A Ferrian Sodium-Amphibole from Vals, Switzerland

By *Leendert van der Plas* (Wageningen)[1]) and *Theodor Hügi* (Bern)[2])

With 2 figures in the text

Abstract

Chemical, optical, X-ray, DTA and TGA data are given for a Ferrian sodium-amphibole, separated from a metamorphic ophiolite in the northern Adula region (near Vals, Kt. Graubünden, Switzerland). Information regarding the following trace elements is added; Ba, Co, Cr, Cu, Mo, Ni, Pb, Sn, Sr, V, Zn. The chemical analysis is as follows: SiO_2 49.22, Al_2O_3 7.78, Fe_2O_3 8.28, FeO 10.49, MnO 0.23, MgO 10.52, CaO 7.45, Na_2O 3.54, K_2O 0.26, H_2O^+ 1.80, H_2O^- 0.32, TiO_2 0.23 = 100.12. The optical properties. comparable to those of ferrohastingsite, are X 1.66—1.67, Y n. d., Z 1.675—1.685, $2V_x$ 0°—48° (axial plane normal to 010, Z = b), $2V_x$ 0°—20° (axial plane parallel to 010, Y = b). Chemical and optical data of some riebeckites, ferrohastingsites, femaghastingsites and magnesiohastingsites from other localities are tabulated.

Introduction

While mapping a part of the northern Adula region, an outcrop of bluish black rocks was encountered SW of the village Vals, Kanton Graubünden, Switzerland. For a description of the geological setting of these rocks, of their constituent minerals and of their probable genesis, the reader is referred to VAN DER PLAS (1959). A summary of these data is given below.

Samples LP 88, LP 88a and LP 452. W of the Hohbühl, coord. 732,6—160,4, alt. 2400 m. A metamorphic ophiolite of presumably Mesozoic age.

---

[1]) Mineralogy and Geology Dept. of the Laboratory of Regional Pedology, Geology and Mineralogy, Agricultural State University, Wageningen, The Netherlands.

[2]) Department of Mineralogy and Petrology, University, Bern, Switzerland.

Macroscopical description:

A massive fine-grained bluish-black rock, showing epidote patches, magnetite octahedrons and fine amphibole crystals, and cut by an albite vein containing *black amphibole* needles of about 4 cm length and not exceeding 1 mm in diameter.

Microscopical description:

The host rock shows patches with and epidote fabric and patches of parallel amphibole prisms with magnetite octahedrons. The size of these patches is about 2 to 3 cm and their shape irregular. The epidote patches consist chiefly of granular or fanlike yellowish epidote with an occasional glaucophane prism (0.2 mm). The patches built up of parallel prisms of a weakly coloured amphibole with magnetite hold several crystals of *amphibole* with *dark greenish blue cores* and light coloured rims. The transitional fabric between these extremes consists of the latter type of amphibole, with light coloured rims set in a matrix of albite and epidote together with separate crystals of a lighter coloured amphibole. The *deep coloured amphibole* in this transitional fabric occasionally shows cores of glaucophane, whereas the glaucophane in the epidote parts frequently occurs in direct contact with epidote.

It became apparent that dark green amphibole is of rather uncommon composition; the same mineral was found to be beautifully developed in an albite vein showing slightly fibrous rims and a less pronounced zonal habit. In the paper mentioned above, this amphibole was called "ferrohastingsite", on the assumption that similarity of optical properties might indicate a similarity of chemical composition. As ferrohastingsite has not yet been described from Switzerland it seemed worth while to carry out a mineralogical investigation. The results of these investigations are reported here.

Optical Properties

Within the zonal crystals the optical properties vary. The range of this variation is as follows:

$$nX \qquad 1.66\text{—}1.67.$$
$$nY \qquad \text{n. d.}$$
$$nZ \qquad 1.675\text{—}1.685.$$
$$nZ\text{—}nX \qquad 0.010\text{—}0.016.$$
$$2V_x \quad 0°\text{—}48° \text{ axial plane normal to } 010,\ Z=b.$$
$$2V_x \quad 0°\text{—}20° \text{ axial plane parallel to } 010,\ Y=b.$$
$$c/Y \quad 20°\text{—}30°$$
$$c/Z \quad 12°\text{—}20°$$

The colour parallel to the c-axis is a pronounced blue.
The colour parallel to the b-axis is olive green.
The colour approximately parallel to the a-axis is yellowish.

Measurements were all carried out in Na light. Values for other wavelengths may differ appreciably from the data listed. Absorption is less strong than with riebeckites. Extinction dispersion in daylight is large and dispersion of the optical axes extreme. Differences between the measurements made in Li light and those made in Na light in the same crystal illustrate this clearly, viz $2V_{xLi}$ 41°, $2V_{xNa}$ 48°. There are strong indications that crossed dispersion is present, but strong absorption makes observations difficult.

BILLINGS (1928) was the first to compile optical and chemical data of hastingsites. These optical data are listed together with the chemical composition in tables 4 and 5. The optical properties of femaghastingsite, magnesiohastingsite and alkalihastingsite conform less well to our measurements than those of ferrohastingsite. The refringence of the amphibole under discussion is, however, rather low for ferrohastingsite but its other optical properties fit well.

In view of the chemical composition of the investigated amphibole it seems appropriate to compare the optical properties with those of riebeckites. MIYASHIRO (1957) recently compiled data of chemically analyzed sodium-amphiboles and came to the conclusion that the literature shows considerable confusion and contains many contradictions concerning the optical descriptions of riebeckites as a result mainly of very strong absorption. Surveying these optical data and comparing them with our observations one is lead to the conclusion that the refringences of riebeckites are always higher, whereas those of magnesioriebeckite conform to those of the amphiboles we investigated. At the moment there are not enough optical data available concerning magnesioriebeckites to draw a conclusion from this fact. The optical properties of our amphibole differ so strongly from those of riebeckites that before the chemical analysis became available riebeckite was not even thought of as a main component of this amphibole. In conclusion it can be stated that the amphibole from Vals is most closely allied to the group of hastingsites as far as the optical properties are concerned. There is some slight indication that magnesioriebeckites have comparable optical properties.

