

A Chromian Ludwigite and a Nickeloan Hörnesite from the Hayama Mine, Fukushima Prefecture, Japan

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Abstract Ludwigite from the Hayama mine, Fukushima Prefecture, is found to contain Cr_2O_3 up to 4.0 wt.%. It occurs as aggregates of prisms in a forsterite rock and some of them involve accessory magnesiochromite that served as the source of chromium after a reaction comparable with a fusion with boron compound, which was supplied from nearby granodiorite body. Fractures cutting ludwigite aggregates comprise a nickeloan hörnesite containing NiO up to 8.4 wt.%, the source of nickel and arsenic will be nickeline included in the forsterite rock at least in part.

Introduction

The principal compositional substitutions of ludwigite are Fe^{2+} for Mg and Al for Fe^{3+} . The former is complete to form its Fe^{2+} analogue vonsenite, whereas the latter is limited within $\text{Fe}^{3+} > \text{Al}$ (PERTSEV & ALEKSANDROV, 1964). Of subordinate importance are titanium (KONEV *et al.*, 1970) and tin (VLISIDIS & SCHALLER, 1974), and chromium of the present find is new to ludwigite.

Ludwigite from the Hayama mine, Fukushima Prefecture, was described by SUGAKI and HASEGAWA (1952a; 1952b) as the first borate mineral in Japan. They found ludwigite in a forsterite rock comprising minor nickel sulphides worked at that time, together with "chromite", which is here identified as magnesiochromite, letting us use this name in place of "chromite" hereafter. The primary nickel ore minerals are nickeline, gersdorffite, pentlandite and a nickel-bearing pyrrhotite. They are disseminated in the forsterite rock, which is a part of ultrabasic mass forming a roof pendant on a granodiorite body. They consider the genesis of nickel minerals to be orthomagmatic origin and that of ludwigite to be contact metasomatic origin after the supply of boron transported by a gaseous material from the granodiorite side.

The present study detected chromium in ludwigite and suggested the source to be remnant inclusions of magnesiochromite in ludwigite aggregates. Also, among fissure minerals cutting forsterite rock and ludwigite aggregates, a nickeloan hörnesite was found with chlorite and hydrotalcite as its first occurrence in Japan.

Occurrence

The ore deposit of the Hayama mine is located about 10 km southeast of Fukushima City and worked for nickel from a few years since 1951. At present only a small dump is left accessible. The ore deposit has been described by SUGAKI and HASEGAWA (1952a), together with the occurrences of nickel sulphides and ludwigite. The ultrabasic mass involving the ore deposit occupies the northeastern to eastern part of the roof pendant and consists of dunite, forsterite rock type I and forsterite rock type II. Ludwigite is exclusively found in the second member. The second and third members occur as a dike-like form with sharp and parallel boundaries to the surrounding dunite with northeast strike and westerly dip.

The materials here examined were collected from the dump and corresponds well with their description. It consists of pale yellowish green granular forsterite up to a millimeter across and is disseminated by ludwigite aggregates up to a few centimeter long and by minor nickel sulphides, such as nickeline, gersdorffite, pentlandite and a nickel-bearing pyrrhotite (Fig. 1). A part of forsterite grains is occupied by clinohumite. Larger aggregates of ludwigite include granular inclusions of magnesiochromite up to a few millimeter across (Fig. 2), and are rarely cut by white filmy veins (Fig. 3), which intersect forsterite rock as well. As stated later, they include nickeloan hörnesite, hydrotalcite and chlorite. Besides the studied ludwigite, a carbonate-rich part in the forsterite rock involves minute ludwigite prisms and their bundles without apparent inclusions of magnesiochromite.

Under the microscope, serpentine is developed among forsterite and clinohumite grains. Ludwigite aggregates clearly cut serpentine. Of ludwigite aggregates, those involving magnesiochromite inclusions have more densely assembled prisms and the outline of aggregate is generally round. Hörnesite-bearing veinlets are always younger than serpentine. Hörnesite is discriminated by its higher birefringence than the associated minerals in the veinlets. Larger crystals of hörnesite in an unanalysed specimen are pure white in colour with a lanceolate shape with striations on {010}, maximum length being 5 millimeters. They are accompanied by whiter flakes of hydrotalcite.

