Mem. Fac. Lit. & Sci., Shimane Univ., Nat. Sci., 1, 34−44, 5 text-figs., 4 tables, March 15, 1968

On Minerals Associated with Ultrabasic Rocks, Found in the Vicinity of Common Boundaries of Shimane, Tottori, Okayama and Hiroshima Prefectures (IV)

——Aluminous Tremolite from the Hirose Mine, Tottori Pref. and Ferrian Tremolite from the Takase Mine, Okayama Pref.——

Jun-ichi KITAHARA

Department of Geology, Shimane University, Matsue, Japan

(Received, November 10, 1967)

Preface

Geology of these area was reported before by the author, so it will not be described on again in this paper.

The sample No. 1 was found at 34 m level of Hirose mine, and the sample No. 2 was discovered at new No. 3 level of Takase mine.

Both of the country rock of these samples are pyroxenite composed of enstatite and diopside, and a little part of them has been affected by residual magmatic autometamorphism, then tremolite was produced.

It can be considered that the addition of SiO_2 and H_2O to these country rocks (pyroxenite) reacted chemically as the following equation.

$$3MgSiO_3\,(\text{enstatite}) + 2CaMgSi_2O_6\,(\text{diopside}) + SiO_2 + H_2O \longrightarrow (OH)_2Ca_2Mg_5Si_8O_{22}\,(\text{tremolite})$$

In this reaction, the metamorphism does not advance so as to produce hornblende. The reason why fluorine does not exist in tremolite as shown in the chemical analysis table, is that pyroxenite was not metamorphosed by granitic rock.

On the other hand, harzburgite has been metamorphosed by dioritic rock, and then asbestiform tremolite in small quantities has been crystallized from the harzburgite. The occurrences are sometimes observed in the region. The general reaction equation may be expressed as follows.

$$MgSiO_3 + Mg_2SiO_3\,(\text{olivine}) + SiO_2 + CaO\,(\text{from diorite}) + H_2O \longrightarrow (OH)_2Ca_2Mg_5Si_8O_{22}$$

Physical Properties

Sample No. 1 is white in colour and fibrous as shown in Fig. 1, and is

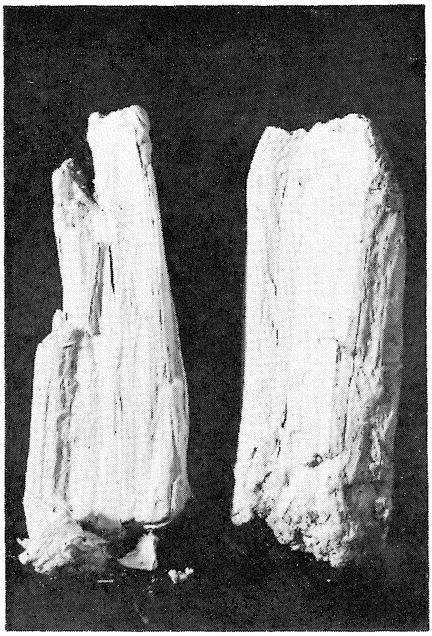

Fig. 1. Aluminous tremolite. (×½)
34 m level of Hirose mine,
Tottori Pref.

Fig. 2. Ferrian tremolite (1). (×½)
New no. 3 level of Takase mine,
Okayama Pref.

Fig. 3. Ferrian tremolite (2). (×½)
ibid.

hygroscopic. Under microscope, it is colourless and its extinction angle is c∧Z=0.8°−3.0°. It is remarkable that its extinction angle is small.

In the case of synthetic amphibole, it is said that all of refractive indices α, γ, double refraction γ-α and extinction angle c∧Z decrease as its content of Al_2O_3 increases.

Sample No. 2 is pale green in colour by naked eye. It may seem fibrous as shown in Fig. 2, and it breaks as shown in Fig. 3 when it is struck. Its specific gravity is G=2.998, and colourless, columnar, extinction angle c∧Z=16.6°, optic axial angle (−)2V=85°48′, refractive indices $\alpha=1.610$, $\beta=1.626$ $\gamma=1.634$, double refraction $\gamma-\alpha=0.024$ under microscopic observation.

In the case of amphiboles, their optical properties are little influenced by replacement of Mg or Si by Na or Al respectively. Their refractive indices relatively increase by replacing Mg with Fe^{++}, or by replacing Al with Fe^{+++}.

X-ray powder data

The X-ray powder data of samples No. 1 and No. 2 were respectively (Figs. 4, 5) recorded automatically by an X-ray apparatus made by Shimazu Co.