X-Ray Investigations

A sample, prepared with the aid of heavy liquids was used in X-ray investigations. Crystals that sank in a mixture of methylene iodide and acetone of S.G. 3.100 were collected, and when examined under a micro-

L. van der Plas and Th. Hügi

Table 1. X-ray powder patterns of ferrian sodium-amphibole and other amphiboles

Ferrian sodium-amphibole from Vals, Switzerland (1)				Hornblende, ASTM 9-434, from Oka, P.Q. Canada (2)			Riebeckite, ASTM 9-436, from N.Roe, Shetland, PHEMISTER et al., 1950 (3)		Riebeckite, from Ras Zeit, Egypt (m 1284), ZWAAN et al., 1958 (5)			
ϑ Co	d Å	I/I₁	hkl	d Å	I/I₁	hkl	d Å	I/I₁	ϑ Fe	d Å	hkl	I
5.62	9.13	30	020	9.03	10	020						
6.07	8.46	100	110	8.45	50	110	8.42	100	6.60	8.42	110	s
10.03	5.14	5	—	—	—	—	—	—	—	—	—	—
10.50	4.91	25	111	4.93	10	111	—	—	—	—	—	—
11.42	4.52	25	040	4.50	10	040	4.51	23	12.36	4.52	040	m
12.24	4.22	10	—	—	—	—	—	—	—	—	—	—
12.77	4.05	10	—	4.00	5b	—	—	—	—	—	—	—
13.25	3.90	15	1̄31	3.89	5b	1̄31	—	—	—	—	—	—
13.72	3.77	5	—	—	—	—	—	—	—	—	—	—
14.07	3.68	5	3̄12	3.65	3b	3̄12	—	—	—	—	—	—
15.20	3.41	35	—	3.38	90	131	3.34	9	16.37	3.43	231̄	m
15.83	3.28	25	240	3.29	70	240	3.27	14	17.11	3.29	240	w
16.21	3.20	5	—	—	—	—	—	—	—	—	—	—
16.66	3.12	65	310	3.09	95	310	3.13	59	17.93	3.14	310	s
—	—	—	—	3.03	5	—	—	—	18.76	3.01	321̄	vw
17.60	2.96	30	—	2.94	65	1̄51.221	—	—	—	—	—	—
18.61	2.80	15	330	2.82	40	330	2.81	11	20.04	2.825	330	w
—	—	—	—	2.76	25	3̄31	—	—	—	—	—	—
19.21	2.72	90	—	2.70	100	151	2.72	23	20.74	2.733	251̄	ss
20.10	2.60	30	—	2.59	70	061	2.60	6	21.82	2.604	161̄	mw
20.55	2.55	40	002	2.568	70	002	2.54	6	22.33	2.548	002	mw
—	—	—	—	2.383	5	350.400	2.38	3	—	—	—	—
22.55	2.33	20	—	2.349	60	3̄51	2.33	5	24.46	2.338	251	mw
23.10	2.28	15	1̄71	2.303	30b	112.1̄71	—	—	—	—	—	—
23.79	2.22	5	—	2.228	5b	2̄42.042	—	—	—	—	—	—
24.14	2.19	5	—	—	—	—	2.18	9	—	—	—	—
24.38	2.17	30	—	2.159	60	3̄32.132	—	—	—	—	—	—
24.64	2.15	5	—	—	—	—	—	—	—	—	—	—

I	hkl	d	2θ	I	d	hkl	I	d	hkl	I	d	2θ
w	402	2.080	27.74			261.202	40	2.058		10	2.06	25.72
vw	45$\bar{1}$	2.016	28.69	4	2.03	351	10	2.019		15	2.02	26.29
						222	10	1.998		15	2.02	26.35
		1.875	31.08			190.152	3	1.957		10	1.961	27.14
vw		1.836	31.81		1.809		5	1.909		5	1.928	27.64
vw		1.807	32.39			$\bar{1}$91	5	1.862	0 10 0	10	1.866	28.65
w	0 10 0			7	1.684		1	1.823				
		1.689	34.96		1.661	0 10 0	3	1.805		5	1.803	29.75
		1.665	35.54	2	1.639	312	3	1.776		<2	1.738	30.98
vw	56$\bar{1}$	1.644	36.08	7	1.619	$\bar{1}$53.082	10	1.698				
m	480	1.618	36.75	3	1.594	172.391	10	1.683	2$\bar{5}$3	10	1.685	32.07
	25$\bar{3}$	1.593	37.42	6		480			600			
w	600	1.517	39.64	2	1.504		25	1.653		20	1.650	32.82
mw	16$\bar{3}$	1.504	40.06		1.458	1 11 0			0 12 0	10	1.632	33.24
m	0 12 0	1.459	41.55	7		600	15	1.614		5	1.617	33.59
		1.440	42.25	2		5$\bar{7}$1	15	1.587		15	1.589	34.26
mw	561	1.386	44.32			2$\bar{6}$3	25	1.557		5	1.562	34.94
w	712	1.349	45.85			0 12 0	12	1.523		15	1.520	36.04
	710	1.321	47.12				10	1.502		10	1.501	36.58
vw	651	1.311	47.57							5	1.474	37.37
sm	0 12 2	1.295	48.37							5	1.457	37.88
	004	1.273	49.51							10	1.440	38.40
m		1.235	51.61							10	1.430	38.72
mw	602	1.197	53.97							5	1.368	40.82
vw		1.168	55.97							10	1.345	41.69
w		1.086	63.07							5	1.318	42.75
m		1.050	67.21									
w		1.029	70.20							10	1.295	43.70
vw		1.018	71.95							<2	1.192	48.64
w		0.987	78.83								cut off	
vw		0.981	80.77									
vw												
mw												
vw												
w												
m												

scope revealed that the light-coloured amphibole variety, forming rims around the more deeply-coloured cores, was present only in very small quantity. It has to be kept in mind, however, that the amphibole crystals on which our observations were made are still slightly zonal.