Chemical Analyses

Microprobe analyses using Link Systems energy-dispersive X-ray spectrometer

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- Fig. 1. Subround ludwigite aggregates (massive, black) in forsterite rock type I. Note that some separate ludwigite needles intersect minor fractures partially filled with serpentine. One polar. Field view: 7.4×1.9 mm.
- Fig. 2. Magnesiochromite (granular, grey) in ludwigite aggregates (prisms, dark grey to black). One polar with condensed light. Field view: 0.8×0.6 mm.
- Fig. 3. Hörnesite (white, center), in veinlets cutting forsterite rock type I. A forsterite grain (right up corner) is enclosed within the veinlet. Minute black prisms are ludwigite. One polar. Field view: 0.6×0.8 mm.

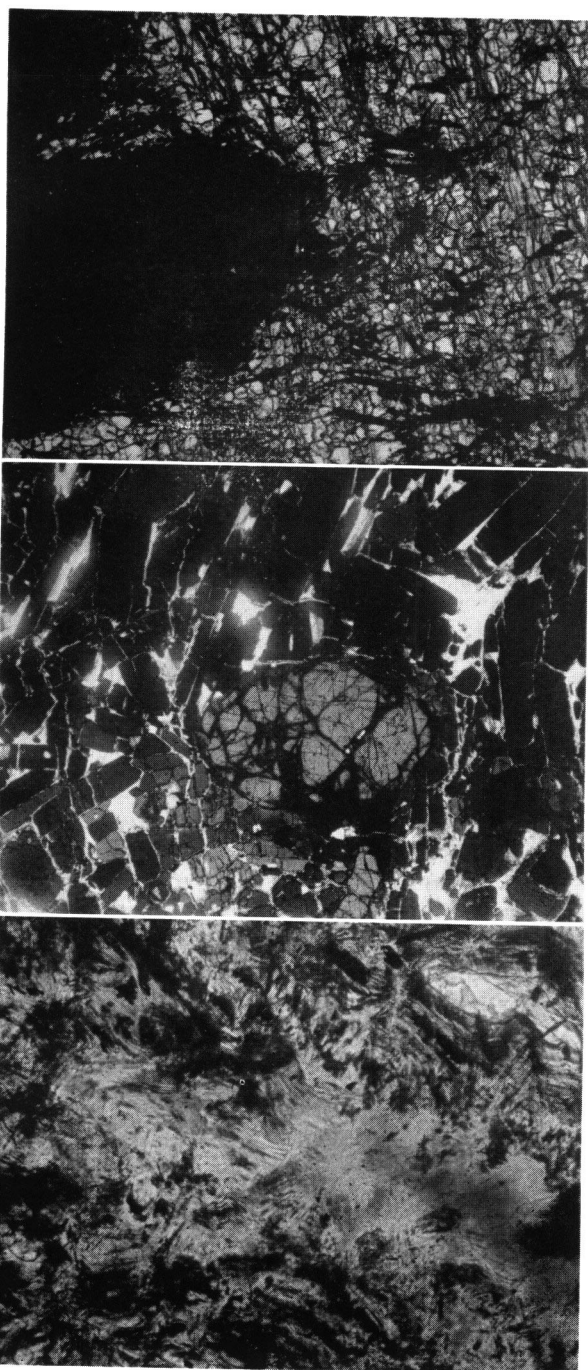


Table 1. Chemical analyses of ludwigite.

	1a.	2a.	1b.	2b.
MgO	37.81	37.19	1.85	1.83
FeO*	5.47	6.54	0.15	0.18
Al ₂ O ₃	2.55	2.46	0.10	0.10
Fe ₂ O ₃	32.45	35.12	0.80	0.87
Cr ₂ O ₃	4.02	1.09	0.10	0.03
B ₂ O ₃ **	17.69	17.59	1.00	1.00
total***	99.99	99.99		

1a. Ludwigite. Cr-rich point. Hayama mine, Fukushima Prefecture. *allotted from total Fe.
calculated. *re-calculated.

2a. Ludwigite. Cr-poor point. Hayama mine, Fukushima Prefecture.

1b. Molecular number. (basis: total metallic cation=4)

2b. Molecular number. (basis: total metallic cation=4)

Empirical formulae:

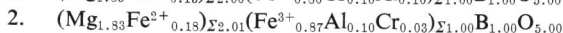
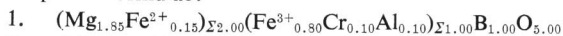


Table 2. Chemical analysis of forsterite

	1a.	1b.
SiO ₂	42.11	0.99
MgO	56.97	2.00
FeO	0.93	0.02
total	100.01	

1a. Forsterite. Hayama mine, Fukushima Prefecture.