From the results, the value of 2 θ, the intensity I/I_1, d and hkl are shown in Tables 1 and 2. The distance of each atom plane, d, corresponds to that of tremolite.

The result of the calculation of unit cell by reciprocal lattice equation with the X-ray powder data in table is as follows.

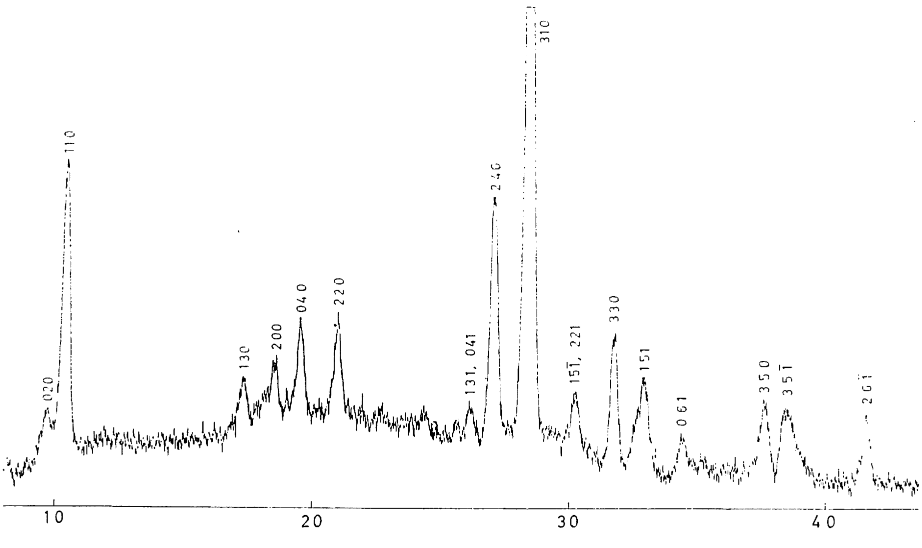

Fig. 4. X-ray diffraction pattern of aluminous tremolite from Hirose mine, Tottori Pref.

$$1/1.5901^2 = 6^2a^{*2}$$

$$a^* = 0.10482$$

As the net plane index (hkl) of $d = 1.5055$ is 0.12.0,

$$b = 18.066\ \text{Å}.$$

$$1/1.5055^2 = k^2b^{*2}$$

$$b^* = 0.05535$$

$$1/1.6529^2 = c^{*2}+0.83852c^*\cos\beta^* \quad (1)$$

$$1/1.4407^2 = 1.25778c^*\cos\beta^*-c^{*2} \quad (2)$$

Table 1. X-ray data for asbestiform tremolite from Hirose mine.

d(Å)	I/I_1	hkl
9.11	1	020
8.46	36	110
5.06	5	130
4.73	3	200
4.55	10	040
4.23	12	220
4.04	1	013
3.46	1	
3.41	3	131, 041
3.29	24	240
3.13	100	310
2.949	5	$15\bar{1}$, 221
2.818	8	330
2.738	4	
2.722	16	151
2.603	5	061
2.392	15	350
2.338	16	$35\bar{1}$
2.165	6	261
2.161	3	
2.023	2	351
2.006	3	370
1.972	2	
1.899	24	510
1.876	1	
1.817	12	530
1.653	10	461
1.642	1	480
1.626	4	1.11.0
1.590	12	600
1.565	1	053
1.534	1	570, $35\bar{3}$
1.505	8	0.12.0
1.440	25	$66\bar{1}$

From (1) and (2),

$$
\begin{aligned}
c^* &= 0.19586 \\
\cos\beta^* &= 0.25319 \\
\beta^* &= 75°40' \\
\beta &= 180°-\beta^* = 104°20' \\
a^* &= 1/a\sin\beta \\
a &= 9.8471\text{Å} \\
c^* &= 1/c\sin\beta \\
c &= 5.2697\text{ Å}
\end{aligned}
$$

From the above values of a, b, c and $\sin\beta$, $a\sin\beta$ or d_{100}, and the volume of the unit cell $V = a\sin\beta\, bc$ can be calculated and the unit cell may be described in the following manner.

$a = 9.847$, $b = 18.066$, $c = 5.270$ Å, $\beta = 104°20'$, $a\sin\beta = 9.54$ Å, $V = 908.7$ Å^3.

