



## VII. Analysis of the spinel ruby

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the tides and currents; and others, a change in the earth's centre of gravity, occasioned either by deposits transported by rivers to the sea, or by the progressive movement of some masses detached from the interior parts of the earth supposed to be concave\*.

[To be continued.]

VII. *Analysis of the Spinel Ruby.* By C. VAUQUELIN, *Inspector of Mines and Member of the French National Institute.* From *Journal des Mines*, No. XXXVIII.

IRON and manganese have long been considered as almost the only metals employed by nature to colour minerals; but though these metals may assume a multitude of different shades according to the proportions of oxygen which they contain, we however often see in nature bodies possessed of colours which neither iron nor manganese ever formed artificially or naturally when pure, and it is probable that we shall one day find many other colouring metals and also stones and earths.

I have already announced that the colour of the emerald, which all chemists ascribed to iron, is owing to the oxyd of chrome. In examining the peculiar red colour of the spinel ruby with the results of the analysis lately made of it by Professor Klaproth, I began to doubt of that rich and beautiful colour being produced by the oxyd of iron, of which the Professor found only 1.5 in 100†. My doubts in this respect were still increased by reading in Bergmann that the ruby fused with borax communicates to it a beautiful green

\* 12. To observe whether there are not daily formed different kinds of stones in the places which are washed by the waters of the sea. C.

† The number, nature and proportion of the principles found by Klaproth in the spinel ruby are stated as follows: Alumine 76; siliceous earth 16; magnesia 8; oxyd of iron 1.5:—Total 101.5.

colour,

colour, as well as by a passage of Klaproth, in which he says, that magnesia extracted from that precious stone, being dissolved in the sulphuric acid, had given to it a green colour. The rubies of different colours preserved in collections, such as the sapphire-blue in the possession of the Hon. Mr. Greville, the green belonging to Mr. Hawkins, and the white in the collection of Mr. Macie of London, authorised me to suspect that iron is not the colouring principle of that stone.

These different considerations induced me to make a new analysis of the spinel ruby: and the result of this labour will prove, that my doubts were not without foundation, and that it not only does not contain a single particle of the oxyd of iron, but that there is even no siliceous earth in it, as announced by Klaproth. The rubies employed for this analysis were crystallised, transparent, and free from any foreign mixture.

EXP. I. A hundred parts of this stone being exposed to a violent heat, lost nothing of their weight, but their tint was weakened and changed to a rose colour.

II. A hundred parts of the same stone reduced to a fine powder, and strongly heated in a charcoal crucible, were agglutinated into one mass of a greenish grey colour.

III. A hundred parts of the small fragments of rubies reduced to an impalpable powder in a mortar of flint, were increased five parts.

IV. I heated for an hour, in a silver crucible, 100 parts of a ruby thus pulverised, with 300 parts of caustic potash: the mixture was not fused; on the contrary it was reduced to a pulverulent mass of a green colour, of which some particles were merely agglutinated. I mixed this with distilled water, in which it was all so nearly dissolved that there remained of it only some particles which weighed scarcely three parts. I poured upon the solution, which remained still mixed with the undissolved matter above-mentioned, some diluted muriatic acid. The first portions of this acid made the solution assume the appearance of a mass as thick as soup (*bouillie*), which was redissolved,

dissolved, at least for the greater part, by additional quantities of the acid. I warmed the solution by a gentle heat, and having filtered it, there remained on the paper three parts of a rose-coloured powder, which was ruby, not decomposed. This I placed apart, that I might operate only on that portion which had been attacked.

V. The muriatic solution above mentioned having been evaporated to dryness by a gentle heat, I poured upon the residuum a large quantity of distilled water: almost the whole of it was dissolved. There remained only five parts of a grey powder, which melted with borax, to which it communicated a green colour.

VI. I subjected these five parts to different tests, which shewed, that they were filiceous earth mixed with a little alumine, and coloured by a matter, of which I shall speak hereafter\*.

VII. I precipitated the muriatic solution of Exp. V. with carbonat of ammonia. When I judged that I had added a sufficient quantity, I boiled the mixture for a quarter of an hour, in order to expel the carbonic acid, and favour the precipitation of the lime or magnesia, if there were any of these in it. By these means I obtained an abundant white precipitate, which I boiled with a solution of caustic potash. The greater part of this precipitate was dissolved. There remained only  $10\frac{1}{2}$  parts of a brown substance inclining to violet, but which turned to a yellowish-green colour, by drying in a gentle heat.

\* In another analysis of the ruby I had for residuum, after the evaporation of the muriatic solution, but five parts and a half of filiceous earth, slightly coloured green, and without any mixture of alumine. This difference arises from the degree of heat given to the matter towards the end of the evaporation, or from the saline mass not being equally stirred throughout. In the latter case it happens that there are parts which dry too much, and others which do not dry sufficiently. Hence it happens that molecularæ of alumine are abandoned by the acid, while molecularæ of silica remain combined; and this was the case in my first analysis.