Part of this sample was put in a Lindeman glass tube and investigated with Co K α radiation using a powder camera, $\varnothing$ 114,6 mm, with a collimator with rectangular aperture. The camera was filled with H_2 gas
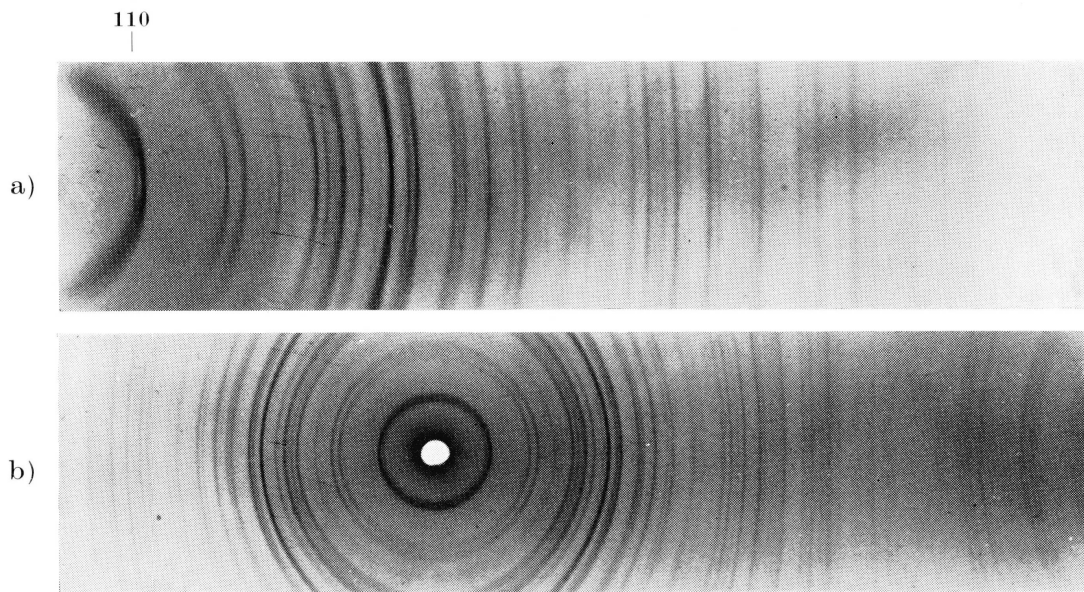
Fig. 1. Ferrian sodium-amphibole from Vals. Co K_{α} radiation.
a) $\varnothing$ 114.6 mm   b) $\varnothing$ 57.3 mm

under normal atmospheric pressure and the film mounted according to the conventional Straumanis-Ievins arrangement. The diameter of the diffraction rings was measured with a low-power travelling microscope. It is our experience that d-values, thus obtained from measurements on a film, are superior to those obtained with a diffractometer unless the diffractometer is very carefully aligned and measurements are made manually on counters all of which is rather time-consuming. In table 1 the d-values are listed as well as the values of θ_{Co}. The pattern is indexed according to JAKOB and BRANDENBERGER (1931) as far as this coincides with the indexing of Perrault. As the paper of PERRAULT, announced for the Can. Min., *6*, part 3, 1959, is still to appear later in 1961, his values have been taken from card 9-434 of the ASTM index. The powder patterns of two riebeckites are given for the sake of comparison.

Another part of the same sample was carefully ground in an agate mortar. The powder was stirred in a 0.005 N NaOH solution and left to

settle for the time prescribed for a given temperature and height of the liquid column. After the grains larger than 8 μ has settled, the supernatant liquid was siphoned off and the fraction < 8 μ was collected with the aid of a centrifuge. The fraction < 0.5 μ was largely disposed of by washing three times with H_2O in a centrifuge and decanting the still somewhat turbid liquid each time. In this way one is sure to get rid of the extremely small crystals that might otherwise cause a broadening of reflections. The sample thus prepared was used in determining the relative intensities of the reflections with the aid of a Hilger and Watts X-ray diffractometer type Y 125 with scintillation counters. This diffractometer is of the monitoring type.

To avoid as much as possible the effects of preferred orientation, three different techniques were used to prepare the sample surface; i: the surface was pressed on a ground glassplate; ii: the surface was pressed on a piece of filter-paper; iii: two tablets were produced in a small hand-press and the surfaces of these tablets ground against each other. After each run the sample was prepared anew. As tests for the best method of preparing unoriented samples of material that might give rise to preferred orientation are still in progress, comment on the characteristics of the three methods would at present be premature. It suffices to report that the results in this case were more or less comparable with respect to reproducibility. On the other hand, samples with a grain-size < 50 μ gave highly unreliable results, i. e., a few peaks with relative intensities < 80 in samples with a grain-size < 8 μ practically disappeared in some of the former traces. The runs made with different scanning speeds were started at $2\frac{1}{2}°$ θ and cut off at 45° θ, or vice versa. The most important peaks were scanned manually on duo-gate counters. The relative intensities of the different diffraction lines are listed in table 1.

DTA and TGA

A DTA was made in normal atmosphere with a heating rate of 8°/min. The trace shows three important exothermic reactions occurring at 670°, 975° and 1090°. The last one is most certainly due to a collapse of the amphibole structure followed by total recrystallization. X-ray investigation of the structure of amphiboles directly after these exothermic reactions was left for subsequent investigation.

A TGA was made in N_2 atmosphere with a heating rate of $2\frac{1}{2}°$/min. After the maximum temperature of the apparatus, viz 1060°, was reached,

the gas supply was cut and the sample was left for one hour at this maximum temperature in a normal atmosphere in order to oxidize the available FeO. Inspection of the sample after cooling, however, showed that total oxidation did not take place. By this method we had hoped to obtain a check on the amount of FeO found in the chemical analysis. The amount of water lost at 1060°C was 1.73%. It is seen in fig. 2 that the TGA trace shows a change of gradient shortly after the important exothermic or endothermic reactions, illustrated by the DTA trace, have taken place. The small secondary reactions accompanying the important exothermic and endothermic reactions are partly due to the technique applied, partly to other influences not to be discussed here.

It needs to be mentioned that the DTA trace is plotted on a scale of which unity along the y axis, is twice as large as along the temperature axis.
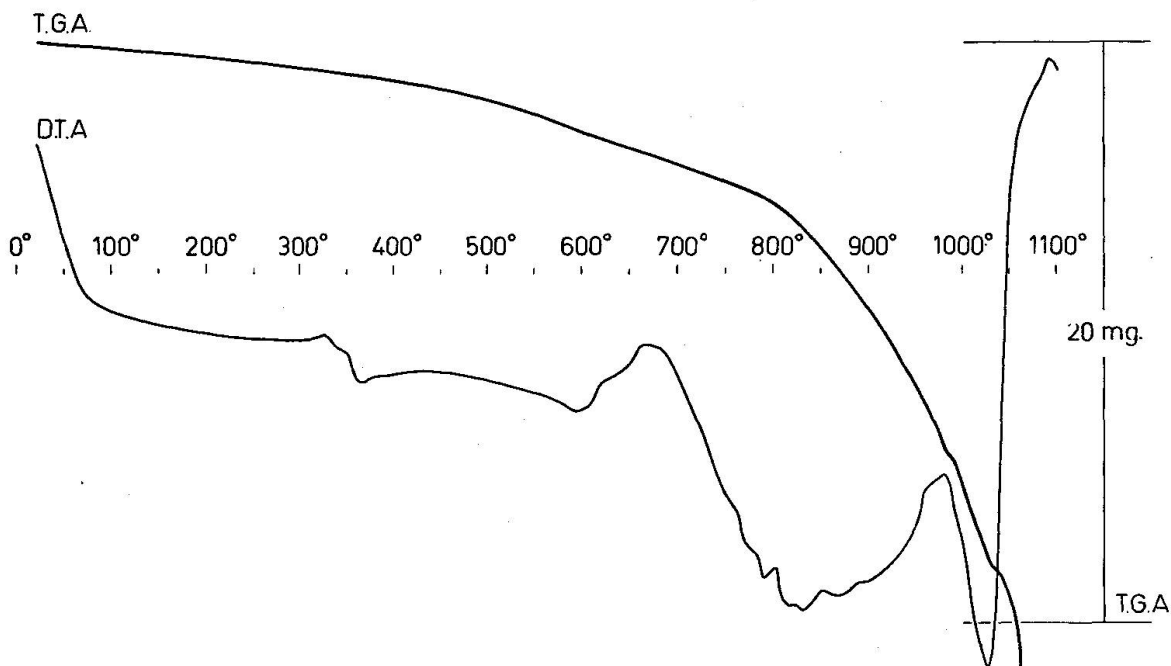

