LUDWIGITES FROM IDAHO AND KOREA.

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INTRODUCTION.

The ferric magnesian borate, ludwigite, which was described by Tschermak in 1874 as a new species from Hungary, was regarded as a rare mineral for 40 years. Within the past few years, however, ludwigite and closely related members of the ludwigite group have been described from six localities in the United States. Recently ludwigites from two additional localities have been received at the United States National Museum. These have been analyzed in the Museum laboratory and are described in some detail below.

LUDWIGITE FROM LEMHI COUNTY, IDAHO.

The specimen of ludwigite from Lemhi County, Idaho (catalogue number 94,145), is labeled "Copper ore, Bruce Estate." No further information accompanies the specimen. Umpleby [1] mentions that a group of claims known as the Bruce Estate extends along the mountain slope near its summit for 2 miles south from Dry Gulch in the Texas district. Lead-silver ore is reported from several claims, but the most interesting feature is a big low-grade copper deposit found in association with large quantities of magnetite. The deposit occurs on the side of a big dike, which is called "syenite" by the miners, but which is probably quartz-diorite, as an abundance of the latter and none of the former was noted in the bowlders in the gulches below.

Description and associated minerals.—The hand specimen is about half light gray and half black in color. The light gray portion is seen in thin section under the microscope to consist of a fabric of idiomorphic crystals of colorless diopside, with interstitial areas of calcite partly replaced by ludwigite, chalcopyrite, and bornite. The ludwigite forms irregular masses and prismatic needles, which are, for the most part, opaque, but which are transparent when very thin. The borate and the ore minerals are intergrown in a manner suggesting contemporaneous deposition. The darker colored portion of the

[1] Umpleby, J. B., U. S. Geol. Survey Bull. 528, p. 89, 1913.

specimen appears to the unaided eye to be made up of pure ludwigite containing irregular masses of bornite. Under the microscope the ludwigite is seen to contain disseminated crystals and ragged grains of diopside. In the replacement of the calcite-diopside rock by ludwigite and sulphides the calcite has been selectively replaced before the diopside was attacked, and residual diopside crystals showing sharp idiomorphic boundaries occur embedded in a mass of ludwigite and bornite. In an advanced stage of the replacement the diopside has been attacked and the crystal outlines destroyed.

Physical properties.—To the unaided eye the Idaho lugwigite is black in color, with a very fine felted structure, in which the fibrous structure is too fine to be detected by the unaided eye, but is manifested by a faint silky luster, which might easily be overlooked, and the material might readily be mistaken for magnetite. The hardness is above 5, as the mineral scratches apatite with ease, but is itself scratched by orthoclase. The streak is moderately dark greenish-brown. The material is not notably attracted by an ordinary magnet of the horseshoe type.

Optical properties.—The ludwigite is transparent in very thin fragments and is intensely pleochroic in tones of brown parallel to the elongation and grass green perpendicular to it. The birefringence is moderate, while the indices of refraction are high. The extinction is parallel to the elongation of the prisms.

Pyrognostics and chemical properties.—This ludwigite yields a small amount of water in the closed tube, all of which is probably extraneous. It is soluble slowly but completely in sulphuric, nitric, and hydrochloric acids. When moistened with sulphuric acid it gives the green flame of boron.

Composition.—The material for analysis was hand selected and was contaminated by small grains of included impurities. The purest pieces of the felted aggregate were selected, ground in an agate mortar, and a small amount of magnetite extracted with a magnet. The remaining material upon analysis yielded the following results:

Analysis of Ludwigite from Lemhi County, Idaho.

Silica (SiO_2)	0.90
Ferric oxide (Fe_2O_3)	35.90
Alumina (Al_2O_3)	2.08
Ferrous oxide (FeO)	5.14
Magnesia (MgO)	36.42
Lime (CaO)	Trace.
Manganous oxide (MnO)	Trace.
Copper oxide (CuO)	2.87
Boric anhydride (B_2O_3)	14.59
Water (H_2O) −105° C	.03
Water (H_2O) +105° C	2.28
Sulphur (S)	.22
Total	100.43

Since several of the constituents which are present in minor amounts are obviously present as impurities, it is difficult to decide which of these should be included as essential to the ludwigite. The copper and sulphur are certainly extraneous, a part of the former and all of the latter being present as bornite. The presence of the bornite introduces some error into the analysis, as it itself contains ferrous iron, and the hydrogen sulphide formed by the action of hydrochloric acid upon it would naturally reduce some ferric iron to the ferrous state. The copper in excess of bornite is probably present as thin staining films of chrysocolla or malachite. These impurities are, however, present in too minor amounts to affect the broader ratios of the ludwigite. The constituents which are probably essential to the mineral yield the following ratios:

Ratios of Ludwigite from Lemhi County, Idaho.

