

THE CHEMICAL COMPOSITION OF ROEBLINGITE

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During the mineralogical and *x*-ray investigations of the Långban minerals which are at present being carried on by Professor G. Aminoff and his associates at the Mineralogical Department of the Natural History Museum, Stockholm, there was recently discovered a mineral analogous in composition to roeblingite. For further investigation of this new mineral, a knowledge of the composition of the Franklin roeblingite is, naturally, of some interest, and, as the data we possess respecting this mineral can hardly be considered sufficient and satisfactory, a sample of roeblingite from Franklin has been made a subject of a chemical analysis.

Roeblingite has been examined and described by S. L. Penfield and H. W. Foote (*American Journal of Science*, Vol. III, 1897). The averages of the percentages of two analyses in close agreement carried out by the latter, and the molecular ratios calculated from them were as follows:

	Average	Mol ratios		
SiO ₂	23.58	0.393	5.61	5.0
SO ₂	9.00	0.141	2.01	2.0
PbO	31.03	0.139	1.99	2.0
MnO	2.48	0.035		
CaO	25.95	0.463		
SrO	1.40	0.014	7.43	7
K ₂ O	0.13	0.001		
Na ₂ O	0.40	0.007		
H ₂ O	6.35	0.353	5.04	5
	100.32			

By means of, as may be seen, a very general approximation of the molecular ratios, the authors succeeded in deducing the proportions SiO₂:SO₂:PbO:RO:H₂O=5:2:2:7:5, which gives the formula H₁₀Ca₇Pb₂Si₅S₂O₂₈, and, consequently, the mineral has been interpreted as being a combination of five molecules of a silicate H₂CaSiO₄, and two molecules of a basic sulphite CaPbSO₄. The correctness of this complex formula is, however, doubted by the authors themselves.

Concerning the execution of the analyses, there may be remarked that, although the authors themselves call attention to the fact that "*the special points of interest connected with this mineral are,*

that this is the first time that a sulphite has been observed in nature . . ." they do not bring forward any quantitative analytical proof of that statement, but merely say that "*the odor of sulphurous anhydride may be obtained when the mineral is dissolved in a little hydrochloric acid, but this test is not very apparent.*" That the authors were too hasty in making this simple test the basis of the declaration that roeblingite is a sulphite will appear from the analysis given below, which will show that all the sulphur is combined as sulphur trioxide.

The "sulphur dioxide" was determined by the authors by dissolving a separate portion of the mineral in hydrochloric acid and bromine water, and precipitating the sulphuric acid as barium sulphate without previously removing the silica and lead from the solution. The barium sulphate precipitate, contaminated with silica and lead, was purified by fusion with sodium carbonate and reprecipitated by means of barium chloride. This method, however, is not to be considered as a very suitable one for removing these contaminations from the barium sulphate, as silica and more especially lead oxide, formed by the decomposition of lead carbonate during the fusion, will be partially dissolved by the leaching of the cake with water, as sodium silicate and sodium plumbite, respectively, and so they will be precipitated again with the sulphuric acid. In this way the authors have obtained an amount of sulphurous anhydride which is from 0.4 to 0.5 per cent too high. Recalculating this to sulphuric anhydride, the percentage is increased from 9.00 to 11.25, for which reason the percentage total of the analysis, with this correction and with an accurate value of the sulphur employed, should be about 2 per cent too high. In spite of this error, Foote has obtained an acceptable total for his analyses, which is due to the fact that the values as found by him of the basic constituents are too high.

The macroscopical and microscopical appearances of the material used by the present writer for a new analysis displayed perfect correspondence with those of the mineral described by Penfield and Foote, and it should be noted especially that, under the microscope, the mineral showed a thoroughly homogeneous structure of interwoven fibrous crystals.

One complete and two partial analyses of portions of the material were carried out by the writer. For each analysis and every separate determination there was used an amount of about 0.5 gram. The analytical methods were the following:

When the mineral was dissolved in dilute hydrochloric acid, no odor of sulphur dioxide was perceptible. However, in order to determine quantitatively minute traces which might be present, a weighed quantity of the mineral was dissolved in hydrochloric acid, under an atmosphere of carbon dioxide, and, after expulsion of the "sulphur dioxide" by boiling the solution, it was led into a measured volume of N/10 iodine-solution by means of a slow stream of carbon dioxide. No consumption of iodine could be observed in this operation, and so all the sulphur must be considered combined in the form of sulphuric anhydride.

For the determination of the sulphur trioxide, the mineral was fused with sodium carbonate, the cake leached with hot water and, after being partially neutralized with hydrochloric acid, the filtrate was cooled to the freezing-point and a current of carbon dioxide passed through the liquid until the red color of phenolphthalein disappeared. The precipitated lead carbonate was filtered off and, after acidifying with hydrochloric acid, the filtrate was evaporated to dryness, the silica separated and the sulphuric acid precipitated with barium chloride. The barium sulphate thus obtained was tested and found to be free from silica and lead oxide.

For the execution of the main analysis, the mineral was dissolved in dilute nitric acid, whereupon the silica was separated by a double evaporation to dryness. For the purpose of removing the nitric acid, the solution was repeatedly evaporated to dryness after the addition of hydrochloric acid. After evaporation, the residues were dissolved in dilute hydrochloric acid, and then there was added to the solution the residue from the evaporation of the silica with hydrofluoric acid, after which the lead was precipitated by hydrogen sulphide, and weighed as sulphate.

