

Chemical and Crystallographical studies
on Calciferous Amphiboles,
Tschermakite-Pargasite Series from Volcanic Rocks

By

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Abstract

Calciferous amphiboles of tschermakite-pargasite series occur mainly in volcanic rocks. These amphiboles can be called oxyhornblende. Chemical composition of calciferous amphiboles may indicate the geological environment which crystallized them.

By X-ray powder diffraction, there are found interesting facts in the relationship between tremolite or actinolite and tschermakite-pargasite series.

Introduction

It has become an important field of investigation of mineralogy to discuss the relationship between the chemical composition and the crystal structure of rock forming minerals. Accordingly, it is essential to clarify the variety of chemical composition and to determine the accurate crystal structures of rock-forming minerals formed under various conditions. From this viewpoint, many excellent studies have been carried out on feldspars, pyroxenes, and other minerals.

In the investigation of amphibole group, it is necessary to obtain the reliable chemical and crystallographical data.

The principal aims of this study are to find the chemical formula, the relationship among the substitutions of some element groups, and to obtain crystallographic data of Al-rich calciferous amphiboles occurring mainly in volcanic rocks.

In this paper, the chemical formula of this variety of amphibole will be described, some informations will be given on the relationship between constituents, and the crystallographic data obtained from the powder patterns of the X-ray diffraction will be described.

Reliable crystallographic data for Al-rich calciferous amphibole will be discussed in future.

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Classification of Natural Amphiboles

The natural amphiboles fall into two classes, orthorhombic and monoclinic. The crystal structures of monoclinic amphiboles were investigated by WARREN (1929, 1930), WARREN and MODELL (1930), WHITTAKER (1949) and ZUSSMAN (1955, 1959).

The crystal structure of tremolite given by WARREN (1930) consists of double chains of SiO_4 tetrahedra running parallel to c-axis. In a half unit cell there are eight 4-coordinate positions occupied by Si atoms, five 6-coordinate positions by Mg ions and two 8-coordinate positions by Ca ions. Hereafter, the 4-, 6- and 8-coordinate positions will be designated by the letters Z, Y, and X respectively. Besides these there is one vacant site called "A" site by Warren.

In monoclinic amphiboles, Z positions are occupied by Si and Al atoms, Y positions by Mg, Fe'' , Ti, Fe''' , and Al ions and X positions by Ca, Na, and/or K ions and occasionally by Mg, and Fe'' ions, causing a collapse of the structure. "A" site is, sometimes, occupied by Na, and/or K ion.

Then we come to the general formula of monoclinic amphibole which is as follows:



where

X: Ca, Na, K, Mg, Fe''

Y: Mg, Fe'' , Fe''' , Ti, Mn, Al

Z: Al, Si

Monoclinic amphibole can be divided into two groups on the basis of chemical composition, i.e. in the first group, X positions are occupied by Mg, and Fe'' , in the other group, by Ca, Na and K.

The former will be called commingtonite group. The latter will be divided into two sub-groups on the basis of the number of Ca-ions occupying X positions. One sub-group is calciferous amphiboles which are higher in Ca-content, and the other is alkali amphiboles lower in that content substituting Na ions for a part of Ca-ions (HALLIMOND, 1943).

In the classification of monoclinic amphiboles, such treatment as mentioned above has been adopted by many authors. Among them WHINCHELL (1945)

found an important information in systematizing amphiboles. MIYASHIRO (1957) made a valuable contribution to the study of alkali-amphiboles, and BOYD (1959) presented a new classification of amphiboles, commenting on the old one which has been current so far.

The crystal structure of orthorhombic amphiboles, anthophyllite, has been established by WARREN and MODELL (1930), and ITO (1950). The anthophyllite structure is "virtually a twinned tremolite, containing only one and the same kind of chains as found in tremolite" (ITO, 1950).

Orthorhombic amphiboles, Anthophyllite group are known only in the composition range $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. This series is miscible with $(\text{Mg}, \text{Fe}'')_5\text{Al}_2\text{Al}_2\text{Si}_6\text{O}_{22}(\text{OH})_2$ (gedrite) (RABBIT, 1948).

In this paper, the subdivisions of Ca-amphiboles are quoted from BOYD's classification (1959).

Table 1. Classification of Calciferous Amphiboles.

tremolite-ferrotremolite	$\text{Ca}_2(\text{Mg}, \text{Fe}^{+2})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
tschermakite-ferrotschermakite	$\text{Ca}_2(\text{Mg}, \text{Fe}^{+2})_3\text{Al}_2\text{Al}_2\text{Si}_6\text{O}_{22}(\text{OH})_2$
edemite-ferroedemite	$\text{NaCa}_2(\text{Mg}, \text{Fe}^{+2})_5\text{AlSi}_7\text{O}_{22}(\text{OH})_2$
pargasite-ferropargasite	$\text{NaCa}_2(\text{Mg}, \text{Fe}^{+2})_4\text{AlAl}_2\text{Si}_6\text{O}_{22}(\text{OH})_2$

There are certain calciferous amphiboles somewhat different from the groups described in Table 1. They are called oxyhornblende. The content of water in them is almost negligible. In this paper, the oxyhornblende will be mainly discussed.

Chemical Analysis of Calciferous Amphiboles

Sampling of Specimens: Calciferous amphiboles used in this study were picked out from the host rocks and agglomerate shown in Table 2. The specimens were crushed into the grains size of which is from 100 mesh to 150

Table 2

Sample	color of sample	host rock
1 (tremolite)	white	contact zone
2	dark green	hornblende porphyrite
3	dark red	hornblende andesite
4	dark green	hornblende andesite
5	black	agglomerate of volcanic ejecta

Locality

Sample 1: Antung-hsien, Liaotung, China

2: Hanyū Village, Ōno Prov. Fukui Pref. Japan

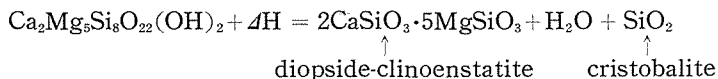
3,4: Shinanozakai, Suwa Prov. Nagano Pref. Japan

5: Gaspan, Parao Island.

mesh. The crushed specimens were separated from magnetic impurities, quartz and feldspars, using an isodynamic separator. After that, the specimens were purified under a microscope. The purified specimens were pulverized into powders in an agate mortar.