Fig. 2. Differential thermal and thermogravimetric analyses curves for the Ferrian Sodium-Amphibole from Vals.
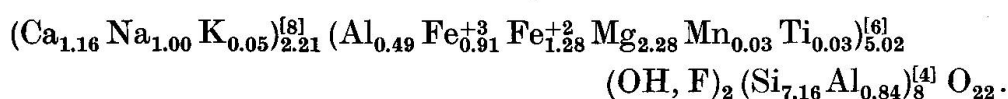
Chemical Composition

Chemical and spectrochemical analyses were carried out on a 99% pure sample of amphibole crystals prepared in the same way as the sample for X-ray analysis by using heavy liquids. The results are listed in table 2.

The analysis (column a) was carried out by means of classical methods. Values of the same sample LP 88 a given in column b) are based on complexing agents (for Ca and Mg) and flame-photometer-methods (for Na and K) and spectrographic methods (for Mn and Ti). The heavy metals have been eliminated in order to get better titrimetric results for Ca and Mg by means of "Komplexon III". We used the HHSNN- and "Eriochromschwarz T"-indicator for Ca and Mg respectively (SCHWARZENBACH 1960) and an EEL-flame-photometer for the alkalis. The differences for these values listed in column a) and b) lie between 0.6% and 4% (for K_2O). MnO and TiO_2 have been checked by means of spectrographic methods (Hilger — automatic large quartz and glass spectrograph E 478, interrupted D.C. carbon-arc, 8 or 12 A, RSV-instrument, Dr. R. Seitner and Co., Type FES/240 GTT 5. Jarrell-Ash microphotometer comparator, Type JA 2100). Table 2a gives some additionel semiquantitative spectrographic results. The $H_2O^{+110°}$-value has been controlled by means of T.G.A. in a Nitrogen atmosphere (see p. 378).

Table 2. *Amphibole from Vals, sample LP 88 a;* W of the Hohbühl; coord. 732,6—160,4, alt. 2400 m; S. G. 3.31; analysts TH. HÜGI and E. SPYCHER

	a)	b)	c)		d)	e)
			Kation aequ. Kations / 23 O			total positive
	Wt %		[based on data of column a)]			charges
SiO_2	49.22		Si	8191	716	28.64
Al_2O_3	7.78		Al	1526	133	3.99
Fe_2O_3	8.28		Fe^{+3}	1036	91	2.73
FeO	10.49		Fe^{+2}	1461	128	2.56
MnO	0.23	0.24	Mn	32	3	0.06
MgO	10.52	10.58	Mg	2609	228	4.56
CaO	7.45	7.28	Ca	1328	116	2.32
Na_2O	3.54	3.64	Na	1142	100	1.00
K_2O	0.26	0.22	K	55	5	0.05
H_2O^+	1.80	1.73				
H_2O^-	0.32					
TiO_2	0.23	0.21/0.22*)	Ti	28	3	0.12
F	n. d.					
	100.12	*) det. H. SCHWANDER			1523	46.03

This analyses leads to the following formula:

$$(Ca_{1.16} Na_{1.00} K_{0.05})^{[8]}_{2.21} (Al_{0.49} Fe^{+3}_{0.91} Fe^{+2}_{1.28} Mg_{2.28} Mn_{0.03} Ti_{0.03})^{[6]}_{5.02}$$
$$(OH, F)_2 (Si_{7.16} Al_{0.84})^{[4]}_8 O_{22}.$$

The ideal amphibole formula has 46.00 positive charges. In order to check the accuracy of the foregoing analysis, the charges of the different kations have been added proportionally in the last column and the total shows a difference of only 0.03.

Table 2a. *Trace element contents of the ferrian sodium-amphibole form Vals* (all values in ppm)

Ba	27	or	BaO	31
Co	6	,,	CoO	8
Cr	22	,,	Cr_2O_3	29
Cu	87	,,	CuO	110
Mo	12	,,	MoO_3	18
Ni	20	,,	NiO	25
Pb	4	,,	PbO	9
Sn	9	,,	SnO_2	11
Sr	47	,,	SrO	55
V	193	,,	V_2O_5	345
Zr	9	,,	ZrO_2	13

Table 2b. *Semiquantitative Fluorescent X-ray spectrographic analysis of ferrian sodium-amphibole, from Vals, sample LP 1,5/7 60;* W of the Hohbühl; coord. 732,6—160,4, alt. 2400 m; analyst R. O. MÜLLER

	Method 1	Method 2	Chemical analysis Column a) Table 2
ZnO	ca. 0.06 %	0.045 —0.100 %	—
CuO	ca. 0.015 %	0.012 —0.029 %	—
NiO	ca. 0.008 %	0.0075—0.016 %	—
V_2O_5	ca. 0.07 %	0.05 —0.13 %	—
TiO_2	ca. 0.115 %	0.097 —0.245 %	0.23 %
MnO	ca. 0.38 %	0.23 —0.66 %	0.23 %

According to the analyst, Dr. R. O. MÜLLER, these values are only approximations and the results are therefore not to be treated as absolute but rather as indications of the real values. For comparison the values of TiO_2 and MnO were also determined in order to test the accuracy of this semiquantitative method. In both cases the figures differ considerably from those found by the first method but fall within the range given by the second method. To comment on the methods themselves is beyond the scope of this paper and it suffices here to state that the values in the first and second columns are the result of two different determinations and calculations based on essentially different theories.