The result of the calculation of unit cell from the X-ray powder data in table 2 is as follows.

$$
\begin{aligned}
1/1.5869^2 &= 6^2a^{*2} \\
a^* &= 0.10503 \\
1/1.5033^2 &= 12^2b^{*2} \\
b^* &= 0.05543 \\
b &= 18.0396\text{Å}
\end{aligned}
$$

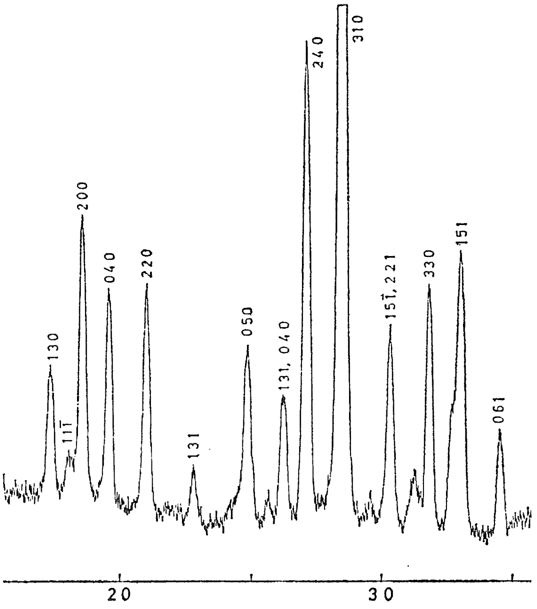

Fig. 5. X-ray diffraction pattern of ferrian tremolite from Takase mine, Okayama Pref.

$$1/1.6507^2 = c^{*2}+0.84021c^*\cos\beta^* \qquad (3)$$
$$1/1.4381^2 = 1.26318c^*\cos\beta^*-c^{*2} \qquad (4)$$

From (3) and (4),

$$c^* = 0.19573$$
$$\beta^* = 75°39'$$
$$\beta = 104°21'$$
$$c^* = 1/c\sin\beta$$
$$c = 5.27370\text{Å}$$
$$a^* = 1/a\sin\beta$$
$$a = 9.82804\ \text{Å}$$

The characteristics of unit cell are generalized as shown below.

$a = 9.828$, $b = 18.040$, $c = 5.274$ Å, $\beta = 104°21'$, $a\sin\beta = 9.52$ Å, $V = 905.8$ Å^3.

Chemical Composition

The results of the chemical analyses and the atomic ratios of the samples

Table 2. X-ray data for tremolite from Takase mine, Okayama Pref.

d(Å)	I/I_1	hkl	d(Å)	I/I_1	hkl
14.37	5	001	2.332	11	$42\bar{1}$
9.02	5	020	2.303	1	$17\bar{1}$
8.42	18	110	2.281	1	$31\bar{2}$, $\bar{3}12$
7.19	13	120	2.185	1	171
5.09	12	130	2.166	15	261
4.90	2	$11\bar{1}$	2.044	4	202
4.77	22	200	2.018	45	$\bar{4}02$, 351
4.52	19	040	2.001	45	370
4.21	19	220	1.968	6	
3.90	4	131	1.891	23	510
3.57	20	050	1.869	1	242
3.46	1		1.815	13	530
3.40	9	131, 041	1.686	1	
3.27	51	240	1.650	18	461
3.12	100	310	1.636	5	480
3.01	1		1.618	11	1.11.0
2.940	30	$15\bar{1}$, 221	1.585	15	600
2.857	2	221	1.558	1	
2.813	18	330	1.534	8	570, $35\bar{3}$
2.738	7	$33\bar{1}$	1.503	12	0.12.0, $\bar{2}63$
2.714	32	151	1.456	2	3.11.0
2.599	8	061	1.438	19	$66\bar{1}$, $\bar{6}61$
2.542	8	$\bar{2}02$	1.398	3	073
2.386	9	350	1.364	3	512
2.344	12	$35\bar{1}$, $\bar{3}51$	1.355	5	710

No. 1 and No. 2 are shown in Tables 3 and 4.

Their chemical formulas are shown as follows respectively, according to the ordinary general formula. Sample No. 1 is noted as $(Na, Ca, K)_{2.08}(Al, Ti, Fe^3, Mg, Fe^2, Ni, Mn)_{5.33}(Si, Al)_{8.00}O_{22.63}(OH)_{1.37}$ and sample No. 2 is indicated as $(Na, Ca, K)_{1.98}(Al, Ti, Fe^3, Mg, Fe^2)_{5.34}(Si, Al)_{7.98}O_{22.60}(OH)_{1.40}$.