Constituent.	Per cent.	Ratios.			
FeO	5.14	0.0715	9745	9.75	1.08×4
MgO	36.42	.9030			
Fe_2O_3	35.90	.2247	2247	2.25	1.00×1
Al_2O_3	2.08	.0204	2288	2.29	1.02×1
B_2O_3	14.59	.2084			
	94.13				

The general formula derived from these ratios is, then—

$$4(Mg, Fe)O.\ \ Fe_2O_3.\ \ B_2O_3.$$

Following Schaller this composition may be interpreted as an isomorphous mixture of magnesioludwigite and ferroludwigite in the molecular proportions of approximately 7 parts of the former to 3 of the latter; or the material is, by weight, 68 per cent magnesioludwigite and 32 per cent ferroludwigite. The essential constituents given above are below recalculated to 100 per cent and compared with the percentages calculated for a mixture of this composition.

		Found.	Calculated.
MgO		38.69	37.26
FeO		5.46	5.38
Fe_2O_3		38.14	39.88
Al_2O_3	2.21	17.71	17.48
B_2O_3	15.50		
Total		100.00	100.00

The material is thus higher in the magnesioludwigite molecule than any ludwigite yet analyzed except the end member itself.

LUDWIGITE FROM KOREA.

Introduction.—The United States National Museum has received from Mr. J. Morgan Clements several specimens labeled ilvaite from Heoth 1 Kol Mine, Korea. (Cat. No. 93729 U.S.N.M.) Since the mineral was obviously the same which Koto had called ilvaite[2] and Higgins had [3] had described as a new species under the name "collbranite," its investigation was deemed necessary. Analysis has shown the material in each of the several specimens to be ludwigite.[4]

Occurrence.—The occurrence of the ludwigite has been well described by both Koto and Higgins in the papers cited, although both authors erred in their identification of the mineral. The deposit, which is mined for gold and copper, occurs as irregular masses of lime-silicate minerals at the contact of granite with limestone. The lime-silicate hornfels in irregularly impregnated with ludwigite, bornite, and chalcopyrite, mingled with some chalcopyrite and a little galena and magnetite. The less metamorphosed limestone contains a little diopside and a uniaxial variety of serpentine, while the more intensely altered phase consists of about equal volumes of calcite and contact-metamorphic minerals. This is impregnated with auriferous sulphides in addition to the ludwigite and diopside, the ludwigite-bearing limestone being the ore body of the Hol Gol Mine. Local bodies of diopside rock and of garnetite occur in the ore-bearing zone. Muscovite is mentioned by Koto as occurring in the ore while, according to Higgins, phlogopite is very abundant, masses of pure phlogopite many tons in weight being encountered at times. It is evident from the descriptions that the ludwigite is common and present in large amount in the mine.

Description of associated minerals.—The specimens examined by the writer are all very similar in appearance, all consisting of sheaves and rosettes of shining black needles of ludwigite embedded in a white or grayish-white granular groundmass. The aggregates of the ludwigite may reach a centimeter in maximum diameter and are rather uniformly disseminated in their matrix. When examined under the microscope in thin section this matrix is seen to consist in the main of calcite in large twinned grains with disseminated irregular grains of colorless diopside. All of the grains of calcite when at the position of extinction between crossed nicols, show numerous minute flakes of a mineral resembling talc as though some magnesia in the original limestone had separated out in this form during metamorphism. Small masses and grains of bornite are visible in one specimen. None of these are included in the thin sections studied and no other ore minerals were seen. The ludwigite is included in the calcite and does not encroach upon the

[2] Koto, B., Geology and Ore Deposits of the Hol-Gol Gold Mine, Journal College Science, Imperial Univ. Tokyo, vol. 27, art. 12, 1910.

[3] Higgins, D. F., Geology and Ore Deposits of the Collbran Contact, Suan Mining Concession, Korea. Economic Geology, vol. 13, p. 19, 1918.