1b. Molecular number. (basis: 0=4)

Empirical formula:

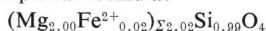


Table 3. Chemical analysis of magnesiochromite.

	1a.	1b.
Al ₂ O ₃	10.58	0.39
Fe ₂ O ₃ *	4.31	0.10
Cr ₂ O ₃	61.35	1.51
FeO*	5.82	0.15
MnO	0.88	0.02
MgO	17.92	0.83
total	100.86	

1a. Magnesiochromite. Hayama mine, Fukushima Prefecture. *allotted from total Fe.

1b. Molecular number. (basis: total cation=3)

Empirical formula:



Table 4. Chemical analysis of nickeline.

	1a.	1b.
Ni	42.85	0.99
Fe	0.04	0.00
As	56.65	1.01
S	0.15	0.01
total	99.68	

1a. Nickeline. Hayama mine, Fukushima Prefecture.
Average of two analyses.

1b. Molecular number. (basis: total atom=2)

Empirical formula:

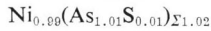


Table 5. Chemical analyses of hörnesite.

	1a.	2a.	1b.	2b.
MgO	19.28	19.63	2.46	2.50
NiO	8.41	7.48	0.57	0.51
As ₂ O ₅	44.31	44.78	1.98	2.00
H ₂ O*	28.01	28.12	8.00	8.00
total	100.01	100.01		

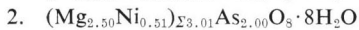
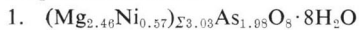
1a. Hörnesite. Hayama mine, Fukushima Prefecture. A nickel-rich point. *calculated.

2a. Hörnesite. Ditto. A nickel-poor point.

1b. Molecular number. (basis: total oxygen=8 in the anhydrous part)

2b. Molecular number. (basis: same as above)

Empirical formulae:



were made on ludwigite (Table 1), forsterite (Table 2), magnesiochromite (Table 3), nickeline (Table 4), and hörnesite (Table 5) included in a single specimen. In Table 1, two ludwigite analyses are given to indicate the range of Cr₂O₃ contents. It is worth mentioning that SUGAKI and HASEGAWA (1952a) had already found 0.68 wt. % of Cr₂O₃ in their analysis, but they ascribed it to the admixed "chromite", which is actually magnesiochromite as just stated. Cr₂O₃ contents in ludwigite is obviously reciprocal to Fe₂O₃ contents. Forsterite is compositionally very close to the end member as pointed out by them. The chemical analysis of magnesiochromite in Table 3 is re-calculated to separate Fe²⁺ from total Fe. Nickeline is very close to NiAs. Hörnesite analyses were made on two grains in separate fractures indicating the range of NiO content. They are re-calculated after the addition of 8H₂O.

X-Ray Powder Data

X-ray powder data for ludwigite from an aggregate involving magnesiochromite (Table 6), nickeline (Table 7), and hörnesite (Table 8) were obtained by the diffractometer method. All of them are well coincident with the known data. Those of the

Table 6. X-ray powder data for ludwigite.

1.		2.			hkl
I	d _{obs.}	I	d _{obs.}	d _{calc.}	
4	7.42	5	7.37	7.39	110
4	6.12	6	6.14	6.14	020
100	5.12	100	5.11	5.12	120
<1	4.62				200
4	3.73	2	3.74	3.74	130
4	3.061	2	3.070	3.070	040
				3.064	230
		1	3.016	3.018	001
25	2.990	5	2.988	2.988	310
4	2.902	5	2.913	2.910	140
6	2.812	1	2.796	2.792	111
10	2.753	10	2.759	2.753	320
70	2.547	80	2.554	2.557	240
70	2.515				211?
2	2.459	2	2.456	2.461	330
2	2.363	2	2.372	2.374	150
<1	2.271	2	2.267	2.271	410
35	2.167	26	2.168	2.169	250
		1	2.153	2.159	041
		4	2.124	2.123	311
18	2.116				141
50	2.027	8	2.035	2.034	321
18	1.995	8	1.997	1.998	160
6	1.946				241?
4	1.917	5	1.919	1.920	350
		5	1.906	1.907	331
4	1.873	5	1.872	1.872	151
4	1.771	2	1.770	1.770	520
10	1.757				421
4	1.721	2	1.724	1.724	170
2	1.704	2	1.705	1.705	360
<1	1.683				450
					431
6	1.664	2	1.666	1.666	161
2	1.644				270
2	1.619				351
		4	1.574	1.576	441
		6	1.535	1.535	080
$a = 9.26\text{\AA}$		$a = 9.242\text{\AA}$			
$b = 12.26\text{\AA}$		$b = 12.280\text{\AA}$			
$c = 3.05\text{\AA}$		$c = 3.018\text{\AA}$			

