Art. XI.—*On the Analysis and Chemical Composition of the Mineral Warwickite;* by W. M. Bradley.

Historical.—The mineral warwickite was first described by Shepard* in 1838 and again more fully in 1839; in the latter article he describes his method of analysis. Shepard named the new species *warwickite*, after the original locality, Warwick, Orange Co., N. Y. The mineral was found in limited quantity as small, slender crystals, imbedded in a highly crystalline white limestone. It had earlier been called hypersthene on account of the brilliant copper-red reflections afforded by its cleavage surfaces. At a second occurrence found by Young and Horton in the vicinity of the first, pieces about half an inch in diameter were obtained. These latter crystals lacked the copper-red luster characteristic of those from the first-mentioned locality, and were in a more or less decomposed condition.

From a qualitative analysis Shepard concluded that warwickite was a fluo-titanate of iron and manganese with a small percentage of yttrium. His results, however, were shown later (cf. Smith, noted below) to be erroneous and need not be discussed here.

In 1846, Hunt† published an article on a supposed new species from Warwick, N. Y., which he called *enceladite.* The material analyzed (I, below) was the impure altered warwickite examined by Shepard, as Hunt himself recognized later. His second analysis‡ (II, below) was made on a purer specimen but showed a loss of nearly 20 per cent, which he attributed to an accident. Hunt's analyses are as follows:

	I		II
SiO_2	18·50		----
TiO_2	28·20		31·50
FeO	10·59	Fe_2O_3	8·10
MgO	22·20		43·50
Al_2O_3	13·84		----
CaO	1·30		----
H_2O	7·35	Ignition	2·00
	101·98		

After the completion of Hunt's analyses several years elapsed before further work was done on this mineral. About 1853, Brush and Smith, then engaged in the re-examination

* This Journal (1), xxxiv, 313, 1838, xxxvi, 85, 1839.
† This Journal (2), ii, 30, 1846. ‡ Ibid., xi, 352, 1851.

of American minerals, pointed out that warwickite possessed a peculiar composition altogether different from what had been supposed, and that the pure mineral had not yet been analyzed. When the mineral had been subjected by the gentlemen named to a careful qualitative analysis, it was found to their great surprise to contain a large amount of boric acid, hitherto overlooked, so that it was to be considered as a boro-titanate of magnesia and iron. The quantitative analysis undertaken by Smith was made with difficulty because of the small amount of material available and from the fact that minute crystals of spinel penetrated those of warwickite. Smith, however, was finally satisfied that the results obtained expressed the true composition. The specific gravity obtained (Brush) was 3·362, and Smith's analysis is as follows:

		Oxygen	Ratio
B_2O_3	27·80	19·06	9
TiO_2	23·82	10·37	5
MgO	36·80	14·46	6
FeO	7·02	2·10	1
SiO_2	1·00		
Al_2O_3	2·21		
	98·65		

Smith regarded the silica and alumina as impurities, the latter arising from the spinel that it had been impossible to separate; this, with a little of the magnesia, he deducted in making out the oxygen ratio from which he derived the formula:

$$6MgO \cdot 1FeO \cdot 2TiO_2 \cdot 3B_2O_3.$$

Method of Analysis.—The material used for the present analysis was obtained from the Brush collection and came from Amity, N. Y., where this mineral is found as a characteristic associate of the granite contacts of the region. The warwickite occurs in minute slender crystals showing the copper-red reflections of the cleavage surfaces which is so characteristic of the pure mineral. It is found in a coarsely crystalline white limestone, intimately associated with a greenish blue spinel, black spinel, magnetite, serpentine, chondrodite and occasional scales of graphite. The limestone rock containing the minute crystals of warwickite was crushed to small fragments and these small pieces, which contained some of the mineral, were carefully selected by means of a glass. This material was again crushed and prepared for treatment with heavy solutions. Potassium mercuric iodide solution, having when concentrated a specific gravity of 3·15, was first used to separate the greater part of the calcite and serpentine. The

final separation was made by means of barium mercuric iodide with a specific gravity of 3·55.

Considerable difficulty was caused by the presence of a greenish blue glassy spinel which in the solution closely resembled the grains of warwickite, but by repeated treatment with the heavy solution the latter was obtained in a quite pure condition. The material was further purified by the action of an electro-magnet which helped to remove some of the remaining foreign material. Finally by means of a very powerful glass the few remaining grains of the associated minerals were as far as possible removed. The final sample obtained amounted to a little over two grams and was quite uniform in character.

The specific gravity, determined by means of the barium mercuric iodide solution and a Westphal balance, was found to be 3·342; this is practically the same as that given by Brush, viz.: 3·351 for small fragments.