In the filtrate from the lead sulphide, the manganese (after the removal of the hydrochloric acid by evaporation with an excess of sulphuric acid) was separated from the strontium and the greater part of the calcium by means of sulphuric acid and ethyl alcohol. From the small amount of lime that remained, the manganese was separated by double precipitation with ammonium persulphate in the slightly sulphuric acidified ammonium-sulphate solution, whereupon the lime was precipitated as oxalate. The calcium and strontium sulphates were converted into carbonates by fusion with sodium carbonate and were dissolved in hydrochloric acid, calcium and strontium oxalates being formed. The collected precipitations

of the oxalates were heated to dryness at a temperature of 100°C., and weighed as $\text{Ca}(\text{Sr})\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. By means of gentle ignition they were then decomposed to carbonates, which were dissolved in nitric acid.

The nitrates were separated by treatment with amyl alcohol, and, finally, the strontium was determined as sulphate.

The determination of the alkalis was carried out according to Lawrence Smith's method. For the determination of water and carbon dioxide, there was employed a sifted powder, about 1 mm. in size, so as to avoid hygroscopical water. A portion of this prepared material, placed in a platinum vessel in a quartz tube, was heated in an electric furnace to a temperature of 1250°C., the water and carbon dioxide being carried into the absorption vessels by a current of air. By this means there were obtained the values for water and carbon dioxide reproduced in the table below. The percentage of hygroscopical water was determined by drying a finely ground portion of the mineral at 105°C. In order to ascertain if any part of the combined water was expelled at this temperature—which was likely when one considers the high value of hygroscopical water—there was also carried out a determination of water with a finely ground portion of the mineral, which gave the result that no combined water was given off at 105°C.

In the following table there are included the calculated values of the analyses, and their averages and molecular ratios.

	I	II	III	Average	Mol. ratios	A.	B.
SiO ₂	23.53	23.55	23.62	23.57	0.3924	0.4063	6.03
CO ₂	0.61	—	—	0.61	0.0139		
SO ₃	10.78	10.82	10.84	10.81	0.1350	0.1348	2.00
PbO	29.99	30.04	30.08	30.04	0.1346		
MnO	2.48	2.50	—	2.49	0.0351		
CaO	23.15	23.09	—	23.12	0.4123	0.4743	7.04
SrO	2.77	2.80	—	2.79	0.0269		
H ₂ O+ 105°	6.15	—	—	6.15	0.3414	0.3414	5.06
H ₂ O— 105°	0.45	—	—	0.45	—	—	—
				100.03			

FeO, ZnO, BaO, MgO, K₂O, Na₂O were absent.

As the molecular ratios of SO₃ and PbO are equal, it may be considered correct to combine these constituents to PbSO₄, the molec-

ular ratio of which, in column A, will then be 0.1348. It may be supposed that the small amount of carbon dioxide occurs as calcite, but it seems to the present writer more probable that this substance, too, is a constituent in the crystal-lattice of roeblingite. Furthermore, the calculation of the carbon dioxide in one way or the other does not decisively influence the formula. According to the quotients in column B, this ought to be written: $2 \text{PbSO}_4 \cdot 7 \text{RO} \cdot 6 \text{SiO}_2 \cdot 5 \text{H}_2\text{O}$; or $2 \text{PbSO}_4 \cdot \text{R}_7\text{H}_{10}\text{Si}_6\text{O}_{24}$, where $\text{R} = \text{Ca, Si, Mn}$.

This formula presents several points of agreement with that stated by Penfield and Foote, and seems to be as complicated as theirs. However, in another manner of writing, the formula $2\text{PbSO}_4 \cdot \text{R}_7\text{H}_{10}(\text{SiO}_4)_6$ is obtained, which shows roeblingite to be a combination of two molecules of lead sulphate and six molecules of an "acid" Ca-Si-Mn orthosilicate, or a combination of 2PbSO_4 with an acid Ca-Sr-Mn salt of the hypothetical acid $\text{H}_{24}\text{Si}_6\text{O}_{24}$. This interpretation of the composition of the silicate group is, from the chemical properties of the mineral—*inter alia*, no combined water is given off under a temperature of 200°C .—preferable to the theory of its being a salt with five molecules of water of crystallization of the—from a valence-chemical point of view, conceivable—acid $\text{H}_{14}\text{Si}_6\text{O}_{19}$.

There is given below, in a table, a comparison between the theoretical percentages and those actually obtained from the analyses, after replacing the carbon dioxide by its equivalent amount of silica, and strontium and manganous oxides by their equivalent amounts of lime, and recalculating to 100 per cent. The agreement

	Found	Calculated for $2\text{PbSO}_4 \cdot \text{Ca}_7\text{H}_{10}\text{Si}_6\text{O}_{24}$
SiO_2	24.90	24.86
SO_3	11.03	11.04
PbO	30.65	30.80
CaO	27.14	27.08
H_2O	6.28	6.22
	100.00	100.00

between the found and the calculated values is, as will be seen, satisfactory, and confirms the correctness of the stated formula. According to its composition, roeblingite should be grouped with

häüyne and noselite, which, too, have three molecules of orthosilicates to one sulphate group.

The chemical analysis of the Långban roebingite, as well as the *x*-ray analytical investigations of the two minerals, will be published by Professor G. Aminoff in the series "Contributions to the Mineralogy of Långban," in *Kungl. Svenska Vetenskapsakademiens Handlingar*.