[4] The analysis has already been published with a short note identifying collbranite with ludwigite. Shannon, E. V., Amer. Mineral, vol. 6, p. 87, 1921.

diopside. Koto[5] concludes that the ludwigite was first deposited, followed by the diopside, after which the deposition of the sulphides and recrystallization of the calcite took place.

Physical properties.—The ludwigite is entirely black in color in the hand specimen and consists of radiating or divergent aggregates of prismatic fibers. The luster is silky. The hardness is about 5.2–5.5. The streak is greenish to brownish-black and is distinctly darker than that of the Idaho ludwigite. A peculiar property of this ludwigite is its magnetism. When powdered to 60 mesh all of the particles can be picked up with a common horseshoe magnet. When powdered very finely and examined under the microscope no magnetite inclusions were found in the mineral and no magnetite was visible on polished surfaces, so that the magnetic property must belong to the borate itself. This is further discussed below.

Optical properties.—Under the microscope very thin needles are transparent, but are very deeply colored, distinctly more so than the Idaho material described above. They are markedly pleochroic, the color parallel to the elongation being brown and that perpendicular to it green, the absorption being greatest in the former direction. Owing to the deep color of the mineral the birefringence is greatly obscured and the optical character could not be determined. The indices of refraction are higher than the range of immersion media at hand.

Pyrognostics and chemical properties.—The mineral yields water (extraneous) in the closed tube. It is slowly soluble in hydrochloric, nitric, and sulphuric acids, and gives the usual reactions for boron and iron.

Chemical composition.—The ludwigite was separated from the accompanying gangue material by the use of heavy solutions. The relatively pure material thus obtained was analyzed with the following results:

Analysis of ludwigite from Korea.

Silica (SiO_2)	0.40
Ferric oxide (Fe_2O_3)	32.49
Alumina (Al_2O_3)	2.32
Boric anhydride (B_2O_3)	16.80
Ferrous oxide (FeO)	10.40
Lime (CaO)	1.86
Manganous oxide (MnO)	.36
Magnesia (MgO)	34.54
Water (H_2O) above 110° C	1.42
Total	100.59

Of the above constituents the silica, water, and lime are quite probably extraneous, the silica and lime being doubtless derived

[5] Koto, Journ. Coll. Sci. Tokyo, 1910, p. 23.

from the included gangue and the water being adsorbed. The remaining constituents yield ratios as follows:

Ratios of ludwigite from Korea.

Fe_2O_3	0.2034	0.2261	0.93×1
Al_2O_3	.0227		
B_2O_3	.2400	.2400	.99×1
Mg_3O	.8566	.8566	1.04×3.4
Fe	.1448	.1499	1.04× .6
MnO	.0051		

These ratios place the Korean ludwigite as a member of the ferroludwigite-magnesioludwigite series having three parts ferroludwigite to 2 parts of magnesioludwigite.

PREVIOUSLY DESCRIBED LUDWIGITES.

LUDWIGITE (FERROLUDWIGITE) Hungary.

The original ludwigite described by Tschermak[6] was from Morawicza in the Banat, Hungary. Here it occurs embedded in a crystalline limestone with irregularly distributed masses of magnetite. The magnetite occurs intimately intermixed with the ludwigite. The material is fibrous and blackish-green to black in color. The formula derived by Tschermak from the analysis is $3MgO.B_2O_3FeO.Fe_2O_3$. Whitfield later analyzed material from this locality and, considering the water essential, arrived at the formula $3RO.R_2O_3$ with R = Mg,-Fe,H_2 and R_2 = B and Fe.[7] Schaller[8] later confirmed the results and formula of Tschermak.

PINAKIOLITE, SWEDEN.

Pinakiolite as described by Flink[9] occurs at Langban, Wermland, Sweden, in bands in granular dolomite with hausmannite, etc. The formula deduced from the analysis is analogous to that of ludwigite, $3MgO.B_2O_3.MnO.Mn_2O_3$.

LUDWIGITE, MONTANA.