Analytical Method: The main portions, that is, SiO_2 , Al_2O_3 , CaO , MgO were determined gravimetrically which is usually applied to silicate minerals. Total iron and FeO were analysed volumetrically, the former by the methods of Zimmermann Reinhardt, and the latter by usual method. TiO_2 and MnO were determined colorimetrically. Alkali metals were determined by the method of flame photometry. Absorbed water was determined by heating the pulverized samples at the temperature between 108° and 110°C for 2 hours in an electric air-oven.

Determination of total water content was difficult technically. ALLEN and CLEMENT (1908) found that tremolite lost 85% of combined water at 923°C . POSNJAK and BOWEN (1931) demonstrated the behavior of water in tremolite by static weight loss experiments: up to 900°C , the theoretical water content of 2.22% was driven off, but the dehydration was very slow up to 850°C . Tremolite heated at 900°C for 24 hours showed several X-ray diffraction lines which are in conformity with those of pyroxene. They therefore concluded that the following reaction might be taken place in the solid state:



The author re-examined the dehydration process with tremolite (Sample No. 1), green hornblende from metagabbro, Shiga island, Fukuoka, Japan, and dark reddish amphibole (Sample No. 3), by differential thermal analysis, with the heating rate of 10°C per minute. The result indicates that endothermic reactions occur at 1040°C in the cases of tremolite and green hornblende, but it does not occur at about 1000°C in the case of dark reddish amphibole. The result shows that there is no combined water in the dark reddish amphibole (see H_2O content in Table 3). WITTELS (1952) reported that dehydration took place at the temperature between 925°C and 1125°C when tremolite, richterite, hastingsite, pargasite and glaucophane were subjected to differential thermal analysis.

The total contents of water of amphiboles will therefore be determined by heating them at a temperature of 1000°C until they have attained a constant weight. Of course, the water content obtained in a way mentioned above should be corrected by the amount of oxidized ferrous iron and of fluorine when they are contained in amphibole. In the present investigation the water content was determined by using Penfield method together with the method mentioned above.

Chemical Composition and Chemical Formula

The results of chemical analyses with calciferous amphiboles which

Table 3. Chemical Composition of Calciferous Amphiboles.

	1	2	3	4	5	6*
SiO ₂	58.54	39.34	39.58	42.05	41.07	39.20
Al ₂ O ₃	0.79	19.91	19.42	18.00	17.97	13.87
Fe ₂ O ₃	0.03	0.00	7.54	2.77	3.59	4.08
TiO ₂	0.04	1.30	3.04	2.80	0.18	6.53
FeO	0.11	7.18	0.57	4.66	7.79	7.33
MgO	23.60	14.10	14.92	15.19	13.37	11.96
MnO	tr.	0.19	0.11	0.11	0.14	0.11
CaO	12.75	14.96	12.30	10.95	12.05	12.37
Na ₂ O	0.59	2.40	2.58	2.12	1.83	1.99
K ₂ O	0.07	0.35	0.20	0.31	0.31	1.45
H ₂ O+	2.52	1.02	0.00	1.15	0.52	0.87
H ₂ O—	0.15	0.00	0.06	0.19	0.57	0.27
Total	99.19	100.75	100.32	100.30	99.39	100.03

6* : Analyst USHIZIMA (HARUMOTO, "CHIKYU" (The Earth)
Vol. 19, 1933.)

Table 4. Atomic Ratio of Analyzed Calciferous Amphiboles
Based on (O, OH)=2400

	1	2	3	4	5	6*
Si	792	570	552	600	610	586
Al ^{IV}	8	230	248	200	190	214
Al ^{VI}	4	110	70	102	125	30
Ti	0	13	32	30	2	74
Fe ⁺³	0	0	79	30	39	47
Fe ⁺²	0	86	7	56	97	92
Mn	0	1	2	2	2	2
Mg	477	304	310	324	297	267
Ca	181	232	183	168	192	198
Na	15	68	70	58	53	57
K	0	6	3	6	6	27
OH	227	99	0	110	50	86
"A"	0	106	56	32	51	82
X	196	200	200	200	200	200
R''	477	391	319	382	396	361
R'''	4	123	181	162	166	151
R''+R'''	481	514	500	544	562	512
Z	800	800	800	800	800	800

occur in volcanic rocks and in some other rocks are shown in Table 3.

In Table 4 are shown the atomic ratios for $O=2400$, which were derived from the results of chemical analyses ($O=2400$, instead of $O=24.00$) Al is divided into two groups, viz, 4-coordinate (Al^{IV}) and 6-coordinate (Al^{VI}). Letters R''' and R'' in these tables represent the trivalent and divalent ions respectively in Y-positions. "A" means the ion occupying "A" site. $R''' + R''$ should be equal to 500 ideally, and nearly equal to 500 in the actual compositions of amphiboles.

The procedure of calculating R''' and R'' is as follow; Si is smaller than 800 in most cases and, therefore, a part of Al is allotted so that $Si + Al^{IV} = 800$. These Si and Al atoms represent the cation forming (Si, Al^{IV})-0 tetrahedra. The remaining Al is regarded as being situated in 6-coordinate positions together with Ti, Fe''' , Fe'' , Mn and Mg. The notations R''' and R'' , so far used, mean $Al^{VI} + Ti + Fe'''$ and $Fe'' + Mn + Mg$, respectively.

Ca is nearly equal to 200 in calciferous amphiboles but sometimes falls below 200. In such a case it is currently considered that the deficient is supplied with Na and/or K. In most cases, however, $Ca + Na + K$ is larger than 200. The excess of Na and/or K is considered to be in the "A" site.

Calciferous amphibole of Sample 1 has a typical formula of tremolite $Ca_2Mg_5Si_6O_{22}(OH)_2$. In other amphiboles, Si is close to 6 atoms, and 8 positions of four fold coordinations are replaced by two Al atoms. Ca is generally 1.8-2.0. Therefore amphiboles of sample 2, 3, 4, 5 and 6 belong to tschermakite-pargasite series. "A" site is occupied by 0.5-1.0 alkali metal ions in these amphiboles, so it may be better to describe these amphiboles as calciferous amphiboles of pargasite-ferropargasite group.

The Ca-amphibole of sample 6 has been described as typical titaniferous amphibole, kaersutite, by HARUMOTO (1933): this sample was used in the experiment of X-ray diffraction in this work. The chemical formula of the kaersutite is graphically represented as $(Na, K, Ca)_3R''_4(Fe''', Al)_{0.3}Ti_{0.7}Al_2Si_6O_{23}(OH)$.

