

ART. XLVI.—*On the chemical composition of Ralstonite*; by  
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A NUMBER of years ago Professor Geo. J. Brush generously gave one of us a specimen containing a large amount of the rare mineral ralstonite associated with thomsenolite from Arksut Fiord, Greenland. Considerable time was spent in picking out the octahedral crystals free from thomsenolite and only a partial analysis was made which was never published; difficulty was found in determining the fluorine, and the material was exhausted before a complete analysis was made. The results were essentially the same as those of Nordenskiöld.\* Since then J. Brandl† has analyzed the mineral, using material which was selected by Professor P. Groth. The results of the three analyses are as follows:

	Nordenskiöld.	Penfield.	Brandl.
Mg	5.52	4.29	3.56
Na	5.66	4.12	5.50
K	tr.	.11	----
Ca	1.99	1.67	1.53
Al	22.94	22.33	22.14
H <sub>2</sub> O	14.84	18.41	10.00
F	----	----	57.12
	<hr/> 49.95		<hr/> 99.85

\* Geol. Fören. i Stockholm. Förhandl., 1874, ii, 81.

† Annalen der Chemie, cxxiii, 7.

Only small quantities were used in making the above analyses owing to the scarcity of material and the difficulty of obtaining it free from thomsenolite. As far as the metals are concerned the three analyses agree remarkably well with one another. Nordenskiöld calculated that the 50.05 per cent of material which was not determined in his analysis, if assumed to be fluorine would not be sufficient to satisfy all the metals, and concludes that the mineral must contain some oxygen. The same would be true in Penfield's analysis. Brandl determined the fluorine directly and found it just sufficient to satisfy the metals; he proposed the formula  $3(\text{Na}_2\text{MgCa})\text{F}_2, 8\text{AlF}_3, 6\text{H}_2\text{O}$ .

The fragments which were left after selecting material for the above analysis by Penfield were carefully saved, and although we could see that they contained large quantities of ralstonite, still it was found impossible to separate the pure mineral from thomsenolite by hand picking. After selecting the purest crystal of ralstonite we could find, we took its specific gravity by just floating it in the Thoulet solution and found it to be 2.560; by the same method we found the specific gravity of cryolite to be 2.974 and thomsenolite 2.979. The great difference in specific gravity between ralstonite and the other two minerals admits of a very perfect separation by means of the Thoulet solution. All the material which we had was crushed and made to pass an eighty-mesh sieve, the finest dust was washed away by means of water and the separation carried on as usual, repeating it several times so as to remove the last traces of thomsenolite. Finally, the purest powder was floated on a solution whose specific gravity was 2.611, a few heavier particles were removed and the solution diluted to the specific gravity 2.551, when all but a trace of the powder sank to the bottom. This material, amounting to over twelve grams, showed no impurity of double refracting thomsenolite when examined under the polarizing microscope, and was used in making the following analysis.

A few remarks are necessary regarding the method of analysis. It was found to be practically impossible to decompose the mineral completely with sulphuric acid; a residue was always left which could not be dissolved by further treatment with sulphuric acid, nor with hydrochloric or nitric acids. For the determination of the metals the mineral was fused with sodium carbonate, the fusion soaked out with water, sulphuric acid was added, and the solution evaporated and ignited till the hydrofluoric and excess of sulphuric acids were expelled. The mass was then dissolved in water and the metals determined according to the usual methods. Sodium was determined once by Smith's fusion method, and again by decomposing the min-

eral as far as possible with sulphuric acid, assuming that the sodium was all in solution and the insoluble portion some compound of aluminum. Water was determined by igniting the mineral in a combustion tube, passing the vapor over dry sodium carbonate and collecting it in a weighed chloride of calcium tube. The fluorine could not be determined by driving off the silicon fluoride. About twenty-five per cent of fluorine was readily driven off; by continuing the decomposition with the temperature of the sulphuric acid about  $160^{\circ}$ , silicon fluoride was slowly, but, in the course of six or eight hours never completely given off. The greatest amount of fluorine which we were able to drive over by this method was about thirty-one per cent. This is not at all in accordance with the statement of Brandl,\* who states that the decomposition commences at  $145^{\circ}$  and is completed at  $160^{\circ}$ . We found it impossible to make a determination according to the method described by him. Our determinations are made according to the Berzelius method by fusing with mixed potassium and sodium carbonates and silica. They are probably too low by about one-half to one per cent, judging from test experiments which we made on cryolite. Our determinations are as follows:

			Mean.	Ratio.		
Mg	4.46	4.31	4.39	.183	.278	1.00
Na	4.25	4.27	$4.27 \div 46$	.093		
K	.12	.12	$.12 \div 78$	.002		
Ca	.03	---	.03			
Al	24.23	24.27	24.25	.882		3.17
F	39.76	40.05	39.91	2.101		7.56
H <sub>2</sub> O	18.72	18.74	18.73			
			91.70			

The ratio of  $(\text{MgNa}_2\text{K}_2) : \text{Al} = 1 : 3$  nearly. This ratio being assumed as correct, the ratio of the fluorine necessary to unite with the metals should be 11, whereas we only find 7.56. The fluorine is therefore not sufficient to unite with the metals and this is fully in accordance with the suggestion of Nordenskiöld. If the metals in our analysis, which are in excess of the fluorine, are united to hydroxyl, which, as has been shown to be the case in several instances, is capable of replacing fluorine, it would be necessary, in order to make the ratio  $(\text{Mg}, \text{Na}_2, \text{K}_2) : \text{Al} : (\text{F} + \text{OH}) = 1 : 3 : 11$ , to have 16.27 per cent of hydroxyl corresponding to 8.61 per cent of water; the remaining 10.12 per cent of water would then be regarded as water of crystallization, and would correspond to two molecules, making the formula of the mineral  $(\text{Mg}, \text{Na}_2)\text{Al}_3(\text{F} + \text{OH})_{11} \cdot 2\text{H}_2\text{O}$ . Making this disposition of the water, our analysis would be:

\* Loc. cit.

		Ratio.		
Mg	4.39	.183	} .278	1.00
Na	4.27	.093		
K	.12	.002		
Ca	.03			
Al	24.25		.882	3.17
F	39.91	2.101	} 3.058	11.00
OH	16.27	.957		
H <sub>2</sub> O	10.12		.562	2.02
	<hr/> 99.36			

It will be seen that the assumption that hydroxyl replaces fluorine not only makes up for the deficiency in the analysis but also leads to a very satisfactory ratio. This assumption is also well supported by actual experiment. When the mineral is cautiously heated in a closed glass tube at first neutral water, by stronger ignition acid water, is driven off. The first that comes off is undoubtedly water of crystallization, afterwards the hydroxyl is decomposed and fluorine comes off in combination with the hydrogen. By drying the air-dry powder at 100° C. there is a loss of only 0.10 per cent; by heating in an air bath to a temperature never exceeding 250° C. the mineral lost 10.37 per cent; the water goes out very slowly; the experiment was carried on for over a week, during the last three days of which the weight remained very constant. If this 10.37 per cent is regarded as water of crystallization, the remaining 8.36 per cent would correspond to 15.78 per cent of hydroxyl, which agree closely with the figures in our last analysis. The ratio of Mg:Na is almost exactly 1:1, there seems to be no simple ratio between F and OH. The excess of the aluminum in the analysis may be owing to some slight impurity. We have never seen perfectly transparent, glassy crystals of ralstonite, and their turbidity may be owing to some slight decomposition; if this is the case the alkalis would naturally be most readily removed, causing the aluminum to be too high. If our fluorine determination should be as much as one per cent too low, which is probably not the case, our results would not be materially changed. Using the actual water of crystallization and hydroxyl determinations and determining the fluorine by difference, we would have for the latter part of our analysis:

		Ratio.		
F	40.79	2.147	} 3.075 ÷ 278	11.06
OH	15.78	.928		
H <sub>2</sub> O	10.37		.576 ÷ 278	2.07

Probably this determination of fluorine by difference 40.79 per cent represents the true amount of that element more closely than the results of our actual determinations.