From a mineralogical point of view it is interesting that Zn and V can be present in amounts as large as approximately 0.1%. As comparable data on the presence of these elements in metamorphic amphiboles is lacking no further comments will be made in this respect.

The composition of the amphibole corresponds to two possible mixtures of pure endmembers of which only the following are possible.

Titaniferous amphibole	$Ca_2(Mg, Fe^{+2})\, Ti$	$Si_6 Al_2 O_{22}(OH, F)_2$
Riebeckite	$Na_2 Fe_2^{+3} Fe_3^{+2}$	$Si_8\quad O_{22}(OH, F)_2$
Glaucophane	$Na_2 Al_2 (Mg, Fe^{+2})_3$	$Si_8\quad O_{22}(OH, F)_2$
Ferrohastingsite	$Na\, Ca_2 Al\, Fe_4^{+2}$	$Si_6 Al_2 O_{22}(OH, F)_2$
Ferrian hastingsite	$Na\, Ca_2 Fe^{+3}(Mg, Fe^{+2})_4$	$Si_6 Al_2 O_{22}(OH, F)_2$
Tschermakite	$Ca_2 Al_2(Mg, Fe^{+2})_3$	$Si_6 Al_2 O_{22}(OH, F)_2$
Tremolite	$Ca_2(Mg, Fe^{+2})_5$	$Si_6\quad O_{22}(OH, F)_2$

The method of assigning the available kations to the endmembers is shown in the following scheme.

		Titaniferous amphibole	Riebeckite and glaucophane	Riebeckite	Ferrian-hastingsite	Ferrian- and ferro-hastingsite	Tschermakite	Tremolite	Rest
			I or II		I or II				
Si	716	18	336		126		105	128	3
Al	84	6			42		36	—	—
Al	49		14		14		35	—	—
Fe+3	91		70	84	21	7	—	—	—
Mg	228								
Fe+2	128	12	126		84		53	80	4
Mn	3								
Ti	3	3	—		—		—	—	—
Ca	116	6			42		36	32	—
Na+K	84		84		—		—	—	—
Na+K	21				21		—	—	—

To take full account of the available Ti, the total amount of Ti is assigned to titaniferous amphibole. The high amount of Fe^{+3} points to at least the presence of a ferri-amphibole and can be assigned to rie-

beckite in combination with the available amount of Na in 8-fold coordination, on the assumption that kations in 10-fold coordination (cf. Heritsch et al. 1957), viz 0.21, form the hastingsite molecule, and must necessarily be sodium. We tried Fumiko Shîdo's variant (1958), assuming that some of the Ca is present in form of $Ca_2 Ca_5 Si_8 O_{22} (OH)_2$. This did not provide a solution, however, which proves that the kations in 10-fold coordination are all sodium. If, however, the hastingsite is in the form of a ferrian hastingsite then the fact that the Fe^{+3} content is insufficient to match the amount of Na in 8-fold coordination, would mean that some glaucophane is present. Both possibilities are listed as II and I respectively. What is left of the Al in 6-fold coordination, viz 0.35, is grouped into the Tschermakite molecule. The remaining ions are used to form tremolite, leaving 0.03 Si and 0.04 of the divalent metal ions as a remainder.

Summarizing we find:

		3%	titaniferous amphibole
35%	or	42%	riebeckite
7%	or	0%	glaucophane
21%	or	7%	ferrian hastingsite
0%	or	14%	ferrohastingsite
		18%	tschermakite
		16%	tremolite

The question as to which of the two possibilities seems to be more in accordance with the optical and X-ray data will now be discussed. The optical data are definitely in favour of the highest possible amount of ferrohastingsite with the lowest possible amount of riebeckite. This leads to the following composition:

3%	titaniferous amphibole
35%	riebeckite
7%	glaucophane
7%	ferrian hastingsite
14%	ferrohastingsite
18%	tschermakite
16%	tremolite

The X-ray powder pattern shows the same characteristics as the pattern of riebeckite, i. e., the presence of four weak lines at approximately d = 1.66; 1.64; 1.62 and 1.59 Å. The patterns of Ca-amphiboles and glaucophane show a different configuration of spacings as was shown by Zwaan and van der Plas (1958). From a structural point of view the

composition has to be such as to take into account the presence of a large amount of riebeckite. A lack of X-ray powder data of chemically analyzed sodium-amphiboles makes it impossible to estimate what percentage of the riebeckite molecule suffices to account for the presence of this typical pattern.

One problem not often treated in papers on amphiboles remains. This concerns the structure of a zonal amphibole. One must imagine a more or less statistical spread of the available kations over the specific sites, showing a gradient of concentration of one over the other from core to rim, in other words a higher concentration of e. g., sodium in a certain diffuse zone in the core gradually giving way to a higher concentration of e. g., calcium in a zone near to the rim? Or has such a zonal crystal to be treated as a multiple shell comprising layers of homoaxial crystals, each layer having a discrete chemical composition and arranged in such a way that within the amphibole the chemical composition changes discontinuously from one shell to the next?

According to the last view a powder pattern involving a mixture of patterns of homogeneous amphiboles is theoretically to be expected. As present knowledge of the X-ray powder pattern of amphiboles is very limited, and as hitherto no attempt appears to have been made to compare the pattern of a zonal amphibole with that of a mixture of pure endmembers, this question must for the moment remain unanswered. Investigations along these lines will not only throw light on the structure of zonal amphiboles, but will also be highly interesting in the light of the metamorphic facies problem.

Concluding Remarks

After examining the ferrohastingsite-like amphibole from Vals, the problem remains of giving it an appropriate name. In the following three tables 3, 4, 5, the chemical and optical properties of a number of amphiboles with certain comparable properties are given. Table 3 lists the chemical composition of a number of riebeckites. From this table it is clear that these amphiboles differ considerably from our amphibole with respect to the contents of Al_2O_3, Fe_2O_3 and CaO. The next table, 4, shows a number of chemically and optically analyzed ferrohastingsites. From this table it can be seen that our mineral has too little Al_2O_3 and FeO. Calculations of the composition in terms of endmembers from which the first five analyses could be derived (BILLINGS analyses) lead to at least 45% of hastingsite molecules in all these cases. This is a much