Calciferous amphiboles of Sample 2, 3, 4 and 5 have high degrees of replacement of R'' position by Mg, approaching to the value of 3.

These minerales present the chemical compositions of pargasite side in the pargasite-ferropargasite group.

If the oxyhornblende is not strictly a primary mineral, but is an alteration product of common green hornblende by oxydation and dehydration, calciferous amphiboles of sample 2, 3, 4, 5 and 6 may be called oxyhornblende. Especially, the reddish amphibole of sample 3 accepts oxydation to a higher degree than others. Amphiboles of sample 3 and 4 are found in the same volcanic rock, andesite, and in chemical composition, they are similar, except for the amounts of Fe_2O_3 and FeO . But they indicate exactly, however, the same number of $(Fe^{+3} + Fe^{+2})$ atoms. Therefore, it may be considered that the reddish amphibole of Sample 3 is an alteration product of the green amphibole of Sample 4.

Table 5. X-ray Powder Diffraction Patterns of Amphiboles
Sample 1. tremolite

h k l	2 θ degree	4 sin ² θ obs.	4 sin ² θ cal.	d (Å)	I
0 2 0	9.75	0.0288	0.0288	9.07	19
1 1 0	10.50	0.0335	0.0334	8.42	109
1 0 $\bar{1}$	17.45	0.0920	0.0923	5.08	10
0 1 1	18.13	0.0994	0.1008	4.90	6
2 0 0	18.62	0.1046	0.1048	4.77	11
0 4 0	19.63	0.1162	0.1152	4.55	11
2 2 0	21.10	0.1341	0.1336	4.21	24
0 3 1	22.86	0.1571	0.1584	3.89	6
1 4 $\bar{1}$	26.30	0.2070	0.2075	3.40	23
2 4 0	27.23	0.2217	0.2200	3.28	41
3 1 0	28.53	0.2429	0.2430	3.13	100
0 5 1	30.36	0.2744	0.2736	2.94	16
3 3 0	31.92	0.3023	0.3006	2.81	27
2 3 1	32.76	0.3182	0.3182	2.73	12
2 5 $\bar{1}$	33.08	0.3242	0.3234	2.71	28
1 1 $\bar{2}$	34.55	0.3527	0.3528	2.59	9
2 0 $\bar{2}$	35.37	0.3690	0.3692	2.54	12
1 3 $\bar{2}$	37.35	0.4104	0.4104	2.40	1
3 0 1	37.75	0.4186	0.4119	2.38	7
4 0 0			0.4192		
3 2 1	38.50	0.4347	0.4407	2.34	14
4 2 0	39.15	0.4490	0.4480	2.30	5
2 7 $\bar{1}$	41.74	0.5075	0.4962	2.16	14
3 3 $\bar{2}$			0.5100		
2 0 2	44.92	0.5831	0.5892	2.02	8
5 1 0	48.00	0.6617	0.6622	1.90	14
5 6 $\bar{1}$	55.65	0.8715	0.8703	1.65	8
4 8 0	56.15	0.8859	0.8800	1.64	2
5 2 1	56.88	0.9073	0.9149	1.62	2
6 0 0	58.40	0.9520	0.9434	1.58	1
1 0 3			0.9519		
1 2 3	59.43	0.9829	0.9802	1.56	2
5 7 0	60.30	1.0090	1.0078	1.53	2
6 2 $\bar{2}$			1.0164		
2 8 2	61.70	1.0518	1.0500	1.50	3
2 12 0	64.75	1.1468	1.1416	1.44	18

Table 5. (Continued)
Sample 2.

h k l	2 θ degree	4 sin ² θ obs.	4 sin ² θ cal.	d (Å)	I
0 2 0					
1 1 0	10.55	0.0338	0.0335	8.42	91
1 0 $\bar{1}$					
0 1 1	18.00	0.0978	0.1001	4.93	4
2 0 0					
0 4 0	19.67	0.1166	0.1168	4.51	6
2 2 0	21.10	0.1341	0.1340	4.21	4
1 4 $\bar{1}$	26.33	0.2075	0.2084	3.39	12
2 4 0	27.25	0.2219	0.2216	3.27	40
3 1 0	28.62	0.2443	0.2431	3.12	100
0 5 1	30.45	0.2759	0.2753	2.93	8
3 3 0	31.95	0.3029	0.3015	2.80	18
2 3 1	32.68	0.3166	0.3181	2.74	15
2 5 $\bar{1}$	33.05	0.3236	0.3253	2.71	19
1 1 $\bar{2}$	34.50	0.3517	0.3499	2.60	10
2 0 $\bar{2}$	35.16	0.3650	0.3664	2.55	6
3 0 1			0.4108		
4 0 0	37.75	0.4183	0.4192	2.38	4
3 2 1	38.40	0.4325	0.4400	2.34	8
4 2 0					
2 7 $\bar{1}$			0.5083		
3 3 $\bar{2}$	41.75	0.5078	0.5275	2.16	8
2 0 2	44.75	0.5837	0.5852	2.02	6
5 1 0	48.02	0.6621	0.6623	1.89	4
5 3 0					
5 6 $\bar{1}$	55.72	0.8734	0.8736	1.65	1
4 8 0					
5 2 1					
6 0 0					
1 0 3					
6 2 $\bar{2}$					
5 7 0					
0 12 0					
4 8 $\bar{2}$					
2 8 2					
2 12 0	64.73	1.1463	1.1560	1.44	10

Table 5. (Continued)
Sample 3, from andesite

h k l	2 θ degree	4 sin ² θ obs.	4 sin ² θ cal.	d (Å)	I
0 2 0					
1 1 0	10.60	0.0341	0.0336	8.35	84
1 0 $\bar{1}$					
0 1 1					
2 0 0					
0 4 0	19.68	0.1168	0.1168	4.51	9
2 2 0					
1 4 $\bar{1}$	26.41	0.2088	0.2082	3.38	16
2 4 0	27.34	0.2233	0.2220	3.27	33
3 1 0	28.70	0.2457	0.2440	3.11	100
0 5 1	30.55	0.2776	0.2752	2.92	12
3 3 0	32.02	0.3042	0.3024	2.80	14
2 3 1	32.75	0.3179	0.3188	2.73	14
2 5 $\bar{1}$	33.14	0.3252	0.3254	2.71	28
1 1 $\bar{2}$	34.62	0.3540	0.3492	2.59	14
2 0 $\bar{2}$	35.20	0.3657	0.3656	2.55	13
3 0 1			0.4122		
4 0 0	37.90	0.4218	0.4208	2.37	5
3 2 1	38.56	0.4362	0.4414	2.33	9
2 7 $\bar{1}$			0.5006		
3 3 $\bar{2}$	41.95	0.5125	0.5076	2.15	9
2 0 2	45.17	0.5899	0.5864	2.01	10
5 1 0	48.43	0.6730	0.6648	1.88	5
5 3 0	50.60	0.7305	0.7332	1.80	7
5 6 $\bar{1}$					
4 8 0	56.05	0.8830	0.8766	1.64	10
5 2 1					
6 0 0					
1 0 3					
6 2 $\bar{2}$					
5 7 0					
0 12 0					
4 8 $\bar{2}$					
2 8 2					
2 12 0	65.08	1.1574	1.1564	1.43	9