Owing to the limited amount of material available for analysis it was desirable to determine the main constituents, B_2O_3, TiO_2, MgO and total iron in one portion. After repeated fusions of the mineral with sodium carbonate the resulting cake was soaked out and the liquid decanted through a filter, the residue being thoroughly boiled with 25^{cc} of sodium carbonate solution and transferred to the filter and finally washed with dilute sodium carbonate solution. The filtrate containing the boron was transferred to a distilling bulb and the determination of boron made by distilling with methyl alcohol, the distillate being collected in ammonium hydroxide and finally evaporated over calcium oxide. The residue left in the bulb after distillation contained a trace of titanium which was recovered and added to the main solution previous to the precipitation of the titanium. The residue from the sodium carbonate fusion was brought into solution by prolonged fusion with acid potassium sulphate, and the resulting cake dissolved in cold water to which had been added strong SO_2 water. The solution was then largely diluted and rather strongly acidified with acetic acid; the titanium precipitation being made in the presence of sodium acetate and brought about by boiling the solution from three to five minutes, strong SO_2 water being added before the boiling point was reached. The precipitate was then filtered and washed with dilute acetic acid and finally weighed as TiO_2. Some of the details of the above briefly outlined method are those recommended by Warren.*

The filtrate from the precipitation of titanium was concentrated and a very small precipitate was collected and added to

* This Journal (4), xxv, 23, 1908.

the main precipitate before igniting. A trace of iron was also precipitated at this point, and this together with a mere trace retained by the main titanium precipitate was recovered by fusing the TiO_2 with acid potassium sulphate and a volumetric determination for iron was made in the usual way with $KMnO_4$. The filtrate from the titanium precipitation containing the iron in the ferrous state was treated with nitric acid to oxidize the iron, and hydrochloric acid added to form enough ammonium chloride to keep the magnesium in solution, when ammonium hydroxide was added to precipitate the iron, etc. Double precipitations of the hydroxides were made and the weight of the mixed oxides obtained. The oxides were then fused with acid potassium sulphate, and the total iron determined as usual by titration with $KMnO_4$. Traces of titanium retained by the precipitate of ferric hydroxide were determined where present by the colorimetric method and corrections for both iron and titanium were made. The amount of the alumina present was as usual arrived at by difference. The filtrate from the ammonium hydroxide precipitation served for the determination of magnesium, which was precipitated as ammonium magnesium phosphate. This was then dissolved, reprecipitated and filtered on a Gooch crucible and finally weighed as magnesium pyrophosphate. The determination of ferrous iron was made by dissolving the mineral in a mixture of hydrofluoric and sulphuric acids, and finally titrating with $KMnO_4$, the modifications of Pratt* being used throughout the above operation.

The results of the analysis follow:—

	I	II	Average		Ratios
B_2O_3	21·21	21·36	21·29	·304	·304
TiO_2	25·06	24·66	24·86	·310	·3328
SiO_2	1·45	1·32	1·39	·0228	
MgO	35·41	36·01	35·71	·884	1·011
FeO	9·11	9·20	9·15	·127	
Fe_2O_3	4·77	4·76	4·76	·0297	
Al_2O_3	2·95	2·87	2·91	·0284	
	99·96	100·18	100·07		

The amounts of sesquioxides found are comparatively small and the ratios obtained from them have no rational relation to those obtained from the percentages of the other constituents. Disregarding the Fe_2O_3 and Al_2O_3 for the present, it will be seen that the other constituents yield,

$$B_2O_3 : TiO_2 : (Mg, Fe)O = 1 : 1·094 : 3·325.$$

* This Journal (3), xlviii, 149, 1894.

This would point to B_2O_3 . TiO_2 . 3(Mg, Fe)O as the formula for the mineral. Since, however, a glassy green spinel is so intimately associated with the warwickite and its separation from it, both on account of its closely similar specific gravity, and because under the microscope it assumes an almost metallic appearance, it is thought reasonable to assign the 2·91 per cent of Al_2O_3 found to its presence in the material analyzed. This assumption would necessitate the subtraction of an equivalent amount of MgO as required by the formula MgO . Al_2O_3. Qualitative and quantitative tests on this spinel have proven it to correspond essentially to the variety known as chlorospinel, in which a little of the Al_2O_3 is replaced by Fe_2O_3. In this particular spinel there was found 8·92 per cent of Fe_2O_3, and corrections for this isomorphous Fe_2O_3 introduced into the warwickite analysis by means of this spinel have been accordingly made.

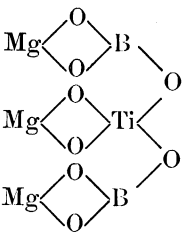
The presence of magnetite associated with the warwickite was proven by testing the impure material by the ordinary magnet. If, as is possible, it was intimately mingled with the warwickite it would be difficult to entirely separate it, as the warwickite itself is attracted easily by the electro-magnet. It seems reasonable therefore to assume that the greater part of the Fe_2O_3 found was contained in magnetite, and that an equivalent amount of FeO to correspond to FeO . Fe_2O_3 should be deducted from the analysis. Treating the analysis in this way we have the following results:

Average		Spinel	Magnetite	III	Calculated to 100		Ratio
B_2O_3	21·29			21·29	23·87	·341	1
TiO_2	24·86			24·86	27·87	·347	1·090
SiO_2	1·39			1·39	1·56	·025	
MgO	35·71	—1·26		34·45	38·63	·957	3·134
FeO	9·15		—1·95	7·20	8·07	·112	
Fe_2O_3	4·76	— ·42	—4·34				
Al_2O_3	2·91	—2·91					
	100·07			89·19	100·00		

The ratios from the corrected analysis yield B_2O_3 . TiO_2 . 3(Mg, Fe)O as before, but with sharper agreement between the theoretical and derived numbers. The formula for warwickite can then be written,

$$(Mg, Fe)_3TiB_2O_8$$

which could be developed into a symmetrical structural formula as follows:—



The theoretical composition corresponding to this formula would be

B_2O_3	=	25·81
TiO_2	=	29·54
$3MgO$	=	44·65
		100·00

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