Table 3. *Chemical analyses and optical properties of some riebeckites*

	1	2	3	4	5	6	7	8
SiO_2	51.94	52.41	47.60	48.28	51.3	55.62	55.44	49.22
Al_2O_3	0.20	0.61	3.49	0.73	2.7	4.54	0.22	7.78
Fe_2O_3	18.64	14.37	11.06	14.23	14.2	12.99	16.77	8.28
FeO	19.39	14.82	18.79	16.98	18.5	3.53	5.23	10.49
MnO	n. d.	1.46	0.99	0.53	0.9	1.25	0.09	0.23
MgO	1.37	5.07	4.56	3.69	n. d.	11.98	12.30	10.52
CaO	0.19	1.33	2.56	2.26	1.1	1.95	2.17	7.45
Na_2O	6.07	4.94	4.72	4.30	6.0	5.58	6.76	3.54
K_2O	0.04	2.10	1.42	0.77	1.4	0.36	0.15	0.26
TiO_2	n. d.	0.45	1.09	3.91	1.9	0.26	0.04	0.23
P_2O_5	n. d.	n. d.	n. d.	n. d.	n. d.	0.07	n. d.	n. d.
H_2O^+	2.58	2.02	2.84	3.32	1.9	1.96	0.55	1.80
H_2O^-	0.31	0.10	0.74	0.36	0.1	0.00	0.05	0.32
F	n. d.	0.30	n. d.	n. d.	0.3	n. d.	0.18	n. d.
							Cl 0.08	
Sum		99.98			100.3		100.03	
$F = O$		0.13			0.1		0.09	
	100.73	99.85	99.86	99.36	100.2	100.09	99.94	100.12

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Z-X	0.008	n.d.	0.011	0.002	0.016	0.010	n.d.	0.010–0.016
X	1.698	n.d.	1.680	1.688	1.701	1.660	n.d.	1.66 –1.67
Y	1.699	1.686	1.687	n.d.	1.710	n.d.	n.d.	n.d.
Z	1.706	n.d.	1.691	1.691	1.717	1.670	n.d.	1.675–1.685
x	indigo	n.d.	n.d.	n.d.	indigo	pale yellow	n.d.	c = blue
y	yellow	n.d.	n.d.	n.d.	brownish yellow	blue	n.d.	b = olive green
z	indigo	n.d.	n.d.	n.d.	indigo	purple	n.d.	a = yellowish
ext.	X/c 0°	n.d.	n.d.	X/c ½°–1½°	X/c 3°–4°	Y/c 28°	n.d.	Y/c 20°–30° / Z/c 12°–20°
2 V	z = ?	n.d.	n.d.	z = 65°	x = ca. 80°	x = 43°	n.d.	x = 0°–48°
disp.	?	n.d.	n.d.	r > v	n.d.	r ≪ v	n.d.	n.d.
b = ?	b = Z	n.d.	n.d.	b = Z	b = Y	b = Z	n.d.	b = Z or Y
S. G.	n.d.	n.d.	n.d.	n.d.	3.32	n.d.	n.d.	3.31
	n.d.	n.d.	n.d.	Z > X > Y	n.d.	n.d.	n.d.	c > b > a

No. 1. Crocidolite, Kliphuis, analyst H. E. VASSAR (PEACOCK 1928, p. 256, No. 1).

No. 2. Riebeckite from aegirine-riebeckite-quartz-syenite, Kogan Zan, analyst T. MIYASHIRO-INOUE (MIYASHIRO, A. and MIYASHIRO, T., 1956, p. 48, No. 9).

No. 3. Riebeckite from quartz-syenite-pegmatite, Kogan Zan, analyst S. KOMATZU (HARADA 1939, ref. MIYASHIRO, A. and MIYASHIRO, T., 1956, p. 48, No. 10).

No. 4. Riebeckite from nepheline-syenite, Mariupol (AINBERG 1930, p. 94 or 606, No. a).

No. 5. Riebeckite from riebeckite-felsite, North Roe, analyst C. O. HARVEY (PHEMISTER et al., 1950, p. 368, No. 1).

No. 6. Magnesioriebeckite from crystalline schists, Bizan, analyst H. HARAMURA (MIYASHIRO and IWASAKI 1957, p. 701).

No. 7. Crocidolite, Cochabamba, analyst H. B. WIIK (ERNST, 1960, p. 36, see also WHITTAKER 1949).

No. 8. Amphibole from albite-vein, Vals, analysts TH. HÜGI and E. SPYCHER, this paper.

Table 4. *Chemical analyses and optical properties of some ferrohastingsites*

	1	2	3	4	5	6	7	8
SiO_2	34.184	37.49	37.40	38.50	36.86	35.42	34.41	37.78
Al_2O_3	11.527	10.81	12.34	10.88	12.10	8.89	9.16	10.63
Fe_2O_3	12.621	7.52	4.16	6.70	7.41	9.73	5.10	8.56
FeO	21.979	25.14	25.84	27.28	23.35	24.48	26.07	24.46
MnO	0.629	0.95	1.24	tr.	0.77	1.17	0.34	0.67
MgO	1.353	1.35	2.20	1.40	1.90	0.17	2.13	0.51
CaO	9.867	9.77	9.72	11.30	10.59	6.93	8.98	8.02
Na_2O	3.290	2.06	1.80	1.22	3.20	5.13	1.41	2.99
K_2O	2.286	1.91	1.36	1.66	1.20	3.23	1.67	2.06
TiO_2	n. d.	0.86	3.20	tr.	n. d.	1.34	5.94	0.73
P_2O_5	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
H_2O^+	0.348	2.01	0.00	1.27	0.60	3.15	3.52	3.13
H_2O^-	n. d.	n. d.	0.60	0.00	0.70		0.10	0.00
F		n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
$F = O$								
	98.084	99.87	99.86	100.21	98.68	99.64*)	99.83	99.54

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Z–X	0.027	0.017	0.024	0.020	n. d.	0.022	0.021	0.017–0.011
X	1.705	1.697	1.698	1.693	n. d.	1.699	1.693	1.695–1.682
Y	1.731	1.713	1.719	1.710	n. d.	1.719	n. d.	n. d.
Z	1.732	1.714	1.722	1.713	n. d.	1.721	1.714	1.711–1.693
x	yellow	yellow	yellow	green-brown	light olive gr.		yellow-green	greenish yellow
y	deep gr. blue	blue-gr.	olive green	brown-green	yellow-green		olive brown-gr.	olive brown-green
z	deep ol. green	olive-green	deep green	blue-green	blue-green		dark green	dark green
ext.	Y/c 13°	Y/c 15°	Z/c 20°	Z/c 17°	Z/c 9°	Z/c 20°	Z/c 12°–13°	Y/c 15°–27°
2 V	25°	16°	47°	small	n. d.	36°	36°	0°–35°
disp.	r≪v	r≪v	r>v	n. d.	n. d.	n. d.	r>v	r<v
b = ?	b = Z	b = Z	b = Y	b = Y	b = Y	b = Y	b = Y	b = Z
	Z>Y>X	Y>Z>X	Y>Z>X	Z>Y>X	Z≧Y>X	Y≦Z>X	Z≦Y>X	Z≧Y>X
S. G.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.