Table 5. (Continued)

Sample 4.

h k l	2 θ degree	4 sin ² θ obs.	4 sin ² θ cal.	d (Å)	I
0 2 0	9.80	0.0291	0.0292	9.03	2
1 1 0	10.55	0.0338	0.0335	8.42	95
1 0 $\bar{1}$					
0 1 1					
2 0 0					
0 4 0	19.65	0.1164	0.1168	4.52	6
2 2 0					
1 4 $\bar{1}$	26.32	0.2072	0.2084	3.39	10
2 4 0	27.26	0.2222	0.2216	3.27	32
3 1 0	28.65	0.2448	0.2431	3.12	100
0 5 1	30.43	0.2755	0.2755	2.94	16
3 3 0	31.95	0.3029	0.3015	2.80	33
2 3 1	32.70	0.3169	0.3185	2.74	9
2 5 $\bar{1}$	33.05	0.3236	0.3253	2.71	16
1 1 $\bar{2}$	34.53	0.3524	0.3505	2.60	7
2 0 $\bar{2}$	35.16	0.3650	0.3664	2.55	9
3 0 1			0.4116		
4 0 0	37.80	0.4197	0.4192	2.38	6
3 2 1	38.50	0.4347	0.4408	2.34	9
4 2 0					
2 7 $\bar{1}$			0.5003		
3 3 $\bar{2}$	41.85	0.5102	0.5074	2.16	7
2 0 2	44.77	0.5800	0.5872	2.02	4
5 1 0	48.18	0.6665	0.6623	1.89	7
5 3 0	50.40	0.7251	0.7207	1.81	4
5 6 $\bar{1}$	55.90	0.8787	0.8768	1.64	6
4 8 0					
5 2 1					
6 0 0			0.9432		
1 0 3	58.32	0.9495	0.9460	1.58	4
6 2 $\bar{2}$					
5 7 0					
0 12 0					
4 8 $\bar{2}$					
2 8 2					
2 12 0	64.85	1.1500	1.1560	1.44	10

Table 5. (Continued)

Sample 5.

h k l	2 θ degree	4 sin ² θ obs.	4 sin ² θ cal.	d (Å)	I
0 2 0	9.80	0.0291	0.0288	9.03	1
1 1 0	10.50	0.0335	0.0331	8.42	103
1 0 $\bar{1}$					
0 1 1					
2 0 0					
0 4 0	19.60	0.1158	0.1152	4.53	11
2 2 0					
1 4 $\bar{1}$	26.27	0.2065	0.2065	3.39	19
2 4 0	27.20	0.2211	0.2188	3.28	28
3 1 0	28.50	0.2423	0.2403	3.13	100
0 5 1	30.35	0.2741	0.2729	2.94	17
3 3 0	31.85	0.3011	0.2979	2.81	32
2 3 1	32.60	0.3151	0.3165	2.75	17
2 5 $\bar{1}$	33.00	0.3226	0.3215	2.71	24
1 1 $\bar{2}$	34.52	0.3520	0.3497	2.60	13
2 0 $\bar{2}$	35.10	0.3637	0.3652	2.56	13
3 0 1			0.4081		
4 0 0	37.75	0.4186	0.4144	2.38	6
3 2 1	38.36	0.4319	0.4363	2.34	16
4 2 0	39.05	0.4468	0.4432	2.30	7
2 7 $\bar{1}$			0.4943		
3 3 $\bar{2}$	41.76	0.5082	0.5038	2.16	18
2 0 2	45.00	0.5857	0.5852	2.01	10
5 1 0	48.05	0.6630	0.6547	1.89	4
5 3 0					
5 6 $\bar{1}$	55.70	0.8729	0.8721	1.65	16
4 8 0					
5 2 1	56.97	0.9097	0.9067	1.62	6
6 0 0			0.9324		
1 0 3	58.15	0.9446	0.9445	1.59	10
6 2 $\bar{2}$					
5 7 0					
0 12 0					
4 8 $\bar{2}$					
2 8 2	61.65	1.0502	1.0460	1.50	11
2 12 0	64.70	1.1452	1.1404	1.44	11

Table 5. (Continued)

6* kaersutite

h k l	2 θ degree	4 sin ² θ obs.	4 sin ² θ cal.	d (Å)	I
0 2 0					
1 1 0	10.50	0.0335	0.0333	8.42	69
1 0 $\bar{1}$					
0 1 1					
2 0 0					
0 4 0					
2 2 0					
1 4 $\bar{1}$	26.30	0.2059	0.2059	3.39	13
2 4 0	27.15	0.2203	0.2196	3.29	32
3 1 0	28.54	0.2429	0.2421	3.13	100
0 5 1	30.33	0.2738	0.2720	2.95	11
3 3 0	31.80	0.3002	0.2997	2.81	21
2 3 1	32.46	0.3126	0.3164	2.75	10
2 5 $\bar{1}$	32.96	0.3220	0.3212	2.71	13
1 1 $\bar{2}$	34.43	0.3504	0.3463	2.61	11
2 0 $\bar{2}$	35.30	0.3677	0.3644	2.54	16
3 0 1	37.66	0.4168	0.4097	2.39	9
4 0 0			0.4176		
3 2 1	38.25	0.4293	0.4385	2.35	10
4 2 0					
2 7 $\bar{1}$	41.66	0.5059	0.4940	2.17	8
3 3 $\bar{2}$			0.5021		
2 0 2	44.88	0.5829	0.5828	2.02	7
5 1 0	48.00	0.6617	0.6597	1.90	6
5 3 0					
5 6 $\bar{1}$					
4 8 0					
5 2 1	56.80	0.9048	0.9113	1.62	7
6 0 0	58.06	0.9426	0.9396	1.59	9
1 0 3			0.9369		
6 2 $\bar{2}$					
5 7 0					
0 12 0					
4 8 $\bar{2}$					
2 8 2					
2 12 0	64.56	1.1410	1.1412	1.44	7

