ART. XII.—*Ludwigite from Montana*; by WALDEMAR T. SCHALLER.*Occurrence and Association.*

THE ludwigite here described was collected at Philipsburg, Montana, by Mr. Donald F. MacDonald and sent to the chemical laboratory of the Survey for determination by Mr. F. C. Calkins. It is stated to occur in metamorphosed limestone with large bodies of magnetite. An examination of a thin section showed that a member of the olivine group was sprinkled throughout the ludwigite and in addition a minute amount of a carbonate and a secondary fibrous mineral was present.

The ludwigite forms small spherulites composed of radiating fibers of a very dark green or nearly black color. In its physical properties it resembles the original ludwigite from Hungary. Under the microscope with high magnification the fibers extinguish parallel and show a strong pleochroism, parallel to the elongation a sea-green, normal thereto a chestnut-brown with stronger absorption in the brown than in the green. The refractive index is much higher than 1.67. The olivine mineral has a mean refractive index of about 1.66 and cleavage sections, parallel to b {010}, showing α and β have refractive indices lying between 1.65 and 1.66. The mineral must therefore be very low in ferrous iron and is referred to forsterite. As no calcium was noted in the analysis, the carbonate is either magnesite or siderite.

Analysis.

The sample free from magnetite but containing a small quantity of forsterite and minute amounts of the colorless fibrous mineral and the carbonate, gave on analysis the following results, the figures in the last column showing the values with the forsterite and carbonate deducted and the analysis recalculated to 100 per cent.

The ferrous iron was determined by a modification of Pratt's method,* using finely ground material. Some experiments conducted by Dr. Hillebrand on samples of this mineral showed that the oxidizing effect of grinding on the ferrous iron was slight. The first value for alumina (1.98 per cent) was obtained as the difference between the gravimetric determination of R_2O_3 and the subsequent volumetric titration

* Hillebrand, W. F. The Analysis of Silicate and Carbonate Rocks, Bull. 305, U. S. Geol. Survey, 1907, p. 138.

Analysis of Ludwigite from Montana.

	Analysis of ludwigite mixed with forsterite and carbonate.			Analysis of ludwigite.	
	1	2	3	Average	
FeO	6.12	5.53	5.74	5.79	7.27
MgO	39.09	38.60	39.42	39.04	33.78
Total iron	36.33	36.01	----	----	----
Fe ₂ O ₃	----	----	----	29.73	37.37
SiO ₂	8.97	8.74	8.85	8.85	----
Al ₂ O ₃	1.98	1.64	----	1.81	2.27
H ₂ O +	.97	----	----	.97	1.24
H ₂ O —	.91	.95	.85	.90	1.13
CO ₂	.28	.43	----	.36	----
B ₂ O ₃	13.48	----	----	13.48	16.94
				<hr/> 100.93	<hr/> 100.00

of the iron with permanganate solution. The iron and aluminum chloride solution was repeatedly evaporated with methyl alcohol to expel all the boric acid. The second value (1.64 per cent) was determined by precipitating the alumina by phenylhydrazine, as described by Allen.* As the two determinations agree fairly well, the presence of a small amount of alumina in the sample seems well confirmed. The higher result of the first case is probably due to the retention of a small amount of boric acid. Whether the alumina belongs to the ludwigite or to one of the accompanying minerals is difficult to decide, but it has here been included in the borate. The boric acid content has also been determined by Wherry and Chapin,† who give as the average of their results 12.82 per cent B₂O₃, a value slightly lower than the one here given.

The water content, though small, is still of sufficient importance to merit consideration. While no definite conclusion has been reached, it is believed that most, if not all, of the water is really unessential to the mineral. The determinations were made on the finely ground material and considerable water was thereby unquestionably taken up by the mineral.‡ As some water may also have been furnished by the secondary fibrous material, it therefore seems justifiable to conclude that a good part, if not all, of the water reported in the analysis is extraneous. It has been entirely omitted in the consideration of the ratios deduced from the analyses.

* Journ. Amer. Chem. Soc., vol. xxv, p. 421, 1903. See also Bull. 305, U. S. Geol. Survey, p. 95.

† Determination of Boric Acid in Insoluble Silicates, E. T. Wherry and W. H. Chapin. Journ. Amer. Chem. Soc., vol. xxx, p. 1691, 1908.

‡ For data on this point, see this Journal, vol. xxv, p. 328, 1908.

Discussion of Formula.

From the figures of the average analysis, the ratios were calculated and found to be as follows :

Ratios of ludwigite analysis.					
MgO	9760	-----	} 7532	4.00	{ 3.57 MgO
FeO	804	-----			
Fe ₂ O ₃	1858	[Less 1475 Mg ₂ SiO ₄	} 2035	1.08	{ .43 FeO
Al ₂ O ₃	177	and .82 MgCO ₃]			
SiO ₂	1475	-----			
CO ₂	82	-----			
B ₂ O ₃	1926	-----	1926	1.02	

The ratios agree well with the formula generally given for ludwigite, $4\text{RO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$. The high water content obtained by Whitfield,* on the Hungarian material, namely 3.62 per cent, is substantiated neither by the analysis of the Montana mineral, as given above, nor by the analysis of the material from Hungary, as described beyond. Yet both samples yield about a per cent of water which is at present impossible to prove foreign to the mineral and may, in time, be shown to be an essential constituent thereof. If the water given off above 107° (H₂O+) be considered as essential to the mineral, a formula of about the proportions $\text{RO} : \text{Fe}_2\text{O}_3 : \text{B}_2\text{O}_3 : \text{H}_2\text{O} = 16 : 4 : 4 : 1$ would result.