Assuming, as it seems fair to do, that our results and conclusions are correct and that the formula which we have proposed is the true one, namely, that the mineral is an isomorphous mixture of  $(\text{MgNa}_2)\text{Al}_3\text{F}_{11} \cdot 2\text{H}_2\text{O}$  and  $(\text{MgNa}_2)\text{Al}_3(\text{OH})_{11} \cdot 2\text{H}_2\text{O}$ , in which formulæ fluorine and hydroxyl play the same part or are isomorphous, let us see if we can in any way account for the variations in the previously published analyses, especially between Brandl's and our own, the only two complete analyses. First, we would emphasize that the greatest care was used in preparing the material for our analysis; the extremes in the specific gravity of the powder which we separated were 2.611 and 2.551, or a variation between the lightest and heaviest of only 0.060. Second, our analysis shows that our material is practically free from calcium, indicating a very complete separation from thomsenolite with which the ralstonite is so intimately associated, and showing that calcium is not an essential constituent of the mineral. Third, we were not limited regarding the amount of material which we could use, as we had an abundant supply of the pure mineral. From the same specimen from which our material was derived, one of us by very careful picking was able to obtain nearly one gram of octahedral crystals, which he supposed were pure but which, as is shown in the analysis near the beginning of this article, contained 1.67 per cent of calcium, showing that a most careful and laborious hand-picking had not been sufficient to free the small crystals wholly from thomsenolite from which the calcium was unquestionably derived. It seems highly probable that other investigators have worked with material containing slight quantities of thomsenolite. Groth,\* for instance, states that the material which he furnished to Brandl for analysis, showed under the polarizing microscope particles of a strongly double refracting mineral with quadratic habit which was unquestionably thomsenolite. If we assume that the mineral is free from calcium as our analysis indicates and that the calcium in the other analyses is all derived from thomsenolite, we should find by calculation the following figures giving the per cent of thomsenolite in the analyzed material and of the mineral free from thomsenolite.

	Nordenskiöld.	Penfield.	Brandl.	Calculated from $(\text{MgNa}_2)\text{Al}_3\text{F}_{11} \cdot 2\text{H}_2\text{O}$
Thomsenolite	11.07	9.28	8.51	- -
Mg	6.20	4.29	3.90	4.46
Na	3.95	4.27	5.05	4.27
Al	24.27	21.19	23.06	22.99
F	----		57.68	58.25
H <sub>2</sub> O	15.68	19.46	10.17	10.03
			99.85	100.00
Ratio $(\text{MgNa}_2) : \text{Al}$	$= 1.17 : 3$	$1.06 : 3$	$0.97 : 3$	

\* Zeitschr. Kryst., vii, 474.

In these analyses the ratio  $(\text{MgNa}_2):\text{Al}=1:3$  very nearly, especially considering the small quantity of mineral which was used in making the analyses and in Brandl's analysis, the only complete one, the fluorine is just sufficient to satisfy the metals, while the ratio  $(\text{MgNa}_2):\text{Al}:\text{F}:\text{H}_2\text{O}=0.97:3:10.88:2.02$ , or nearly  $1:3:11:2$ , the same as required by the formula proposed by us, only in this case the compound is a pure fluorine compound, containing no hydroxyl. Following Brandl's analysis we have given the percentage composition calculated from the above ratio in which the  $\text{Mg}:\text{Na}=1:1$ . It will be noticed how closely the figures agree with the analysis of Brandl.

The great difference in the proportion in which the metals are united,  $(\text{MgNa}_2):\text{Al}=1:3$  in ralstonite and  $\text{Ca}:\text{Na}:\text{Al}=1:1:1$  in thomsenolite, would account for the decided change in the formula derived from an analysis of a mixture of ralstonite with a little thomsenolite. Brandl's formula,  $3(\text{Na}_2\text{MgCa})\text{F}_2, 8\text{AlF}_3, 6\text{H}_2\text{O}$ , is therefore a little too low in  $\text{AlF}_3$ . The difference in the deportment of the mineral when treated with strong sulphuric acid may be owing to the fact that although the fluorine compound is readily decomposed by that acid so that Brandl was able to determine the fluorine by driving over  $\text{SiF}_4$ , the hydroxyl compound in our mineral in some way hinders the decomposition of the fluorine compound, perhaps by being in itself with difficulty decomposed and inclosing and thus protecting some of the molecules of the fluorine compound from decomposition.

In thin sections under the microscope all of the ralstonite appears very transparent and free from visible inclusions and decomposition products. Some of the crystals on the original specimen were colored yellow and where one of these had been cut through, the yellow substance was seen to consist of a very thin film, probably of iron oxide, coating the crystal. The larger crystals were zonal in structure, the zones lying parallel to the faces of the octahedron. This zonal structure is scarcely perceptible in ordinary light, being indicated by faint greyish streaks running parallel to the contours of the cross section, which could not be resolved by the use of high powers into visible inclusions. In polarized light the zonal structure was more perceptible; all of the crystals show slight double refraction and a division of the cross sections into fields reminding one of the double refraction of analcite. The slightly double refracting ralstonite with its absence of cleavage is in marked contrast to the strongly double refracting thomsenolite, showing brilliant polarization colors, blue of the second order, distinct cleavage and inclined extinction.

In closing we wish to express our thanks to Professor Geo. J. Brush for his liberality in providing us with the rare material for carrying on this investigation.

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