Table 5. (Continued)
actinolite from Mt. Iratsu, Ehime Prefecture, Japan.

h k l	2 θ degree	4 sin θ obs.	4 sin θ cal.	d (Å)	I
0 2 0	9.60	0.0280	0.0282	9.21	7
1 1 0	10.50	0.0335	0.0335	8.42	100
1 0 $\bar{1}$	17.40	0.0915	0.0924	5.10	9
0 1 1	18.10	0.0989	0.1009	4.90	6
2 0 0	18.67	0.1052	0.1052	4.65	10
0 4 0	19.66	0.1166	0.1152	4.51	15
2 2 0	21.10	0.1341	0.1340	4.21	33
1 4 $\bar{1}$	26.33	0.2075	0.2076	3.39	10
2 4 0	27.25	0.2219	0.2204	3.27	35
3 1 0	28.60	0.2440	0.2439	3.12	100
0 6 0	29.45	0.2578	0.2592	3.03	7
0 5 1	30.35	0.2741	0.2737	2.94	12
3 3 0	31.90	0.3020	0.3015	2.81	43
2 3 1	32.82	0.3191	0.3189	2.73	11
2 5 $\bar{1}$	33.05	0.3236	0.3237	2.71	21
1 1 $\bar{2}$	34.55	0.3527	0.3533	2.59	8
2 0 $\bar{2}$	35.40	0.3697	0.3696	2.54	8
4 0 0	37.75	0.4186	0.4132	2.38	8
3 0 1			0.4208		
3 2 1	38.50	0.4347	0.4414	2.34	9
4 2 0	39.15	0.4490	0.4496	2.30	6
2 7 $\bar{1}$	41.75	0.5078	0.4965	2.16	8
3 3 $\bar{2}$			0.5107		
2 0 2	44.92	0.5837	0.5904	2.02	7
5 1 0	48.10	0.6643	0.6647	1.89	16
5 3 0	50.30	0.7224	0.7223	1.81	8
5 6 $\bar{1}$	55.63	0.8710	0.8724	1.65	8
4 8 0	56.10	0.8845	0.8816	1.64	3
5 2 1	56.87	0.9068	0.9180	1.62	6
6 0 0	58.20	0.9460	0.9468	1.53	6
1 0 3			0.9524		
6 2 $\bar{2}$	60.40	1.0121	1.0192	1.53	3
5 7 0			1.0103		
4 8 $\bar{2}$	61.20	1.0365	1.0356	1.51	3
0 12 0			1.0368		
2 8 2	61.65	1.0502	1.0512	1.50	6
2 12 0	63.84	1.1495	1.1420	1.44	13

X-Ray Power Diffraction of Calciferous Amphiboles

Experimental: Five powder samples of calciferous amphiboles used in the investigation are shown in Table 2, and the others are actinolite from Mt. Iratsu, Ehime Pref. Japan, and kaersutite from Utsuryo island, Korea (chemical composition in the Table 3, 6*).

X-ray powder diffraction patterns of seven samples of calciferous amphiboles were obtained by the Shimazu recording diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and Ni filter. The diffractometer was operated under the following conditions.

Voltage:	35 KV
Current:	10 mA
Scanning speed:	1° per minute
Chart speed:	1 cm/min.
Range:	500 cps.
Time constant:	2 second
Slite:	Divergence 1.5 mm, Scatter 0.20 mm, Receiving 0.15 mm

2θ angles were measured at the maximum of diffraction peaks and calculated by silicon diffraction pattern using the method of least squares. The assignment of the peaks of tremolite was made by comparison with $4 \sin^2 \theta$ obs. and calculated $4 \sin^2 \theta$ on the basis of the unit cell dimension, $a_0=9.78 \text{ \AA}$, $b_0=17.80 \text{ \AA}$, $c_0=5.26 \text{ \AA}$, $\beta=106^\circ 2'$ (WARREN 1930) as space group I 2/m. The assignment of actinolite was made by the same treatment (cell dimension $a_0=9.89 \text{ \AA}$, $b_0=18.14 \text{ \AA}$, $c_0=5.31 \text{ \AA}$, $\beta=105^\circ 48'$ space group I 2/m ZUSSMAN, 1955). Other calciferous amphiboles, pargasite groups and kaersutite, were indexed by analogy with the very similar patterns of tremolite, actinolite.

The final least-squares treatment yields the cell dimensions as given in Table 6.

The final assignment of lines together with the calculated (on the basis of the unit cell data given in the Table 6) and observed $4 \sin^2 \theta$, and, observed spacings and intensities are given in Table 5.

Table 6 A Reciprocal Lattice Dimensions of Ca-Amphiboles

	a^*	b^*	c^*	β^*
Sample 1 (tremolite)	0.1618	0.0848	0.3059	$73^\circ 51'$
Sample 2	0.1619	0.0854	0.3047	$73^\circ 53'$
Sample 3	0.1622	0.0857	0.3045	$73^\circ 45'$
Sample 4	0.1620	0.0853	0.3050	$73^\circ 47'$
Sample 5	0.1611	0.0848	0.3048	$73^\circ 45'$
kaersutite	0.1615	0.0851	0.3033	$74^\circ 37'$
actinolite	0.1621	0.0848	0.3061	$73^\circ 52'$

Table 6 B Lattice Dimension of Ca-Amphiboles (space group I 2/m)

	a_0 (Å)	b_0 (Å)	c_0 (Å)
Sample 1 (tremolite)	9.92	18.18	5.17
Sample 2	9.91	18.06	5.27
Sample 3	9.90	17.99	5.27
Sample 4	9.91	18.09	5.26
Sample 5	9.96	18.17	5.27
kaersutite	9.89	18.12	5.27
actinolite	9.89	18.17	5.24

The X-ray powder diffraction data for 5 samples of pargasite group, tremolite and actinolite are compared in Table 5. In their d values, there is no remarkable difference between pargasite group and actinolite or tremolite group. In relative intensities of diffraction patterns, however, the pargasite group has a notable difference from both the tremolite and actinolite group as shown in Table 7. This problem will be discussed in future.

