

THE COMPOSITION OF THE ALUMINIAN LUDWIGITE
FROM CRESTMORE, CALIFORNIA*WALDEMAR T. SCHALLER AND ANGELINA C. VLISIDIS,
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ABSTRACT

The black crystals of the aluminian ludwigite (Woodford's mineral B) from the limestone at Crestmore, California, gave on analysis: $B_2O_3=18.15$, $MgO=40.67$, $FeO=5.60$, $MnO=0.02$, $Al_2O_3=10.97$, $Fe_2O_3=22.59$, $TiO_2=1.50$, $SnO_2=0.24$, $H_2O- =0.07$, $H_2O+ =0.05$, insoluble=0.48; total=100.34 per cent. Specific gravity 3.64. The formula is $(Mg_{3.80}, Fe_{0.29}^{+2})(Al_{0.81}, Fe_{1.06}^{+3}, Ti_{0.07}, Sn_{0.01})B_{1.96}O_{10}$ or essentially $Mg_2(Fe^{+3}, Al)BO_3O_2$. This ludwigite has the highest known content of Al_2O_3 of any member of the ludwigite ($Mg \gg Fe^{+2}$)-vonsenite ($Fe^{+2} \gg Mg$) series.

The black crystals of ludwigite in the limestone at Crestmore, California, have been known for some time to contain an unusually high percentage of aluminum for a ludwigite. An unpublished spectrographic analysis by T. G. Kennard indicated a high percentage of Al_2O_3 as did an incomplete chemical analysis by J. D. Lauder milk whose results showed that the mineral was an anhydrous iron (mostly ferric with only a few per cent of FeO) magnesium borate and identified the mineral as ludwigite (A. O. Woodford, written communication).

This ludwigite is Woodford's mineral B. Woodford, Crippen, and Garner (1941, p. 375) state "Slender, black orthorhombic prisms up to 20 mm. in length have been found in the Sky Blue limestone (e.g. at station 31, Wet Weather quarry)." (The thickest single crystal observed by W.T.S. is 2 mm. thick.) Woodford (1943) gives the optical properties as X=pale green, Y=slightly darker green, Z=dark brown. The alpha index of refraction is given as 1.791, probably ± 0.002 and the birefringence $(\gamma-\alpha)=0.095 \pm 0.010$, hence $\gamma=1.886 \pm 0.010$.

Because of the aluminum present these values are considerably lower than those given for several ludwigites by Larsen (1921).

This occurrence differs from nearly all other occurrences of ludwigite in that the mineral is present in the limestone as single isolated crystals, mostly with many brilliant faces in the prism zone. Edgar H. Bailey, U. S. Geological Survey, also observed and measured goniometrically some crystals with terminal faces (Woodford, 1943). The usual mode of occurrence of ludwigite as finely fibrous masses, with either parallel or interwoven or radiating fibers apparently is not known for Crestmore.

A suite of the limestone specimens containing this ludwigite was sent to Schaller by Edgar H. Bailey some years ago and furnished the material used for the analysis presented here. Single larger crystals of ludwigite

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are sparsely and irregularly distributed throughout the limestone although occasionally several crystals may be grouped together and aggregates of very minute crystals occasionally are present, especially where associated with colored silicates. Very minute and long hairlike crystals are closely associated with the larger ones or may be present by themselves. Some of the crystals are apparently deeply etched whereas others seem to be the result of skeletal growth. Long curved forms of ludwigite are present at many places; if the two ends meet they will enclose limestone.

In the preparation of material for analysis, a total weight of two kilograms of the limestone was dissolved in cold 1:3 HNO_3 , yielding $78\frac{1}{2}$ grams of insoluble material of which $9\frac{1}{2}$ grams, or about 12 per cent, was ludwigite. The remainder was chiefly forsterite and a humite group mineral, probably clinohumite. No other acid insoluble borate mineral was noted. The two kilograms of limestone therefore consisted approximately of 96% carbonate, $3\frac{1}{2}$ % acid insoluble silicates, and $\frac{1}{2}$ % ludwigite. Even this low percentage of ludwigite is high for its per cent occurrence in large masses of the limestone as only the richest portions of the limestone were used. To the ludwigite crystals so obtained were added several grams of additional material previously separated and purified by Edgar H. Bailey. Before the separated crystals obtained from the limestone were crushed, several dozen of the best crystals were selected by handpicking and preserved for goniometric measurement. It was from this lot of crystals that those used in the crystal structure studied by da Silva, Clark, and Christ (1955) were selected.

For the final purification of the Crestmore ludwigite the electromagnet, isodynamic separator, methylene iodide, and handpicking were all used. In washing out the dust of the crushed sample, the wash water appeared greenish (olive-green) due to the translucency of the dust particles. This translucency indicates a low content of FeO in the ludwigite. The analyzed sample is not magnetic, that is, it does not move when tested with a small alnico magnet.

The analysis presented no unusual difficulty although the values obtained for MgO are a little high due probably to the inclusion in the ludwigite crystals of a little periclase or brucite, as discussed below.

The results of the analysis are given in Table 1.