Nomenclature of Tremolite

Winchell (1932) restricted the name tremolite to the nearly pure magnesian type with less than 10 mol. percent and the name ferrotremolite to the nearly pure iron type with more than 90 mol. percent $(OH)_2Ca_2Fe_5Si_8O_{22}$: all intermediate compositions be called actinolite. Tremolite grades into about 10

Table 3. Aluminous tremolite from Hirose mine, Tottori Pref.

	Wt. %	Mols		Atom. Ratios	Ditto when (O, OH, F) =24
SiO_2	55.69	928	Si	928	7.673
TiO_2	0.02	0.3	Ti	0.3	0.005
Al_2O_3	2.92	29	Al	58	0.480
Fe_2O_3	1.82	11	Fe^2	22	0.182
FeO	0.57	8	Fe^3	8	0.066
NiO	0.16	2	Ni	2	0.017
MnO	0.01	0.1	Mn	0.1	0.001
MgO	23.75	594	Mg	594	4.911
CaO	12.72	227	Ca	227	1.877
Na_2O	0.60	10	Na	20	0.165
K_2O	0.21	2	K	4	0.033
H_2O_+	1.50	83	H_+	166	OH 1.373
H_2O_-	0.30		O	2902.7	O 22.627
Total	100.27				

Atom. Ratios on the basis of 24 (O, OH, F).

Si	7.673	8.00			
Al	0.327		Na	0.165	
Al	0.153	5.33	Ca	1.877	2.08
Ti	0.002		K	0.033	
Fe^3	0.182		OH	1.373	
Mg	4.911		F	—	
Fe^2	0.066		O	22.627	
Ni	0.017				
Mn	0.001				

$100Mg/(Mg+Fe^2+Fe^3+Mn) = 95.2$

(Analyst : J. Kitahara)

percent of the ferrotremolite molecule.

Sundius (1946) restricted the term tremolite to the type with less than approximately 15 mol. percent of $(OH)_2Ca_2Fe_5Si_8O_{22}$, and proposed that the nearly iron rich type be named ferroactinolite.

The calling of names tremolite, actinolite and ferroactinolite has here been selected for minerals with 0 to 20, 20 to 80 and 80 to 100 mol. percent $(OH)_2Ca_2Fe_5Si_8O_{22}$ respectively. It is propounded to limit the names tremolite, actinolite and ferroactinolite to these calcium amphiboles in which the replacement of Si by Al is less than 0.5 atoms per formula unit, then the replaced amount of Si by Al is small. In the tremolite-ferroactinolite series, the amounts of Fe replacing Mg range commonly from 0 to 50 percent.

The samples of the both mines can be called tremolite from the chemical

Table 4. Ferrian tremolite from Takase mine, Tottori Pref.

	Wt. %	Mols		Atom. Ratios	Ditto when (O, OH, F) =24
SiO_2	56.29	938	Si	938	7.817
TiO_2	0.03	0.4	Ti	0.4	0.003
Al_2O_3	1.02	10	Al	20	0.167
Fe_2O_3	3.18	20	Fe^3	40	0.333
FeO	1.39	19	Fe^2	19	0.158
NiO	tr	—	Ni	—	—
MnO	0.0	0	Mn	0	0.0
MgO	23.27	582	Mg	582	4.850
CaO	12.18	218	Ca	218	1.817
Na_2O	0.54	9	Na	18	0.150
K_2O	0.13	1	K	2	0.017
H_2O^+	1.51	84	H_+	168	1.400
H_2O_-	0.20		O	2879.8	22.600
Total	99.74				

Atom. Ratios on the basis of 24 (O, OH, F).

Si	7.817	7.98			
Al	0.167		Na	0.150	1.98
Al	—	5.34	Ca	1.817	
Ti	0.003		K	0.017	
Fe^3	0.333		OH	1.400	
Mg	4.850		F	—	
Fe^2	0.158		O	22.60	
Ni	—				
Mn	0.0				

$100Mg/(Mg+Fe^2+Fe^3+Mn)=90.8$

(Analyst : J. Kitahara)

composition, for Al of Z site (4 coordination) is smaller than 0.5 atom in the unit formula. The total sum of Al content (Y site and Z site) in sample No. 1 from Hirose mine is 0.48 atom, and it is relatively rich as tremolite, so the sample was said aluminous tremolite. The content of ferric iron in sample No. 2 from Takase mine is 0.33 atom and rich as tremolite, so it was called ferrian tremolite.