When the unit cell dimensions of pargasite groups and those of tremolite or actinolite group are compared, there is no remarkable difference in the a_0 values, but the b_0 values of pargasite group are smaller than that those of tremolite and actinolite with a difference range of 0.06 Å-0.19 Å, and the c_0 values of pargasite group and actinolite is larger than that of tremolite with a difference range of about 0.1 Å.

Table 7 Relative Intensities of Some X-ray Diffraction Patterns.

h k l	Sample 1 tremolite	actinolite	Sample 2	3	4	5	kaersutite 6*
1 1 0	109	100	91	84	95	103	69
2 2 0	24	33	4	0	0	0	0
3 3 0	27	43	18	14	33	32	21
1 0 $\bar{1}$	10	9	0	0	0	0	0
2 0 $\bar{2}$	12	8	6	13	9	13	8
2 0 0	11	10	0	0	0	0	0
4 0 0							
3 0 1	7	8	4	6	5	6	8

Graphical Representations and Chemical Formula of Calciferous Amphiboles from Volcanic Rocks.

In order to compare with the chemical compositions of calciferous amphiboles from volcanic rocks, a number of reliable data were collected from numerous literatures. They are shown in Table 8, which was compiled in the

Table 8 Analyses of Calciferous Amphiboles Calculated to Atomic Ratios Based on (O, OH)=2400

No.	Si	Al	Ti	Fe'''	Fe''	Mn	Mg	Ca	Na	K	OH	R'''	"A"
8	649	170	9	155	5	9	299	144	44	3	n.d.	183	0
9	597	250	78	51	91	1	247	173	75	29	37	176	77
10	584	243	72	45	90	1	266	197	57	26	86	144	80
11	700	228	16	41	80	6	334	178	29	6	95	185	13
12	573	200	31	124	1	7	301	178	67	28	n.d.	128	73
13	676	127	12	118	94	1	272	182	31	7	64	123	20
14	589	238	22	86	45	2	328	192	49	16	210	135	57
15	588	237	23	116	14	1	318	187	43	16	203	164	46
16	688	189	—	62	305	—	58	197	60	75	39	139	132
17	681	167	19	55	113	4	292	176	39	20	64	141	35
18	673	135	24	160	35	5	298	178	39	21	19	216	30
19	622	220	47	52	73	n.d.	315	192	92	31	20	188	115
20	610	174	96	98	46	1	280	196	63	11	20	274	70
21	609	206	10	92	342	13	33	169	65	40	217	127	74
22	607	218	30	137	103	—	222	201	68	20	46	222	89
23	603	248	56	82	61	—	264	194	61	22	48	245	77
24	599	226	46	84	80	—	291	194	66	29	72	201	89
25	598	265	3	117	97	3	254	205	33	51	48	186	89
26	597	296	62	47	68	4	218	202	49	63	35	264	114
27	595	230	48	76	74	—	303	199	81	17	67	197	97
28	595	195	35	127	103	7	231	220	29	13	150	187	62
29	592	261	29	86	47	—	321	196	66	24	59	197	86
30	587	305	19	80	27	—	310	188	90	37	40	210	115
31	585	258	41	60	73	1	272	175	64	29	205	185	68
32	585	389	13	27	111	—	270	164	33	12	23	227	9
33	581	321	28	61	28	9	308	198	73	35	25	218	106
34	575	227	68	90	88	1	264	169	90	25	110	228	84
101	760	36	—	9	17	2	461	172	68	23	190	5	63
102	782	20	1	3	3	—	485	205	11	3	201	7	19
103	790	22	—	1	7	1	485	188	6	1	196	13	—
104	791	22	1	5	12	2	524	197	23	16	—	20	36
105	788	29	2	—	6	—	490	193	13	4	142	21	10
106	792	21	2	15	48	2	467	190	22	9	63	32	21
107	739	73	—	31	175	—	284	195	9	—	218	43	4
108	750	84	8	—	3	1	502	202	52	12	23	53	66
109	771	71	2	8	146	5	321	180	103	11	49	54	94
110	758	54	—	39	101	1	333	222	32	2	121	51	56
111	742	124	4	23	68	3	349	210	12	11	92	97	33
112	717	137	10	29	80	6	348	172	34	10	134	103	16
113	732	125	10	87	131	—	254	172	35	13	33	164	20
114	702	124	12	27	116	1	343	175	53	3	165	77	31
115	701	118	5	40	105	—	338	204	28	—	180	69	32
116	695	125	—	22	125	—	353	197	28	6	203	42	31
117	666	180	10	31	100	2	310	196	45	8	190	97	49
118	665	255	15	83	153	—	121	175	84	10	75	233	69
119	662	188	9	54	166	4	246	196	68	24	71	122	88
120	646	183	15	25	153	—	295	192	55	—	204	84	47
121	642	199	18	36	160	—	272	181	41	12	200	102	34
122	614	211	29	45	149	—	251	184	53	11	229	128	48
123	638	193	12	39	188	—	255	181	39	9	206	94	29
124	631	178	31	32	190	3	257	182	29	27	202	103	39
125	630	209	15	57	137	—	276	197	51	24	130	126	72

Table 8 (Continued)