VIII. These

VIII. These  $10\frac{1}{2}$  parts were dissolved by the sulphuric acid. The solution had a greenish colour. This solution mixed with the saturated carbonat of potash, precipitated a greenish matter, which, when washed and dried, weighed two parts. A small portion of this precipitate melted with borax communicated to it a beautiful emerald green colour\*. This matter, which I placed apart, I shall speak of hereafter.

IX. As I had dissolved in the sulphuric acid 10.5 of matter, and as the carbonat of potash precipitated only 2, there must have remained 8.5 in the solution. Suspecting therefore that the matter was retained there by an excess of the carbonic acid, I boiled the liquor for some minutes, and I obtained a white granulated precipitate, weighing 16 parts, which by calcination were reduced to 8. This matter, combined with the sulphuric acid, gave a salt crystallized in tetrahedral prisms, terminated by pyramids with four faces, the taste of which was first sweet, and afterwards bitter; which was not precipitated by the saturated carbonat of potash; was only partly so by ammonia; and, in a word, which presented all the characters of sulphat of magnesia. The ruby therefore, according to this experiment, should contain 8 parts of magnesia in 100; but as  $\frac{1}{2}$  part was wanting in that subjected to experiment, we may estimate the quantity at 8.5.

\* In heating the colouring matter of the ruby with borax over charcoal, and stopping the operation before the effervescence had ceased, I have twice obtained a vitreous globule of a red colour, perfectly similar to that of the ruby; but in heating again this red globule, the effervescence was renewed, and the globule became of an emerald green colour. In vain did I afterwards try to make the red colour re-appear, whether I applied the exterior or the interior flame of the blow-pipe. It is even very difficult to obtain, in the first instance, the vitreous globule of a red colour. It is necessary for that purpose that the colouring matter should not touch the charcoal; that it should not be added till the borax is melted; and that it should be heated with the exterior flame. Though I often attempted to produce this phenomenon, I never succeeded but twice.

X. I united the five parts of Ex. VI. and the two parts of Ex. IX; boiled them five or six times successively in a porcelain vessel with concentrated nitric acid, evaporating each time to dryness. The matter at first assumed a beautiful dark green colour, and at the end of each operation it boiled and was puffed up like alum. At last, when the greater part of the acid was evaporated, and the matter began to dry, it assumed an orange yellow colour. After treating the matter in this manner, I mixed with it a little pure caustic potash; and when the mixture was well formed and reduced to a kind of paste, I diluted it with distilled water, in which almost the whole of the matter was dissolved. Nothing remained but a little grey matter which weighed about  $1\frac{1}{2}$  parts, and which I found to be siliceous earth. The alkaline solution had a weak golden yellow colour; and as it contained an excess of alkali, I added, in order that it might be saturated, a few drops of nitric acid. By this addition there was produced a slight white precipitate, which weighed at most one part, and which appeared to me to be alumine. The liquor had then a reddish colour.

XI. As I suspected, from all the phenomena which had appeared during the course of this analysis, that the colouring matter of the ruby was chrome, I mixed the liquor of the preceding experiment, first, with nitrat of lead, and I immediately obtained a precipitate of a beautiful orange-yellow colour; second, with nitrat of mercury, and there was produced a deposit of a cinnabar red colour; and, third, with the nitrat of silver, which gave a precipitate of a crimson red colour. I was convinced by these phenomena that the ruby, like the emerald of Peru, contains a certain quantity of chrome, to which it is indebted for its colour. But it seems difficult at first to reconcile the colour of the emerald with that of the ruby, by referring them to the same substance; for nothing seems more remote from green than red. If we however recollect that this metal is susceptible  
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of assuming different colours according to the quantities of oxygen which it absorbs; that when it is saturated with this principle, it is red and acid; and when it contains less, it is green, and in the state of an oxyd, we shall readily conceive how this oxydated metal may colour the emerald and the ruby. It follows then from these considerations, that chrome exists in the emerald in the state of an oxyd, and in the ruby in the state of an acid; and that this acid is there, doubtless, in a saline combination with alumine or magnesia, and perhaps with both at the same time. With regard to the proportion of the chromic acid in the ruby, I have not been able to determine it very accurately, on account of the affinity which it has with alumine, from which it is difficult to separate it completely. I am however of opinion that it may be estimated, without committing any very sensible error, at between 5 and 6 parts in 100 of ruby.

XII. I now return to the solution of alumine in caustic potash (Exp. VII.). I super-saturated it with the muriatic acid, and precipitated it afterwards by the carbonat of ammonia. The deposit washed and kept at a red heat for a considerable time weighed 85 parts. This matter had all the properties of alumine. As I had however scarcely found any filiceous earth during the course of this analysis, and as Klaproth says that he obtained 16 in 100 parts of this stone, I wished to assure myself whether there might not be some of it remaining in the alumine. For that purpose I dissolved the 82 parts above-mentioned in the sulphuric acid, and I indeed obtained an insoluble residuum which weighed three parts, and which was filiceous earth. This, with the  $1\frac{1}{2}$  part obtained (Exp. X.), makes  $4\frac{1}{2}$  parts. But it must be recollected, that during the pulverisation of the 100 parts of ruby, the details of the analysis of which I have explained, 5 parts were taken from the mortar of flint; from which it follows, that the  $4\frac{1}{2}$  parts of this substance found in the course of these operations did not belong to the ruby. Whatever  
method

method I employed, and whatever care I took, I could never obtain a larger quantity, and therefore it is very probable that Klaproth was deceived in this respect.