The present analysis differs from those of other low FeO ludwigites in its high percentage of Al_2O_3 (and correspondingly low Fe_2O_3). Many analyses of ludwigite show small amounts of Al_2O_3 , usually from 1 to 3 per cent. The relatively large amount of TiO_2 present is surprising as no other titanium mineral has been noted from the Crestmore limestone, although golden yellow sphene is reported by Woodford (1943, p. 360) as

TABLE 1. ANALYSIS OF ALUMINIAN LUDWIGITE FROM CRESTMORE, CALIFORNIA
Analyst, Angelina C. Vlisidis

				Average
B ₂ O ₃	18.29%	17.91%	18.26%	18.15%
MgO	40.86	40.48	40.66	40.67
FeO	5.59	5.62	5.60	5.60
MnO	.01	.03	—	.02
Al ₂ O ₃	11.02	10.92	—	10.97
Fe ₂ O ₃	22.56	22.61	—	22.59
TiO ₂	1.50	1.50	—	1.50
SnO ₂	.31	.17	—	.24
H ₂ O ⁻	.07	—	—	.07
H ₂ O ⁺	.05	—	—	.05
CaO	None	—	—	None
Insoluble	.50	.54	.41	.48
				100.34

Specific gravity 3.64.

Total Fe as Fe₂O₃=28.78, 28.93, average 28.86 per cent.

Total R₂O₃ (gravimetric)=41.28 per cent which agrees well with the sum of 28.86 total iron+10.97 Al₂O₃+1.50 TiO₂=41.33.

being "very abundant in some pegmatites. Larger brown crystals are also fairly common."

The atomic ratios calculated from the average analysis are given in Table 2.

The formula is calculated from the analysis on the basis that the formula contains 10 oxygen atoms, that is, a total charge of -20. The equivalent e is defined as,

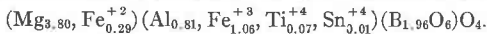
$$e = \frac{\text{formula weight}}{\text{valence of cation} \times \text{number of cations in formula}}$$

The factor $f=20/\sum e$ is an average common multiplier such that $e'=f \times e$ yields the total positive charge in each individual oxide; $e'/(valence of cation)$ is the number of cations.

These ratios are close to the standard formula of ludwigite, 4R₀·R₂O₃·B₂O₃. That of the bivalent group is a little high. The ratios of B (1.96) and of the sum of Al, Fe⁺³, Ti, Sn (1.95) are so nearly identical that it would seem as if a small quantity (estimated as less than one per cent) of an acid-soluble magnesium-rich second phase (periclase?, brucite?) was present in the sample, as an undetected impurity, accounting for the high ratio (4.09) of the bivalent elements Mg, Fe⁺², Mn. Observation of a polished mount of many fragments of the ludwigite crys-

TABLE 2. ATOMIC RATIOS CALCULATED FROM AVERAGE ANALYSIS OF ALUMINIAN LUDWIGITE FROM CRESTMORE, CALIFORNIA

	Analysis	e	$e' = 3.764 \times e$	Atomic ratios
B ₂ O ₃	18.15%	1.563	5.885	B 1.96 = 2 × 0.98
MgO	40.67	2.017	7.594	Mg 3.80
FeO	5.60	.156	.587	Fe ⁺² .29
MnO	.02	.001	.002	Mn .00
Al ₂ O ₃	10.97	.646	2.431	Al .81
Fe ₂ O ₃	22.59	.849	3.194	Fe ⁺³ 1.06
TiO ₂	1.50	.075	.283	Ti .07
SnO ₂	.24	.006	.024	Sn .01
	99.74	5.313	20.000	
H ₂ O ⁻	.07			
H ₂ O ⁺	.05			
CaO	.00			
Insoluble	.48			
	100.34			
				$f = \frac{20}{5.313} = 3.764$



tals as well as a thin section of the limestone carrying the ludwigite shows several colorless inclusions completely embedded in the ludwigite and hence not amenable to nitric acid attack until the surrounding ludwigite is dissolved away.

On a weight percentage basis the composition of this ludwigite can be interpreted to be approximately:

- 48½ per cent MgO-Fe₂O₃ borate
- 36½ per cent MgO-Al₂O₃ borate
- 10 per cent FeO-Fe₂O₃ borate
- 4½ per cent MgO-TiO₂ borate
- ½ per cent MgO-SnO₂ borate

The ludwigite-vonsenite series must then be considered at least a three component system—4MgO·Fe₂O₃·B₂O₃, 4MgO·Al₂O₃·B₂O₃, and 4FeO·Fe₂O₃·B₂O₃.

Five boron minerals are known from Crestmore. Axinite has been described by Eakle (1917). Murdoch and Webb (1940, p. 553) state "The axinite [from Inyo County] looks almost exactly like that found at Crestmore, in Riverside County, California." Axinite was also listed by Woodford (1943) as were danburite, datolite, ludwigite, and tourmaline. Axinite, datolite, and tourmaline are also mentioned by Burnham (1959) as occurring at Crestmore. Two other borate minerals, serendibite

(Richmond, 1939) and vonsenite (Eakle, 1920), apparently as yet not reported for Crestmore, occur in the several other limestone quarries surrounding Riverside.

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