1. Ludwigite. Willis Quadrangle, Montana, U. S. A. After LEONARD *et al.* (1962). Fe/Mn radiation. Camera Method. JCPDS Card No. 15-797.
2. Ludwigite. Hayama mine, Fukushima Prefecture, Japan. Co/Fe radiation. Diffractometer method.

Table 7. X-ray powder data for nickeline.

1.		2.			hkl
I	d _{obs.}	I	d _{obs.}	d _{calc.}	
10	3.14	10	3.14	3.14	100
100	2.66	100	2.660	2.654	101
		10	2.521	2.521	002
90	1.961	60	1.964	1.965	102
80	1.811	35	1.810	1.810	110
20	1.497	5	1.497	1.497	201
20	1.475	10	1.481	1.481	103
30	1.328	5	1.331	1.331	202
$a=3.609\text{\AA}$		$a=3.620\text{\AA}$			
$c=5.019\text{\AA}$		$c=5.042\text{\AA}$			

1. Nickeline. Locality unknown. Fe/Mn radiation. Camera method. After BERRY and THOMPSON (1962).
2. Nickeline. Hayama mine, Fukushima Prefecture, Japan. Co/Fe radiation. Diffractometer method.

Table 8. X-ray powder data for hörnesite.

1.		2.		hkl	1.		2.		hkl
I	d _{obs.}	I	d _{obs.}		I	d _{obs.}	I	d _{obs.}	
20	7.94	3	7.94	110	6	2.240	2	2.241	060
100	6.69	100	6.74	020	6	2.197			22 $\bar{2}$
2	4.56			001	20	2.088	2	2.090	13 $\bar{2}$, 350
20	4.38	2	4.39	11 $\bar{1}$	6	2.042	1	2.043	260
10	4.00	3	3.99	220	10	2.012	1	2.011	061
2	3.91	8*	3.90	20 $\bar{1}$	10	1.988	1/2	1.988	44 $\bar{1}$
6	3.80			021	10	1.963			401
6	3.66	4	3.65	111	10	1.911	2	1.916	24 $\bar{2}$
10	3.36	10	3.36	040	6	1.874			42 $\bar{2}$
30	3.22	4	3.23	13 $\bar{1}$, 310	2	1.845			55 $\bar{1}$
50	3.01	4	3.01	201	6	1.774	1/4	1.776	15 $\bar{2}$
30	2.779	2	2.786	240	25	1.692			44 $\bar{2}$
30	2.734	1	2.738	221	25	1.680	10	1.681	080
50	2.712	3	2.712	041	20	1.661			460
10	2.659	1	2.667	330	20	1.658			152,370
2	2.592				20	1.653			600
16	2.545	3	2.554	24 $\bar{1}$, 33 $\bar{1}$	4	1.620			53 $\bar{2}$
16	2.465			40 $\bar{1}$	2	1.617			55 $\bar{1}$
20	2.330	3	2.328	11 $\bar{2}$					
6	2.284			002					

1. Hörnesite. Rezbanya, Hungary. After KORITNIG and SÜSSE (1966). JCPDS Card No. 19-752. Cu/Ni radiation. Camera method.
2. Hörnesite. Hayama mine, Fukushima Prefecture, Japan. Cu/Ni radiation. Diffractometer method. *intensity enhanced due to admixed hydrotalcite.

last one were obtained on a mixture with chlorite and hydrocalcite. The unit cell parameters were not calculated on this reason. The unit cell parameters of ludwigite, $a=9.242$, $b=12.280$, $c=3.018\text{\AA}$, give the calculated density 3.82 g/cm^3 , which is close to the measured value 3.752 g/cm^3 on the material analysed by SUGAKI and HASEGAWA (1952a).