No. 1. Ferrohastingsite from nepheline-syenite, Dungannon, ADAMS and HARRINGTON 1896 (BILLINGS 1928, p. 288, No. a).

No. 2. Ferrohastingsite from nepheline-syenite, Almunge, QUENSEL 1914 (BILLINGS 1928, p. 288, No. b).

No. 3. Ferrohastingsite from nordmarkite, analyst W. H. HERDSMAN (BILLINGS 1928, p. 288, No. c).

No. 4. Ferrohastingsite from metamorphic limestone, Custer Cy., analyst E. V. SHANNON (BILLINGS 1928, p. 288, No. d).

No. 5. Hudsonite from pegmatite, Cornwall, analyst S. WEIDMAN 1903 (BILLINGS 1928, p. 288, No. e).

No. 6. Ferrohastingsite from alkalisyenite, Beverly (WRIGHT 1900).

No. 7. Ferrohastingsite from pyroxene-granite, Mariupol (AINBERG 1930, p. 87 or 599, No. a).

No. 8. Ferrohastingsite from mariupolite, Mariupol (AINBERG 1930, p. 89 or 601, No. a).

*) Sum is 98.64 instead of 99.64 as given in AINBERG's paper.

L. van der Plas and Th. Hügi

Table 4 cont.

	8a	9	10	11	12	13	14	15
SiO_2	38.82	37.51	38.89	38.03	38.89	37.33	39.28	49.22
Al_2O_3	9.07	8.50	11.88	11.59	10.22	12.78	11.73	7.78
Fe_2O_3	5.57	11.41	7.56	6.81	9.53	8.58	6.77	8.28
FeO	25.87	23.21	21.88	23.72	21.40	21.65	22.85	10.49
MnO	0.25	1.70	0.66	1.11	0.48	1.36	0.20	0.23
MgO	1.91	0.56	2.68	2.87	2.23	1.48	2.78	10.52
CaO	11.79	7.91	10.66	9.75	9.08	9.46	11.62	7.45
Na_2O	2.79	3.79	1.75	2.30	3.78	3.49	0.50	3.54
K_2O	0.92	2.10	1.99	1.90	0.97	1.89	1.69	0.26
TiO_2	0.58	0.73	0.65	0.22	1.43	1.32	0.73	0.23
P_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H_2O^+	2.31	2.32	1.19	1.20	1.84	0.81	1.97	1.80
H_2O^-	0.27	0.33	(0.02)	n.d.	n.d.	0.22	0.12	0.32
F	0.06	0.14	0.21	0.05	n.d.	n.d.	0.52	n.d.
Cl	0.20							
	100.41	100.21					100.76	
$F = O$	0.07	0.06					0.22	
	100.34	100.15	100.00	99.55	99.85	100.37	100.54	100.12

Z–X	0.018		0.018	0.018	0.019	0.010–0.016
X	1.695		1.694	1.706	1.688	1.66 –1.67
Y	1.710		1.710	1.723	1.707	n.d.
Z	1.713		1.712	1.724	1.716	1.675–1.685
x	greenish brown	light brownish	green-yellow		pale yellow brown	c = blue
y	olive green	dark green	dark ol. green		green	b = olive green
z	bluish green	green-brown	dark blue-green		br. green-green blue	a = yellowish
ext.	Z/c 16½°		Z/c 17½°		Z/c 21°	Y/c 20–30° Z/c 12–20°
2V	29°		32°	20°	46°	0°–48° (x)
disp			r>v			
b = ?			b = Z	b = Z	b = Y Y>Z>X	b = Z or Y c>b>a
S. G.	3.32		3.390	3.458		3.31

No. 8a. Ferrohastingsite from the Obira mine, Kyushu, Japan (MATSUMOTO 1960).

No. 9. Taramite from nepheline-syenite, Mariupol, MOROZEWICZ 1925 (AINBERG 1930, p. 89 or 601, No. aI).

No. 10. Ferrohastingsite from granite, analyst M. KLÜVER (FOSLIE 1945, p. 85, No. IV).

No. 11. Hornblende from pegmatite, Österkär, P. GELJER 1913 (FOSLIE 1945, p. 85, No. V).

No. 12. Hastingsite, White Mountains, analyst W. KUNITZ 1930 (FOSLIE 1945, p. 85, No. VII).

No. 13. Hastingsite from aegirine-hastingsite-biotite-nepheline-syenite, Fukushinzan, analyst H. YOSHIZAWA (MIYASHIRO, A. and MIYASHIRO, T., 1956, p. 48, No. 7).

No. 14. Hastingsitic hornblende from hornblende-biotite-quartz-monzonitic syenite, analyst T. MIYASHIRO-INOUE (MIYASHIRO, A. and MIYASHIRO, T., 1956, p. 48, No. 8).

No. 15. Amphibole from albite-vein, Vals, analysts TH. HÜGI and E. SPYCHER, this paper.

Table 5. Chemical analyses and optical properties of some femaghastingsites and magnesiohastingsites

	1	2	3	4	5	6
SiO$_2$	38.04	38.633	39.23	39.23	43.30	49.22
Al$_2$O$_3$	13.50	11.974	11.94	14.38	10.69	7.78
Fe$_2$O$_3$	6.21	3.903	5.92	2.92	3.94	8.28
FeO	15.85	11.523	12.04	8.56	7.00	10.49
MnO	1.21	0.729	0.10	0.65	0.35	0.23
MgO	7.26	10.200	11.01	13.01	16.02	10.52
CaO	12.42	12.807	11.21	11.70	9.73	7.45
Na$_2$O	3.21	3.139	2.33	3.05	4.58	3.54
K$_2$O	1.68	1.489	0.99	0.98	0.66	0.26
TiO$_2$	1.06	5.035	7.99	4.53	1.55	0.23
P$_2$O$_5$	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
H$_2$O$^+$	n. d.	n. d.	0.36	0.36	1.80	1.80
H$_2$O$^-$	n. d.	n. d.				0.32
F	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
	100.44	99.432	99.54*)	99.37	99.62	100.12

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Z–X	0.021	0.033	0.029	0.029	0.017	0.010–0.016
X	1.679	1.670	1.676	1.676	1.653	1.66 –1.67
Y	1.694	1.692	1.692	1.692	1.663	n. d.
Z	1.698	1.703	1.705	1.705	1.670	1.675–1.635
x	light brown	light brown	yellow	yellow	pale yellow	c = blue
y	brown	brown	deep brown	deep brown	green	b = olive green
z	green brown	brown hint of gr.	deep brown	brown	green	a = yellowish
ext.	Z/c 11°	Z/c 15°	Z/c 16°	Z/c 16°	Z/c 40°	Y/c 20°–30° Z/c 12°–20°
2 V	60°	80°	76°	76°	64°	0°–48° (x)
disp.	r < v	r < v	r > v	r > v	low	
b = ?	b = Y	b = Y	b = Y	b = Y	b = Y	b = Z or Y
S. G.	3.518	n. d.	n. d.	3.159	3.160	3.31
	Y > Z > X	Y > Z > X	Y = Z > X	Y = Z > X	n. d.	c > b > a

No. 1–6. BILLINGS 1928, p. 290, No. f, g, h/, h₂, i.

