All these alkalies occasioned copious precipitations. All the precipitates, after washing and drying, were found to re-dissolve in marine acid; and, from all these solutions, the original substance was precipitated, unaltered, on diluting them with water.

In strong fire, from 142 to 156 degrees, this substance discovers a much greater fusibility than any of the known simple earths. In a small vessel, made of tobacco-pipe clay, it melted, and glazed the bottom; and on a bed of powdered flint, pressed

smooth in the manner of a cupel, it did the same. Magnesia, or chalk, would indeed vitrify in the clay vessel; but on flint, no one of the known earths shews any tendency to vitrification in that heat *. In a cavity, scooped in a lump of chalk, this substance, in the heat above mentioned, run into a small round bead, smooth, whitish, and opaque, not in the least adhering to the calcareous mass. On a bed of powdered quicklime it formed a brownish scoria, which in great part had sunk into the lime, and seemed to have united with it. On Mr. HENRY'S magnesia, uncalcined, it melted and sunk in completely, leaving only a slight brownish stain on the surface where it had lain. On beds of the baroselenite and barytic quicklime, it likewise melted and sunk in, leaving a discoloured spot behind; but whether it really united with the substrata, or only penetrated into their interstices, could not be determined with certainty, on account of the smallness of the quantity of the mineral I had to work upon.

On a bed of powdered charcoal, in a crucible closely luted, this substance likewise melted; and therefore it may be pre-

* It may be proper just to mention, that I find this to be a very commodious and sure method of trying, in small, whether any given earthy body be fusible with other earths. If the body is disposed to vitrify with any proportion of clay or flint, for instance, it will equally vitrify when a little of it is applied, or even dusted only, on the bottom of a small cup made of clay, or on a smooth close bed of finely powdered flint. The body, in this mode of application, seems to unite with only just so much of the matter of the substratum as is requisite for their most perfect fusion together, and has nothing else in contact with it, so that no deception can arise; whereas, if *mixed* with the same matter, there might be no appearance of fusion, unless certain favourable proportions of the two should chance to be hit upon; and even then, if the quantity be small, it would not be certain but that the fusion might have originated from the matter of the crucible.

found not to have owed its fusion, in the above experiments, to the same cause to which some of the common simple earths, in certain circumstances, owe theirs, namely, their union with the matter of the vessel or support, that is, with an earth or earths of a different kind from themselves; but to possess a fusibility strictly its own, which takes place in a fire of 150 degrees, or perhaps less.

As charcoal in fine powder assumes a kind of fluidity in the fire, similar to that which powdered gypsum exhibits in a small heat, its surface had changed from concave to horizontal, and the bead had sunk to the bottom; it was rough and black on the outside, and whitish within. On repeating the experiment in a cavity scooped in a piece of charcoal, the result was a blackish bead like the former, only smooth on the outside, with something of metallic brightness, not unlike that of black-lead. Both beads were very light, and had a considerable cavity within. All the internal part was whitish, without the least metallic aspect; and the external glossy blackness appeared to be only the stain which charcoal powder communicates, in strong fire, to some earthy bodies that have a tendency to vitrify. By boiling in concentrated marine acid a part of the beads was dissolved, precipitable as at first by water; but an accident prevented the process from being continued sufficiently to determine whether the whole could be dissolved or not.

By this fusibility in the fire; solubility in one only of the common mineral acids, and parting with the acid in a heat below ignition; precipitability by water, and non-precipitability by Prussian lixivium; this substance is strongly discriminated from all the known earths and metallic calces. And as it suffers no decomposition from any of the alkalies, in any of

the usual modes of application, I presume, it cannot be considered as a combination of any of those earths or calces with any of the known acids; for all the combinations of this kind would, in one or other of the above methods of trial, have had the earth or metal disengaged from the acid.

Whether this substance belongs to the *earthy* or *metallic* class, I cannot absolutely determine; but am inclined to refer it to the earthy; because, though brought into perfect fusion, in contact with inflammable matter, and in close vessels, it does not assume the appearance which metallic bodies do in that circumstance.

Examination of the black particles.

These particles, which bore but a very small proportion to the other matter, were in form of shining black scales, very thin, and very light. One grain weight of them, carefully picked out, exposed to a fire which was gradually raised to about 90°, and continued in all about 40 hours, in a vessel loosely covered, was almost wholly dissipated, and what little remained was perfectly white. Marine acid had no effect on it.

Fifteen grains of the entire mineral lost, in the same fire, three grains. After separating from another portion of the mineral, by washing and otherwise, a considerable quantity of the white matter, 15 grains of the remainder, containing of course more than its due proportion of the black, lost five grains; so that it seems principally to be the substance on which the blackness depends that is destroyed or dissipated by fire. The same quantity, 15 grains, of common black-lead lost in the same fire above 14 grains, the residuum weighing less than one grain.