Genesis of Ludwigite and Hornesite

In order to discuss the genesis of ludwigite, it is necessary to consider at least two steps of formation of mineral associations both corresponding to those of ultrabasic rocks. Firstly, there was a dunite with accessory magnesiochromite and nickeline. Subsequently, an oxidizing condition prevailed to convert the olivine into near end member forsterite. If Fe^{2+} in forsterite is oxidized into Fe^{3+} , it could no longer be present therein, but form such Fe^{3+} -bearing mineral as magnesioferrite if there is excess magnesium, which could be generated from olivine through the process of serpentinization thereof. Magnesiochromite and nickeline seems to have survived without any significant change. Thus, the dunite was supposedly converted into a magnesioferrite-bearing rock including forsterite with an extremely high content of forsterite molecule.

Although the form of boron compound incorporated from the side of granodiorite is unknown, it was capable of reacting with magnesioferrite and magnesiochromite in the manner comparable with a boron fusion. The formation of denser aggregates of ludwigite crystals in a forsterite rock can be explained like this. However, there is another mode of occurrence of ludwigite at the locality. Namely, it occurs as separate minute needles dispersed in forsterite rock. In this case, the rock contains visible dolomite, which involves needles of ludwigite as well as the forsterite rock. Therefore, it is very probable that a part of magnesium in such ludwigite was supplied after the dissociation of dolomite.

That the reaction forming ludwigite is comparable with a kind of boron fusion means that a higher temperature condition and reaction-supporting circumstance were necessary to terminate the reaction of boron-bearing material with the existing minerals. In the present locality, ludwigite is the unique borate mineral realized to date. While in the other locality of ludwigite, it is found as a constituent of kotoite-marble as in Hol Kol, Suian, North Korea (WATANABE, 1943) and in the Neichi mine, Iwate Prefecture, Japan (WATANABE *et al.*, 1963), where kotoite is the most dominant borate mineral. The form of boron-bearing compound coming from the granitic rock side is unknown but can be simply signified as B_2O_3 (WATANABE, 1943). In case of formation of kotoite, the reactant with boron-bearing material is considered to be periclase or brucite if hydrated in advance. Despite its high reactive nature with acids, calcite at the occasion of kotoite formation is not attacked but merely recrystallized. The absence of kotoite in the present case is interpreted as the lack of such a reactive phase in a considerable quantity in the rocks that existed prior to the

incorporation of boron.

Hörnesite is a rare secondary mineral in the oxidized zone of ore deposit and in skarn (PALACHE *et al.*, 1951). At the Hayama mine, possible sources of arsenic are nickeline and gersdorffite, which suffer an incipient stage of alteration represented by the formation of bright green halo around the grains in the forsterite rock (SUGAKI & HASEGAWA, 1952a). The existence of hörnesite requires magnesium capable of combining with arsenate ion. If the alteration of nickeline and gersdorffite is made ideally, or without any loss of nickel and arsenic, the ratio of nickel to arsenic should be unity, while the ratio of total cation to arsenic in annabergite and hörnesite is 3: 2, therefore, the addition of any divalent cations or the loss of arsenate ion is needed. In the present material, the ratio of nickel to arsenic is about 1: 4, suggesting the partial loss of nickel if all the sources of nickel are the nickel arsenide and arsenosulphide realized to date. The chemical compositions of analysed hörnesite need excess arsenic relative to nickel. Also, hörnesite is intimately associated with hydrotalcite, which is highly reactive with acids and has an isomorphic analogue of nickel. If the genesis of nickeloan hörnesite is considered after the reference to above evidences, the following conclusion can be derived. At the stage of serpentinization of forsterite rock, a part of magnesium formed hydrotalcite which is capable of taking up nickel. If the original olivine contains a small amount of nickel, it may finally lead to the formation of nickeloan hydrotalcite. If any solution containing arsenate ion reacted with such a nickeloan phase as nickeloan hydrotalcite, nickeloan hörnesite will be formed. Seeing from the quantity of nickel arsenides in this locality, that of hörnesite is significantly larger, needing the other source of arsenic than nickel arsenides. At the present stage, the source of additive arsenate ion cannot be definitely specified.

Annabergite from Laurium, Greece, contains a small amount of Mg and is suggested to grade into nickeloan hörnesite (PALACHE *et al.*, 1951). Under a superficial condition, nickel ion behaves in the similar manner to magnesium, as well as the case of formation of nickel-bearing hydrous silicates of magnesium.

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