Mo.	Occurrence	Locality	Authors
8	Lava	Sanbe-Volcano, Simane	FUKUTOMI
9	Black basaltic rock	Takaisi, Simane, Japan	T. TOMITA
10	Volcano ejecta	Uturyoto Korea	A. HARUMOTO
11	Andesite	Yufuin, Oita	I. SUNAGAWA
12	Andesite	Shabozan, Formosa	T. ICHIMURA
13	Agglomerate	Kobilyana, Sattu, Sirinei, Hokkaido	J. HARADA
14	Gray black agglomerate	Bentesnima, Niigata	U. KAWANO
15	Gray black agglomerate	Bentensima, Niigata	Y. KAWANO
16	Umptekite	Wansau, Wis.	WEIDMAN (1907)
17	Quartz latite	Sheep Cr., Colo.	LARSEN & <i>Others.</i>
18	Quartz latite	Dry Guch., Colo.	LARSEN & <i>Others.</i>
19	Sodic lavas	Kilimanjaro. E. Africa,	WASHINGTON & MERWIN
20	Volcanic lapilli	Linosa, Mediterranean	WASHINGTON & MERWIN
21	Umptekite	Almunge, Sweden	QUENSEL
22	Essexitic phonolite	Tejedatal	KUNITZ
23	Hornblende basalt	Todtenköptchen, Rhön	GALKIN
24	Volcanic bomb	Isleta-Krater	KUNITZ
25	Andesite	Stenzelberg, Sie-berg	FAMMELSBURG
26	Hornblende-monchiquites	Copinshay, Orkney	FLETT
27	Trachy dolerite	Madeira	KUNITZ
28	Hornblende-andesite	Sabozan, Formosa	T. ICHIMURA
29	Tephrite	Grosspriessen, Bohemia,	KUNITZ
30	Crystal	Billin, Bohemia	PENFIELD & STANLEY
31	Tuff breccia	L. Balaton, Hungary	VENDL.
32	Large phenocrysts in basalt	Seigertshausen, Hesse	TRENZEN
33	Crystal	Lukow, Bohemia	KRUETZ
34	Crystal	Yödödö, Korea	KAWANO
101	Crystalline limestone	Russell, N.Y.	KREUTZ
102	Limestone contact	Ossining, N.Y.	ALLEN & CLEMENT
103	Crystalline limestone	Switzerland	KREUTZ
104	Limestone contact	Sarabsburg, N.Y.	RARSONS
105	Dolomite marble	Less, Mass.	PENFIELD & STANLY
106	Limestone contact	Pierrepont, N.Y.	PARSON
107	Limestone	New Hampshire	KUNITZ
108	Cipotin limestone	Diagdalik	BARTHOUS
109	Amphibole-biotite granite	Haut du Faite	WEYBERG
110	Gabbro	Washington, D.C,	CLARKE
111	Margin of xenolith in gabbro	Sudbury. Ont.	JONES
112	Quartz-am.-diorite	Butte-Ptumas Cos, Cal.	CLARKE
113	Xenolithic crystal in granodiorite	Signal Peak, Colo.	PABST
114	Hornblende-gabbro	Garabal Hill, Scotland,	NOCKOLDS
115	Diorite	S, Felix, Cortegana,	KUNITZ
116	Diorite	Bornthal, Saxony	KUNITZ
117	Hornblende gabbro	Beaver creek, Cal.	TURNER
118	Leucite porphyrite	Ernstshofen, Hesse	KLEMM
119	Granodiorite	Ilemen Mts., Ural,	BELYANKIN
120	Diorite	Brocken, Harz.	KUNITZ
121	Diorite	Eulengebirge Silesia	KUNITZ
122	Appinitic diorite	Garabal Hill	NOCKOLDS
123	Gabbro	Lindentels Odenwald	KORITNIG
124	Glen Tilt diorite	Glen Tilt, Scotland	DEER
125	Diorite	Beerberg, Thuringia	KUNITZ

same way as Table 4. Unfortunately, the contents of H_2O^+ and H_2O^- of some members are not determined separately, and the total H_2O contents of some of them are not determined. In such cases, therefore, atomic ratios were calculated on the basis of $O=2300$, excluding the oxygen in H_2O .

In Fig. 1 are plotted the alkalis in "A" site against R''' , which is similar to the diagram devised by HALLIMOND and MIYASHIRO. The author is of the opinion that the alkalis in the vacant site as well as R''' are compensating the deficient charge due to the substitution of Al for Si. The figure shows their tendency to be grouped by geological environments.

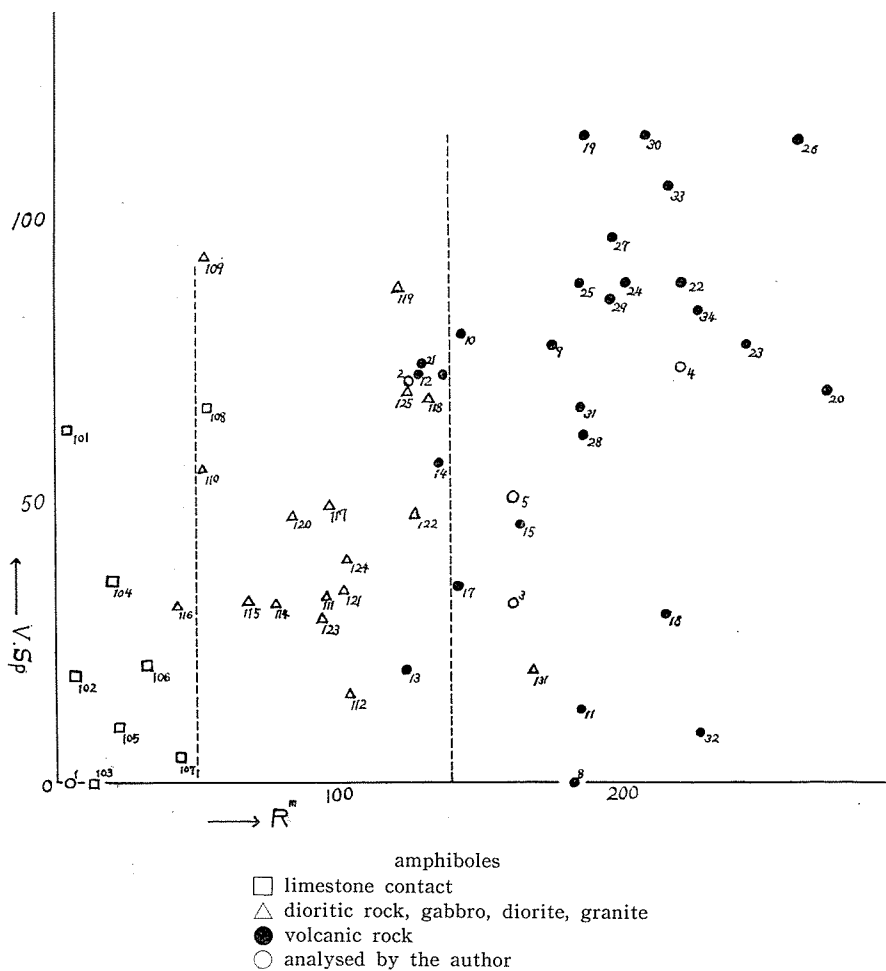


Fig. 1.

Calciferous amphiboles from volcanic rocks fall on the upper right part of the field (R''' 's are from 150 to 250 and Na, K from 0 to 100).