Ludwigite was found by Calkins[10] to occur abundantly with magnetite and forsterite in a contact-metamorphic deposit in limestone at the Redemption iron mine in the Philipsburg district in Montana. This material has been analyzed by Schaller[11] who found it to contain more magnesia and less ferrous iron than the original Hungarian ludwigite. He assigned to the Montana material the formula $3MgO.B_2O_3.(Mg,Fe)O.Fe_2O_3$ and predicted the existence

[6] Tschermak, G., Min. Mitth., vol. 59, 1874.
[7] Whitfield, Amer. Journ. Sci., vol. 34, p. 284, 1887.
[8] Schaller, W. T., U. S. Geol. Survey, Bull. 490, p. 30, 1911.
[9] Flink, G., Zs. Kryst., vol. 18, p. 361, 1890.
[10] Calkins, F. C., Geology and Ore Deposits of the Philipsburg quadrangle, Montana. U. S. Geol. Survey, Prof. Paper 78, p. 162, 1913.
[11] Schaller, W. T., U. S. Geol. Survey Bull. 490, p 28.

of a magnesia member free from ferrous iron, this molecule being in excess in the Montana material and having the formula

$$3MgO.B_2O_3.MgO.Fe_2O_3.$$

MAGNESIOLUDWIGITE, UTAH.

Magnesioludwigite, the magnesia end-member of the ludwigite group predicted by Schaller from his work on the Montana ludwigite, was found by Butler in nearly pure form in the Mountain Lake mine in Utah [12]. The material is ivy-green in color and it occurs in a contact metamorphosed limestone with ordinary ludwigite, magnetite, etc.

LUDWIGITE, UTAH.

Ludwigites which are apparently ordinary in composition and contain ferrous iron have been found in several localities in the Cottonwood-American Fork area in Utah [13]. The mineral occurs in large amounts mixed with magnetite and lime silicates in contact metamorphosed limestones. The material from these occurrences has not been analyzed.

VONSENITE, CALIFORNIA.

Vonsenite, described by Eakle [14] from Riverside County, California is a member of the ludwigite group which is much higher in iron than other members of the group, even the pure ferroludwigite end member as is shown by the following comparison:

	Vonsenite.	Ferroludwigite, theory.
B_2O_3	14.12	16.6
Fe_2O_3	34.82	37.9
MgO	10.71	28.5
FeO	39.75	17.0
	99.40	100.0

The material occurs with magnetite in contact zones in limestone.

GENERAL DISCUSSION.

The above descriptions include all known occurrences of the minerals of the ludwigite group. The compositions of those which have been analyzed may be expressed by the following formulas:

Ludwigite (ferroludwigite), Hungary .... $3MgO.B_2O_3.FeO.Fe_2O_3$.
Magnesioludwigite, Utah .... $3MgO.B_2O_3.MgO.Fe_2O_3$.
Pinakiolite, Sweden .... $3MgO.B_2O_3.MnO.Mn_2O_3$.
Vonsenite, California .... $3(Fe,Mg)O.B_2O_3.FeO.Fe_2O_3$.
Ludwigite, Montana .... $3MgO.B_2O_3.(Mg,Fe)O.Fe_2O_3$.
Ludwigite, Idaho .... $3MgO.B_2O_3.(Mg,Fe)O.Fe_2O_3$.
Ludwigite, Korea .... $3MgO.B_2O_3.(Fe,Mg)O.Fe_2O_3$.

[12] Butler, B. S., and Schaller, W. T., Magnesioludwigite, a new mineral. Wash. Acad. Sci. Journ., vol. 7, No. 2, pp. 29–31, 1917.

[13] Butler, B. S., Ore Deposits of Utah. Prof. Paper U. S. Geological Survey, no. 111, p. 243, 1920.

[14] Eakle, Arthur S., Vonsenite, a preliminary note on a new mineral. Amer. Mineral., vol. 5, p. 141, 1920.

The above type of formula was adopted by Tschermak and continued by Flink and Schaller. It is supported by the ratios of the three end members thus far found. The ratio of B_2O_3 to Fe_2O_3 seems invariably constant. It is possible to interchange the ratios of the bivalent bases, however, and the minerals can almost equally well be expressed by any of the following formula types: $3RO.B_2O_3.RO.Fe_2O_3$; $2RO.B_2O_3.2RO.Fe_2O_3$; $RO.B_2O_3.3RO.Fe_2O_3$.

The general formula for the group is thus $4(Mg,Fe,Mn)O.(B,Al)_2O_3.(Fe,Mn,Al)_2O_3$.