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Though no conclusion can be drawn from these experiments respecting the comparative *loss* of black-lead and the *pure* black matter of this mineral, on account of the heterogeneous parts intermixed with the latter, the *colour* of the residua seems to afford a sufficient discrimination between them; that of black-lead being dark reddish brown, but the others purely and uniformly white.

As this substance could not now be supposed to be either iron mica, or the common kind of black-lead, suspicion fell upon molybdæna. I had not, at that time, had an opportunity of procuring a specimen of molybdæna to compare it with; but from the singular and strongly-marked properties of the molybdænic acid, discovered by SCHEELÉ, it was judged, that a very small quantity of it, when disengaged from the sulphur with which it is naturally combined, would easily be distinguishable.

HJELM'S process for disengaging the sulphur, by repeatedly burning linseed oil upon the molybdæna in a crucible, and afterwards abstracting successive quantities of the same oil from it in a retort, was tried on a portion of the Sydney-Cove mineral, from which much of the white matter had been separated as above mentioned. The black coal, remaining in the retort, became yellow by calcination, as that of molybdæna should do; but in this yellow powder, no vestige of molybdænic acid could be discovered.

Another quantity of the mineral was submitted to SCHEELÉ'S own process, *viz.* repeated abstractions of *diluted* nitrous acid; but, instead of becoming whiter every time, and at length white as chalk, which molybdæna should do, the blackness of this matter continued unaltered to the last.

There is one circumstance in Mr. SCHEELÉ's experiments, which, though omitted by those who have given abstracts of them, may deserve, on the present occasion, to be more particularly noticed. He reduced the molybdæna into fine powder, and poured upon it *concentrated* nitrous acid: "the mixture," he says, "was hardly lukewarm in the retort, when it passed all "together into the recipient with great heat;" and it was for *this* reason that he afterwards used *diluted* acid. Presuming that this violent action of the concentrated nitrous acid might afford a decisive criterion of molybdæna, I had the black residuum, after five or six abstractions of the diluted acid, ground fine upon a levigating glass, and returned into the retort, with six times its weight of smoking spirit of nitre. The heat was increased cautiously far beyond lukewarm, but no commotion could be perceived, except the explosions already mentioned, which always took place when the mixture was near boiling. The distillation was continued to dryness, and repeated five times with the smoking acid; but the mineral remained just as black as it was at first.

Now, as SCHEELÉ's molybdæna is slowly decomposed by the diluted nitrous acid, and rapidly acted upon by the concentrated acid, while the black part of this mineral obstinately resists both, I think we cannot hesitate to conclude, that this black substance is not SCHEELÉ's molybdæna. There are some other circumstances which confirm this conclusion, although, taken singly, they would not, perhaps, be of much weight, considering the great proportion of other matter here mixed with the black. The principal of these circumstances are, that it yields no flowers before a blow-pipe, and that its particles seem to have no flexibility or elasticity, the only difficulty
of

of reducing it into fine powder arising from a property of another kind, unctuousity.

The difference, above taken notice of, between this black matter and common black-lead, consists only in the former leaving on calcination a white substance, seemingly siliceous, and the latter a brown ferruginous one. In their aspect, unctuousity, resistance to acids, and the volatility (in open fire) of that part in which the blackness consists, they perfectly agree; and they appear to agree also in the nature or constitution of this volatile part; for the Sydney-Cove mineral, as well as black-lead, deflagrates and effervesces very strongly with nitre, produces an hepatic impregnation on fusion with vitriolated alkali, but none with pure alkali, and is manifestly rich in inflammable matter, without sulphur.

It seems, therefore, that this substance is a *pure* species of plumbago, or black-lead, not taken notice of by any writer I have met with. FOURCROY, in the last edition of his Chemistry, looks upon iron as an essential component part of black-lead, to which, accordingly, he gives a new name expressive of that metal, *carbure de fer*. LAVOISIER, in his Elements of Chemistry, lately published, mentions a *carbure* of zinc also, and says that both these carbures are called plumbago, or black-lead. The quantity of mineral I had been furnished with was too far exhausted, before I met with this observation, to admit of any further experiments, for determining the presence of zinc in it; but those already stated, with the recollection of some circumstances attending them, persuade me, that *that* metallic body has no share in its composition. Neither before the blow-pipe, nor in calcination, was there any appearance of the peculiar flame, or flowers, by which

zinc

zinc is so strongly characterised: if any such appearance had taken place, it could not have escaped notice, as some of the calcinations were particularly attended to during the process, though with a different view, the discovery of sulphur or arsenic. The white matter which remains after the calcination is certainly not calx of zinc, for it was not acted on by spirit of salt, cold or hot, while the calces of zinc are dissolved rapidly by that acid, even in the cold.

