



# XXXIX. Short reports from the chemical laboratory of Trinity College, Dublin (nos. 2 and 3)

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XXXIX. *Short Reports from the Chemical Laboratory of Trinity College, Dublin (Nos. 2 and 3).* By J. EMERSON-REYNOLDS, M.D., M.R.I.A., Professor of Chemistry, University of Dublin\*.

No. 2.—*On Franklandite, a new Mineral Borate.*

MANY analyses have been made from time to time of sodio-calcic borates, brought chiefly from the Peruvian province of Tarapaca. Most of the analyses seem to show that the specimens of borates examined were mixtures of some predominant mineral, such as the well-defined Ulexite, with varying quantities of one or more borates containing a larger proportion of sodium than Ulexite. I have lately had the opportunity of examining a specimen of a borate from Tarapaca which has the same components as Ulexite, namely sodium, calcium, boron, oxygen, and water, but which is much richer in alkali than that mineral, and which seems to be a nearly pure specimen of the mineral with which I supposed Ulexite to be often associated. The specimen I analyzed was brought from Peru by Mr. Graves, and was kindly placed in my hands for examination by the Rev. Dr. Haughton.

The specimen consists of a felted mass of long, thin, inter-laced fibres, which are white in colour and possess a silky lustre. Under the microscope, the fibrous crystals taken from the cleanest portions of the mass were seen to be free from any but traces of granular coating, and presented the same general aspect.

The hardness is not greater than 1 ; and the specific gravity proved to be 1.65.

The mineral is easily fused, first losing much water.

The taste of the mineral is first slightly saline, owing to the presence of a little admixed common salt, and is afterwards somewhat alkaline. It is slightly soluble in water, but is easily and almost completely dissolved by dilute hydrochloric and nitric acids, the minute residue consisting of particles of clay.

When portions of the mineral mass were digested with nearly ice-cold water, a sensible quantity of chloride was dissolved out. The solution, evaporated on a glass microscopic slide, afforded the well-known crystals of sodic chloride. A little calcium was also dissolved by the water. In some of my earlier experiments upon this body I was led, through the carelessness of a junior assistant, to suppose that the percentage of chloride present was much greater than it is

\* Communicated by the Author, having been read before the Royal Irish Academy.

shown to be in the analysis given further on. The specimen taken for this analysis was carefully picked by myself from the best parts of the mass and the selected portions then mixed.

The analytical process was conducted in the following way:—

A weighed quantity of the borate was dissolved in pure dilute nitric acid; to the solution excess of silver nitrate was added, and the precipitated chloride of silver filtered off and determined. The excess of silver was then separated from the filtrate by just sufficient hydrochloric acid; a calculated excess of pure oxalic acid was next added, and the solution then rendered alkaline by ammonia. The calcic oxalate thus separated was determined in the usual way. The filtrate from the oxalate precipitate was then acidulated with hydrochloric acid, and a small quantity of sulphuric acid separated and estimated with the aid of baric nitrate, the excess of the latter being in turn removed by treatment with sulphuric acid. The solution was now transferred to a platinum dish and evaporated to a small bulk, some pure oil of vitriol added, and the heating continued in order to destroy any oxalic acid present. After evolution of gas had ceased, the liquid was allowed to cool and then treated with pure concentrated hydrofluoric acid, and heat applied to volatilize the boric fluoride. The hydrofluoric-acid treatment was twice repeated, and the heating then continued until the temperature ultimately rose to redness. The residue, consisting of sodic and potassic sulphates, was weighed, the potassium present determined with platinic chloride, and from the data obtained the proportion of potassic and of sodic sulphates then calculated.

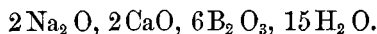
The total water was determined by ignition of a weighed quantity of the mineral in a combustion-tube with pure dry litharge; the water was collected in a calcic-chloride-tube and weighed, the whole operation being conducted as in the ordinary process of organic analysis.

In order to determine by difference the percentage of boric anhydride in the mineral, the small quantity of sulphate present was assumed to be in the form of calcic sulphate, while the chlorine found was supposed to be combined with the whole of the potassium and with its equivalent of sodium. The residual sodium and calcium were then calculated into their oxides, in accordance with the general practice of mineralogists. The sum of the percentages of impurities, sodic oxide, calcic oxide, and water, subtracted from the hundred parts, then gave the percentage of  $B_2O_3$  by difference. This result was controlled by a direct determination as potassic boro-fluoride, made in the following way. The borate was dissolved in the least possible quantity of dilute hydrochloric acid; a slight excess of

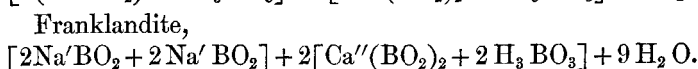
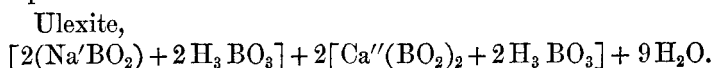
pure oil of vitriol was then added, and the liquid diluted with twenty volumes of strong alcohol. Calcic sulphate and most of the sodic sulphate separated out; the filtrate when evaporated, after addition of an excess of pure potassic hydrate, was treated with pure hydrofluoric acid, the mixture evaporated to dryness, and the insoluble salts washed away from the resulting potassic boro-fluoride by solution of potassic acetate (1 to 4 of water) followed by alcohol. Estimation of boric oxide by means of the boro-fluoride is always unsatisfactory, owing to the solubility of the body, and to the large volume of potassic acetate solution required for the removal of the saline impurities; nevertheless it is useful as a check on the indirect determination of the boron compound. The numerical value obtained by the latter method is much more worthy of confidence, though probably slightly in excess of the true amount.