Now, to establish the proportions of the principles of the ruby, I must here observe, that of 100 parts subjected to analysis, 97 only were attacked; but 97 having furnished 85 of alumine (Exp. XII.), 3 of which were to be taken away for the filiceous earth, 100 would have given 82.47; 8.5 of magnesia having been obtained from these 97, 8.78 would have been found in 100. In the like manner, instead of 6 of the chromic acid, we should have had 6.18. Thus, 100 parts of spinel ruby consist of alumine 82.47, magnesia 8.78, chromic acid 6.18. Loss 2.57. Total 100.

XIII. To prove the correctness of the results of the preceding analysis, I repeated it by following another method. I heated 100 parts of ruby, reduced to a fine powder, for several hours with concentrated fulphuric acid. I obtained a solution, almost complete, by the addition of a sufficient quantity of water. There remained nothing but 5 or 6 parts of a grey powder, which had all the characters of filiceous earth, and which was only mixed with a little chrome.

The solution evaporated to the consistence of syrup gave radiated crystals without solidity; but these crystals, re-dissolved in water, and the solution mixed with a sufficient quantity of the sulphat of potash, gave octaedral crystals of alum. The whole 100 parts of the ruby thus dissolved in the fulphuric acid furnished me, in several successive crystallisations, with about 800 parts \* of alum, without reckoning the latter portions which I could not entirely separate from the mother water. This mother water had a green colour, and a bitter slightly metallic taste. I diluted it with water, and mixed with it a solution of the carbonat of potash. There was formed a greenish white precipitate, which was a mixture of alumine and the oxyd of chrome. The liquor filtered

\* The same article in the *Annales de Chemie*, Messidor An. VI. states this product at 775. EDIT.



and exposed to heat deposited a white powder, which, washed and dried, weighed 17 parts, that were reduced to 8·3 by calcination. They consisted of magnesia, still mixed with a few particles of oxyd. The precipitate formed in the mother water by the carbonat of potash was treated with a solution of caustic potash. By these means the alumine was dissolved, and the oxyd of chrome remained without undergoing any sensible alteration : it weighed 5 parts.

This analysis perfectly confirms the former ; for, some slight differences in the proportions excepted, it absolutely gave the same results. It proves above all that the ruby does not contain siliceous earth, and that the small quantity found in the products was furnished by the mortar in which the stone was pounded.

I must here observe, that it does not always happen that the whole mass of the ruby is dissolved during the first operation. There remains sometimes several parts which have undergone no alteration. This depends on the time employed for ebullition, and still more on the degree of fineness to which the stone is reduced before it is subjected to trial. But when that happens, after having washed the residuum, which is insoluble in the acid, it must be dried, pounded again, and treated in the same manner as before. Nothing then ought absolutely to remain but the siliceous earth belonging to the mortar.

XIV. The muriatic acid dissolves the ruby also : but a considerable portion of it is required ; because it volatilises in a moderate heat, and without a strong degree of heat it makes no sensible impression on that substance. I observed that this acid dissolves the principles of the ruby in the same proportions as they hold between themselves in the stone ; for the portion not attacked absolutely preserves the same shade of colour as that which it had before subjected to the action of the acid. This proves that it does not dissolve one principle in preference to another, and that they are in a state of real combination in the ruby.

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From these considerations it would appear natural to consider the ruby as a saline substance, composed of two bases, alumine and magnesia, and of an acid called the chromic acid.

When I announced to the National Institute that I had not found magnesia in the ruby, I was however far from imagining that Klaproth was deceived; so much confidence did I place in the labours of that able chemist. I chose rather to conclude at that time, that the ruby I had examined was different from his. But I was in an error in that respect, as I was convinced by a new analysis, which I made of about 16 grammes of the same ruby; and it was from this latter labour, carried on in a manner somewhat different, that I established the proportions of the principles of this stone, as already enumerated. This proves the necessity of employing rather large masses, in order to find small quantities of matter. I thought it my duty to make this public acknowledgment, both that I might render justice to accuracy and to the sagacity of a man who has given so many proofs of it, and to avoid the reproach which might have been thrown out against me, of wishing to conceal an error into which I had fallen.

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VIII. *Description of a remarkable Spring of Fresh Water, which rises through the Water of the Sea. By the Abbé SPALLANZANI. From the Journal de Physique, Vol. XXIX.*

THIS spring rises through the salt water at the distance of sixty-five feet from the shore and about a mile from Spezzia. It raises itself some inches above the surface of the sea, and forms a sort of accumulation, shaped like a button of about twenty feet in diameter. This button, when the sea is perfectly calm, is full of watery radii, exceedingly perceptible. The water of which they are formed seems a little turbid; and this is very apparent, especially when it has