The Si content of calciferous amphiboles from volcanic and plutonic rocks (diorite, hornblende-granite and gabbro, cited from HALLIMOND's study) is shown in Fig. 2. It is evident that the Si content increases somewhat regularly with the decrease of R''' . As the Ca-content of calciferous amphiboles is usually from 150 to 200, substitutions such as $(R'', \text{Si})-(R''', \text{Al})$, and $R'''-R''$ (Na, K)

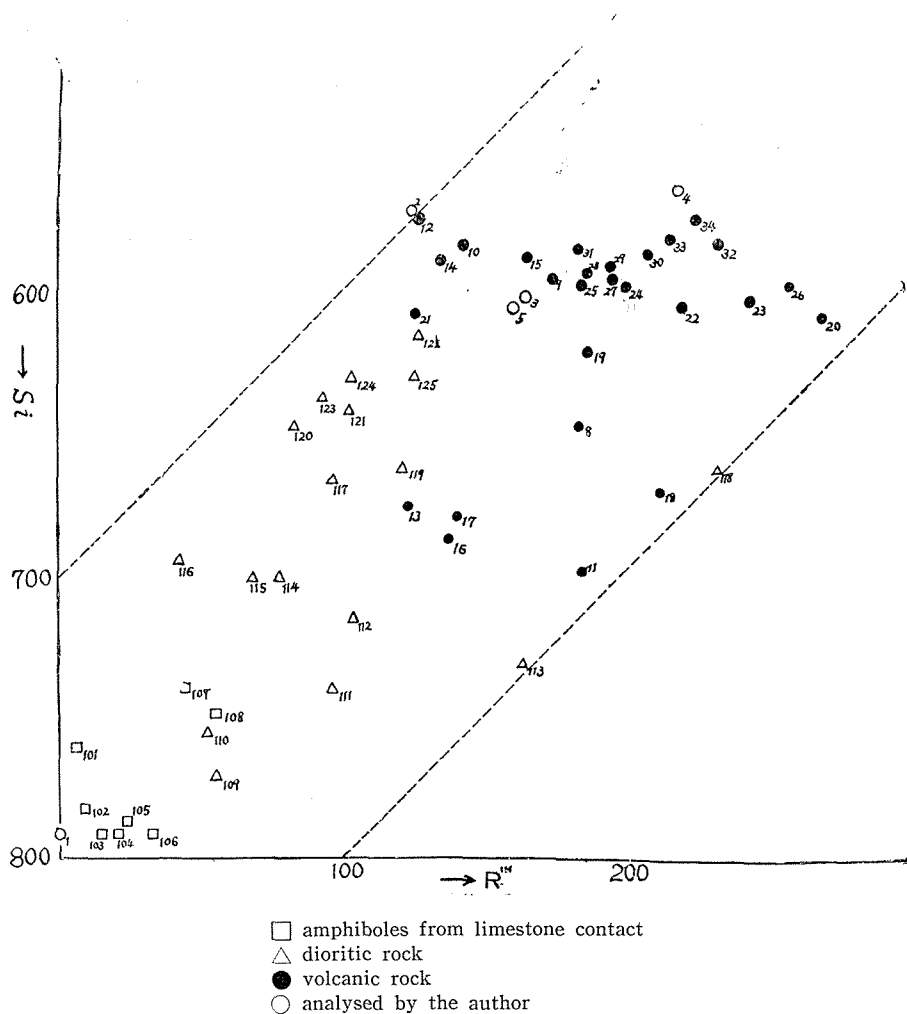
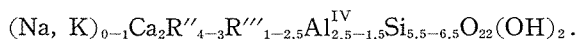


Fig. 2.

might take place. Therefore, the Si content may increase with the decrease of R''' .

The actual Si and R''' contents in calciferous amphiboles from volcanic rocks are about 550–650 and about 100–250 respectively, and the actual Na, K content in their vacant site is about 0–100 as shown in Fig. 1.

Thus, the author established the chemical formula of calciferous amphibole from volcanic rocks as follow:



The calciferous amphiboles represented by the above formula belong to tschermakite-pargasite series.

As for the great part of amphiboles from the volcanic rocks, chemical compositions could not be represented by the above formula.

The chemical compositions of these specimens could not be explained only by the substitution of metal ions.

The (OH) contents of the calciferous amphiboles from volcanic rocks are shown in Fig. 3. The figure shows a tendency for the OH content to be

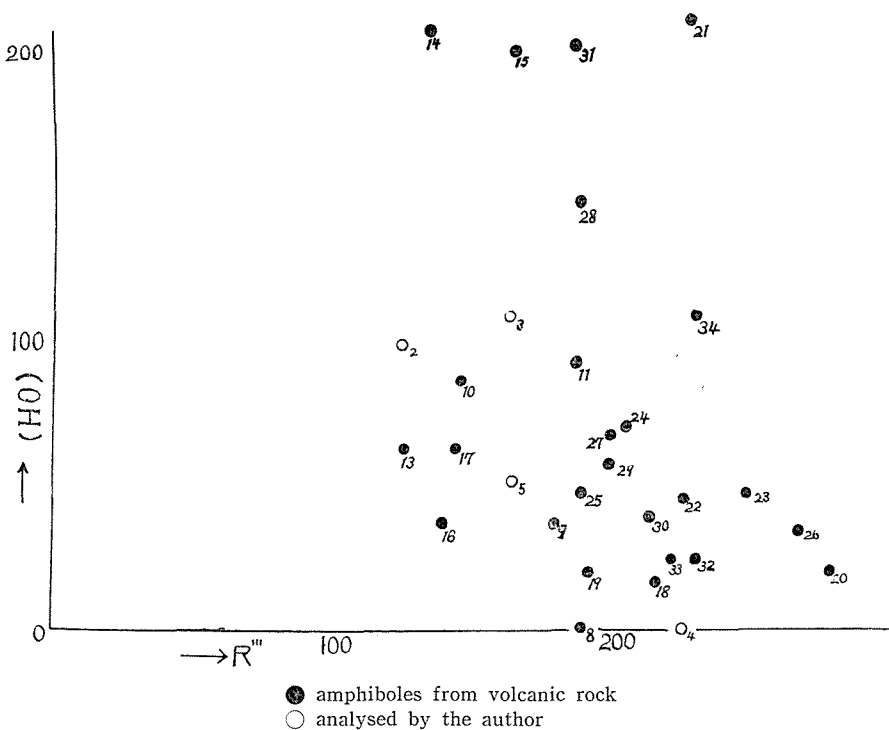


Fig. 3.

smaller than 200. It is from 0 to 100. As a matter of course, in determination of the contents of radicals-OH, F, errors are especially liable to be introduced, as is well known.

If the definition of oxyhornblende already discussed in this paper is the current view, calciferous amphiboles from volcanic rocks may be the alteration product of calciferous amphiboles corresponding to tschermakite-pargasite series by dehydration and oxydation.

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