		Experiment.		
Theory.		I.	II.	III.
B <sub>2</sub> O <sub>3</sub> .....	43·61	43·76 (by diff.)	41·81 (direct)	
CaO .....	11·63	12·10	...	11·94
Na <sub>2</sub> O .....	12·87	12·37		
H <sub>2</sub> O .....	28·04	27·92	...	27·66
(Na, K)Cl =				
2·41 .....				
CaSO <sub>4</sub> + 2aq. } = 1·44 ... }	...	3·85		
96·15		100·00		

If we exclude the impurities present and deal with the residue only (96·15), the analytical data (I.), when discussed in the usual way, lead well to the empirical formula which may be stated thus, according to the custom amongst mineralogists:—



Our insight into the constitution of compound borates is so limited that it is scarcely safe to assign to a new member of the class, as I believe this body to be, a “rational” formula; nevertheless it is possible to express the composition of the compound in such a way as to exhibit very clearly its probable relationship to Ulexite; for the two minerals may be thus represented:—



I have ventured to assign to the new mineral the name

“Franklandite,” with the permission of the distinguished chemist whose researches on the organo-boron compounds have contributed so materially to extend our knowledge of those interesting bodies.

Although the formulæ given above for the two minerals are not in any true sense “constitutional,” they make one point clear, namely that the substitution of one molecule of sodic oxide ( $\text{Na}_2\text{O}$ ) for three molecules of water is capable of converting Ulexite into Franklandite, so far at least as composition is concerned. As a change of this kind can evidently be effected by various indirect means, it is to be expected that mixtures of the two borates in different proportions would be found; and the observed differences in the analytical results afforded by some specimens of native sodio-calcic borates seem to indicate that such mixtures are not uncommonly met with.

No. 3.—*On the Composition of Lievrite, as determined by Mr. Early's method.*

Of the several methods which have been devised for the analysis of ferroso-ferric silicates, that which has been published by Mr. William Early\*, Demonstrator of Chemistry in this Laboratory, is probably the most easily managed. The advantages attending its use are chiefly felt in analyzing silicates, which are either insoluble in, or attacked with difficulty by the ordinary acids; but it can also be used with great convenience in the analysis of silicates easily acted upon by acids. Lievrite is a silicate belonging to the latter class; and as the formula of the mineral is by no means definitely fixed, I requested Mr. Early to analyze by his method a portion of a particularly fine crystal which I obtained some time ago from the well-known Elba locality, our chief aim being to determine with precision the relative amounts of ferrous and ferric compounds present in the specimen.

The analysis was conducted in the following manner:—

1.54 grm. of the finely and recently powdered mineral were mixed with 20 cubic centims. of hydrofluoric acid (containing 20 per cent. of real acid); and the mixture was boiled for five minutes in a deep platinum crucible with a rather loosely fitting cover. 10 cubic centims. of diluted sulphuric acid (1 part to 2 of water) were then added, and the boiling continued for a few minutes. The contents of the crucible were then washed into a flask with air-free water, and the amount of iron in the ferrous condition determined as rapidly as possible by standard potassic permanganate solution. Another quantity of the mineral was acted upon by strong hydrochloric acid; perfect decomposition was effected and a gelatinous

\* Chemical News, October 9, 1874.

mass formed; the product was evaporated to dryness, and the silica separated in the usual way. The acid filtrate from the insoluble silica was then saturated with chlorine gas, and ammonia afterwards added in slight excess; the mixture produced was then boiled in a closely covered beaker in order to remove the excess of ammonia, the solution rapidly filtered, and the precipitate collected and ignited with the usual precautions and weighed. The product contained all the iron as ferric oxide, the alumina, the manganese as  $Mn_2O_3$ , and a trace of silica. The silica was separated from this mixture by hydrochloric acid; and the filtrate was subjected to the double treatment with pure caustic soda for the separation of alumina. The iron and manganese were then separated by the baricarbonate method. From the weight of iron thus found, that previously ascertained to be present in the ferrous state was deducted; the difference represented the weight of metal in the ferric condition. The filtrate from the first precipitate caused by ammonia had the calcium separated from it as oxalate; and the latter was determined in the usual way; the filtrate from the calcium precipitate was then evaporated to dryness and the residue heated to expel ammoniacal salts; the product of this treatment was dissolved with the aid of a few drops of hydrochloric acid, the magnesium separated by means of baric hydrate and estimated, while the alkalis in the filtrate were converted into chlorides and weighed, and the potassium separated by platinic chloride. No trace of lithium was detected in the mineral.

2·841 grms. of the freshly powdered and unaltered mineral were heated gradually to redness in a hard glass tube connected with a weighed chloride-of-calcium tube; a current of dry air was at the same time slowly drawn through the apparatus. The water collected weighed ·012 grm. = ·422 per cent only.

The percentage composition of the specimen analyzed by Mr. Early may be thus stated, when the metallic and other components are calculated as oxides:—

$SiO_2$ .....	29·93
$FeO$ .....	31·83
$Fe_2O_3$ .....	20·16
$MnO$ .....	3·02
$CaO$ .....	13·71
$MgO$ .....	·30
$Al_2O_3$ .....	·36
$K_2O$ .....	·20
$Na_2O$ .....	·29
$H_2O$ .....	·42
	<hr/>
	100·22