The formula as written by Tschermak for the original ludwigite (ferroludwigite) assumes 1 molecule of trimagnesium borate, $3MgO, B_2O_3$, plus 1 molecule of ferrous ferrate, $FeO.Fe_2O_3$; while Schaller deduces for magnesioludwigite 1 molecule of trimagnesium borate plus 1 of magnesian ferrate, $MgO.Fe_2O_3$. Pinakiolite, which is the best evidence in support of the above type of formula, is written 1 molecule of trimagnesium borate plus 1 of manganous manganate. Vonsenite, as written by Eakle, obviously does not agree with this series. An interesting hypothesis is developed from the observation that the ludwigite from Korea, described above, is decidely magnetic. It is to be remembered that the molecule ferrous ferrate is the magnetite molecule, and it is quite conceivable that this compound might preserve its magnetic properties even when united chemically with the borate molecule in a ludwigite. Assuming, for the sake of discussion, that in ludwigites which are markedly magnetic the ferrous iron is present as ferrous ferrate, while in those which are not notably magnetic the ferrous iron is present as borate, the following formulas may be written for the several occurrences:

Hungarian ludwigite; not sensibly magnetic: $3(Mg,Fe)O.B_2O_3.MgO.Fe_2O_3$.

Idaho ludwigite; not sensibly magnetic: $3(Mg,Fe)O.B_2O_3.MgO.Fe_2O_3$.

Vonsenite; not sensibly magnetic. Very close to $3FeO.B_2O_3.MgO.Fe_2O_3$.

Montana ludwigite; moderately magnetic: $3MgO.B_2O_3.(Mg,Fe)O.Fe_2O_3$.

Korean ludwigite; decidedly magnetic: $3MgO.B_2O_3.(Fe,Mg)O.Fe_2O_3$.

Of course, the term magnetic as here used is relative only, as all ludwigites are attracted to a sufficiently powerful electromagnet, as are all iron-bearing materials. The magnetism as stated above is in terms of an ordinary horseshoe magnet. While not put forward as a definite conclusion, this evidence is recommended as worthy of consideration. These interpretations may, in part, explain the anomalous variation in optical properties observed in ludwigites which should otherwise fall in a uniform series between ferro- and magnesioludwigite.[15]

A second point with reference to the composition of ludwigite which deserves mention is the water content, which is often reported in analyses and which is not released at a temperature much above 110° C. The results are collected below:

Mineral.	Locality.	Analyst.	Water below 110°.	Water above 110°.
Ludwigite	Hungary	Whitfield		3.62
Pinakiolite	Sweden	Flink		.47
Ludwigite	Montana	Schaller	1.13	1.24
Do	Hungary	do	.51	.82
Do	Idaho	Shannon	.03	2.28
Do	Korea	do		1.42

Schaller, after some consideration, decided to regard the water as extraneous. Whitfield, on the other hand, considered the water found by him in the Hungarian material as essential and basic. On the whole, the former seems the more reasonable view, especially since emphasis has been placed upon the fact that adsorbed water, properly so-called, may be held tenaciously up to the point of fusion.[6] Those ludwigites which show the largest content of water are distinctly fibrous in structure and thus possess the maximum of surface area.

Magnesia and ferrous iron seem entirely isomorphous in ludwigites as known. Boric anhydride and ferric iron are apparently always definite and constant in their ratio to each other although both may be susceptible of replacement to a slight extent by alumina. Examples intermediate between pinakiolite and ludwigites proper have not yet been found.

With regard to the occurrence of the ludwigites, one fact is obvious and important. Members of the group in every known occurrence are contact metamorphic minerals in limestone. The boron emanations in the contact zone seem to form ludwigite in the event that the supply of silica is deficient, whereas tourmaline forms under the same conditions where the supply of silica is ample. Ludwigite is not known in association with free quartz. The evidence seems to indicate that ludwigites are probably rather common products of contact metamorphism in limestone. The minerals may have largely been overlooked, as the black varieties closely resemble black tourmaline, or magnetite, while light-colored varieties may closely simulate amphiboles, etc., which are frequent in lime-silicate contact

[15] Larsen, Esper S., Mineral Tables, in press.
[16] U. S. Geol. Survey, Bull. 700, pp. 64–69, 1919.

zones. Under the microscope ludwigite resembles ilvaite to a remarkable degree, as shown by the misidentification of the Korean material by no less an authority than Koto. Acicular black minerals in contact altered limestones should be critically examined, as ludwigite is more rationally to be expected in such associations than is tourmaline. Ludwigite may simulate tourmaline in megascopic appearance and boron reaction, magnetite in appearance and magnetic properties, and ilvaite in appearance, solubility in acids, and quantitative optical properties.