No. 1. Femaghastingsite from akerite, Cuttingsville.

No. 2. Femaghastingsite from essexite, Mt. Johnson.

No. 3. Titaniferous femaghastingsite from diorite, Montreal. NiO is 0.04, SrO is 0.01.

No. 4. Magnesiohastingsite from essexite, Montreal.

No. 5. Magnesiohastingsite from metamorphosed limestone, Iron Hill.
   N.B. The optical properties of No. 4 and 5 are not determined on the analyzed material.

No. 6. Amphibole from albite vein, Vals, analysts TH. HÜGI and E. SPYCHER, this paper.

   *) Sum is 102.12 instead of 99.54 as given in BILLINGS' paper.

higher figure than was found in the amphibole under discussion. These calculations also show that the analyses given by BILLINGS do not all lead to a satisfactory solution in terms of endmembers. The first analysis might even be wrong, the sum of Al and Si being smaller than 8 and the amount of Ca + Na + K being larger than 3. The same applies to analysis no. 5, which can only be brought to a matching set of endmembers by using SHÎDO's variant. The last table, 5, compares the analyses of femaghastingsites and magnesiohastingsites given by BILLINGS with those of our amphibole, showing that here too, disregarding the printer's error in no. 3, a considerable difference exists.

Summarizing, the amphibole under consideration may not be called a riebeckite or a hastingsite. This leaves us with the problem of finding a name for an amphibole that is of widespread occurrence in the metamorphic rocks of certain parts of the Swiss Alps, and is also reported from other regions.

Formerly these amphiboles were called hastingsites on the assumption that similarity of optical properties indicates similarity of chemical composition. This, however, we have shown to be a *fallacy*. In the past the problem of a name would have been solved by proposing a new one for this mineral. The confusion in the nomenclature of amphiboles, is, however, so enormous, that only specialists could find a way out of this chaos. The authors, prefer, therefore, to wait until a sound proposal for a reclassification of amphiboles is made, based on chemical analysis, X-ray data and optical properties. Such a reclassification must necessarily take into account genetical relationships. For the time being the amphibole should be referred to as a *ferrian sodium-amphibole*.

Acknowledgments

References

AINBERG, L. (1930): The hornblendes from the Mariupol alkaline body. Bull. Geol. Prosp. Serv., U.S.S.R., *49*, p. 587—617 or 75—105 (text in russ. with engl. summ.).

BILLINGS, M. (1928): The chemistry, optics and genesis of the hastingsite group of amphiboles. Amer. Miner., *13*, p. 287—296.

ERNST, W. G. (1960): The stability relations of magnesioriebeckites. Geoch. Cosmoch. Acta, *19*, p. 10—41.

FOSLIE, S. (1945): Hastingsites and amphiboles from the epidote-amphibolite facies. Norsk. geol. Tidsskr., *25*, p. 74—98.

HERITSCH, H., PAULITSCH, P. und WALITZI, EVA M. (1957): Die Struktur von Karinthin und einer barroisitischen Hornblende. Tschermak Min. Petr. Mitt., F. 3, *6*, p. 215—225.

JAKOB, J. und BRANDENBERGER, E. (1931): Chemische und röntgenographische Untersuchungen an Amphibolen. I. Mitteilung: Die Osannite von Alter Pedroso. Schweiz. Min. Petr. Mitt., *11*, p. 140—162.

MATSUMOTO, Y. and MIYAHISA, M. (1960): Ferrohastingsite from the Obira mine, Kyushu, Japan. Journ. Min. Soc. Japan, *4*, 372—382, in Japanese [Engl. Abstr. in Min. Abstr. 1961, *15*, 42].

MIYASHIRO, A. and MIYASHIRO, T. (1956): Nepheline syenites and associated alkalic rocks of the Fukushin-zan district, Korea. Jour. Fac. Sci. Univ. Tokyo, Sec. II, *10*, p. 1—64.

MIYASHIRO, A. (1957): The chemistry, optics and genesis of the alkali-ampiboles. Jour. Fac. Sci. Univ. Tokyo, Sec. II, *11*, p. 57—83.

PEACOCK, M. A. (1928): The nature and origin of the amphibole-asbestos of South Africa. Amer. Min. *13*, p. 241—285.

PHEMISTER, J., HARVEY, C. O. and SABINE, P. A. (1950): The riebeckite-bearing dikes of Shetland. Min. Mag., *29*, p. 359—374.

PLAS, L. VAN DER (1959): Petrology of the northern Adula region, Switzerland (with particular reference to the glaucophane-bearing rocks). Leidse Geol. Meded., *24*, 2, p. 415—599.

SCHWARZENBACH, G. (1960): Die komplexometrische Titration. Stuttgart 1960.

SHÎDO, FUMIKO (1958): Plutonic and metamorphic rocks of the Nakoso and Iritôno districts in the Central Abukama Plateau. Jour. Fac. Sci. Univ. Tokyo, Sec. II, *11*, p. 131—217.

WHITTAKER, E. J. W. (1949): The structure of Bolivian crocidolite. Acta Cryst., *2*, p. 312—317.

WRIGHT, F. E. (1900): The Alkalisyenite from Beverly, Mass. U.S.A. Tschermak Miner. Petr. Mitt., N.F., *19*, p. 308.

ZWAAN, P. C. and PLAS, L. VAN DER (1958): Optical and X-ray investigation of some pyroxenes and amphiboles from Nagpur, Central Provinces, India. (Including blanfordite, manganese-bearing aegirite-augite, juddite and tirodite). Kon. Nederl. Akad. Wetensch. Amsterdam, Ser. B., *61*, p. 265—277.