While the ratios agree well with the general formula of ludwigite, the amount of ferrous iron is too small (even by referring all the ferrous iron in the analysis to ludwigite and none to either the forsterite or the carbonate) for the formula $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{MgO} \cdot \text{B}_2\text{O}_3$. From the data given above, the formula for the Montana ludwigite may be written $.57\text{MgO} \cdot .43\text{FeO} \cdot 3\text{MgO} \cdot \text{B}_2\text{O}_3$, showing an isomorphous mixture of a *ferrous* ferric magnesian borate with a *magnesian* ferric magnesian borate, the latter being in excess.

As has been previously shown by the analyses of Ludwig and Sipöcz and of Whitfield and confirmed by the analysis given beyond, the Hungarian mineral approximates closely to the definite formula $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{MgO} \cdot \text{B}_2\text{O}_3$, though one analysis by Ludwig and Sipöcz shows a slight deficiency in the ferrous iron. The mineral from Montana, however, is very much lower in the ferrous iron and correspondingly higher in the magnesia, the ratios of $\text{B}_2\text{O}_3 : \text{Fe}_2\text{O}_3 : \text{FeO} + \text{MgO}$ remaining constant. There is here, then, sufficient evidence of the existence of magnesian ferric borate, $\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{MgO} \cdot \text{B}_2\text{O}_3$, free from ferrous iron, not yet found in nature in the pure state but preponderant in the Montana ludwigite, being present

* Whitfield, this Journal, vol. xxxiv, p. 284, 1887.

in isomorphous mixture with the corresponding ferrous ferric magnesian borate, to the extent of 57 per cent or over half. If some of the ferrous iron present in the sample belongs to the forsterite or the carbonate, the percentage of the magnesian borate would be still greater.

Ludwigite from Hungary.

For comparison with the above, an analysis was also made of the ludwigite from Hungary. The quantitative analysis, made on the finely radiating black mineral, is as follows:

Analysis of ludwigite from Hungary.

	1	2	3	Average
FeO	15·84	15·68	15·80	15·84
MgO	28·88	28·88	----	28·88
Total iron as Fe ₂ O ₃ ..	53·35	52·74	53·72	----
Fe ₂ O ₃	----	----	----	35·67
H ₂ O—	·50	·52	----	·51
H ₂ O+	·78	·86	----	·82
CO ₂	·90	----	----	·90
Insol.	·32	·40	----	·36
B ₂ O ₃	[17·02]	----	----	[17·02]
				<hr/> 100·00

The ratios from the average analysis give, after deducting sufficient MgO for the CO₂ to form magnesite, the formula FeO.Fe₂O₃.3MgO.B₂O₃, as shown below.

Ratios of ludwigite analysis.

FeO	·220	·99
MgO	·702	3·06
Fe ₂ O ₃	·223	1·00
B ₂ O ₃	·243	1·09
CO ₂	·020	----

Summary.

The isomorphous relation of the FeO and MgO in ludwigite can be well shown by bringing together the available analyses, which also shows how closely the mineral from Hungary agrees with the calculated values for the pure ferrous-iron ferric magnesian borate. The first column gives the calculated values for FeO.Fe₂O₃.3MgO.B₂O₃, the second, third, fourth, and fifth the analyses of the Hungarian mineral and the sixth that of ludwigite from Montana.

Analyses of ludwigite.						
	1	2	3	4	5	6
	FeO.Fe ₂ O ₃ 3MgO.B ₂ O ₃	Ludwigite from Hungary analyzed by:				Ludwigite from Montana
		Ludwig & Sipöcz	Schaller	Whitfield	Ludwig & Sipöcz	
FeO --	17.01	17.67	15.84	15.78	12.46	7.27
MgO --	28.61	26.91	28.88	30.57	31.69	33.78
Fe ₂ O ₃ -	37.81	39.29	37.67	35.93	39.92	37.37
Al ₂ O ₃ -	-----	-----	-----	-----	-----	2.27
B ₂ O ₃ --	16.57	15.06	[17.02]	12.04	16.09	16.94
MnO --	-----	tr.	-----	0.16	tr.	-----
H ₂ O --	-----	-----	0.51	-----	-----	1.13
H ₂ O +	-----	-----	0.82	3.62	-----	1.24
SiO ₂ --	-----	-----	0.36	-----	-----	-----
CO ₂ --	-----	-----	0.90	-----	-----	-----
	100.00	98.93	100.00	100.16	100.16	100.00

The second analysis (column 5) by Ludwig and Sipöcz shows a slight replacement of the ferrous iron by magnesia, carried out to a much larger extent in the mineral from Montana. All new occurrences of ludwigite should be carefully examined chemically, as the possibility of the existence of the ferrous-iron free magnesian borate is strongly indicated by the above analyses.

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