Structure of Tremolite

Crystal structure of amphiboles is expressed by the parallel adojoining of two SiO_3 chains in pyroxenes $-Si_4O_{11}$. Ca atom occupies the large site between the 6 and 8 coordinates (X site), and Na, K atoms also in the same site. M_1, M_2 and M_3 in the 6 coordinate (Y site) is occupied by the smaller Mg, Fe^2, Fe^3 and Al atoms. Recent investigations have proved that these structures are not of the closest packing of ions, as their sites are occupied equally by larger or smaller ions. In most amphiboles, Al in their unit formula can be replaced by at most two Si ions. Lattice vacancy of the A site is occupied, in the tremolite structure, wholly or partly Na and K atoms. General formula of amphiboles rich in Ca is given by $X_{2-3}Y_5Z_8O_{22}(OH)_2$, in which X=Ca, Na, K, Mn ; Y = Mg, Fe^2, Fe^3, Al, Ti, Mn, Cr, Li, Zn ; Z = Si, Al. OH ion is replaced, wholly or partly, by F, Cl, and in some amphiboles it may be replaced by O. Lattice vacancy (A site) of tremolite may be replaced by Na and K, and Ca in the X site may also be replaced by them. Al, without occupying vacancies, and Ca, without being replaced by Na, may enter into the structure of tremolite, and the balance of the atomic valency can be held by the relation Mg, Si $\rightleftharpoons$ Al, Al.

M_1, M_2 and M_3 are in the position of 6 coordinate and occupied by Y cations. M_4 is in the position of 6 or 8 coordinate and occupied by X cations. In synthetic hornblende, replacement of cations in the position of M_1, M_2 and M_3 by Fe, Mg and Al has a serious effect upon the size of the unit cell, while replacement of Si by Al or that of Mg by Fe^3 have no marked effects. In synthetic monoclinic amphiboles, the increase and decrease of b axis in the unit cell are most seriously affected by their chemical composition. The replacement of $Al^{IV} \leftrightarrow Si$ has no marked effect upon b axis. It is well known that the length of b axis is variable according to all content for those types rich, poor or zero in Al, but the reason is not yet known. Elongation of b axis results from the detaching of the adjoining double chain by large atom introduced, as that of Fe^2 replacing Mg. Small Al atom in M_2 does not always cause the shortening of b axis, as other bonds may remain in open state. The b axis is elongated by 0.25 Å with the random existence of Al in

M_1, M_2, M_3 and M_4 site. Fe, Al^{IV} seem to be concentrated in M_2, and the increase of b axis depends upon the average size of cations in M_2 site. Average value of b also depends upon the size of ions in M_4 site and the ratio Al/Si.

The reason why the length of unit cell of sample No. 1 is near that of synthetic tremolite (18.054 Å) is that, atomic ratio of Fe of 6 coordination is 0.07 and that of Al of 6 coordination is 0.15, then the b axis length is scarcely influenced from them. Al of 4 coordination is 0.33, and it does not influence on b axis length.

The b axis length of sample No. 2 shows a near or somewhat smaller value compared with that of synthetic tremolite. The reason can be explained as follows : though ferrous 0.16 atom increases the b axis length, ferric 0.33 atom decreases it a little, or else it may be due to the warping of b axis.

The increase of asin β results from the increase of the average size of atoms in the 8 coordinate. The minimum value of asin β occurs in such case as when all Si are in the 4 coordinate, and, at the same time, Mg and Al occupy the 8 coordinate. The maximum value of asin β occurs, on the other hand, when one-eighth of Si is replaced by Al, and all Fe^2 ions occupy the 8 coordinate.

The value of asin β of the sample No. 1 is 9.54 and larger than that of the sample No. 2 (9.52). It may be due to the fact that Al atom of 4 coordination of the sample No. 1 is 0.33 and that of the sample No. 2 is 0.16.

The c axis is slightly elongated, if the double chain is not twisted, and the chain turns to be normal as the size of the cation in M_2 position increases. The chain contracts around smaller ions, and expands with larger ions. The elongation of c axis of the untwisted chain must occur, accompanying with that of b axis by M_2, but it may also occur when the chain is not twisted.

The c axis length and b axis length of the sample No. 1 almost coincide with those of the synthetic tremolite respectively.

The c axis length of the sample No. 2 is a little longer than that of synthetic tremolite. The reason is that the c axis is influenced more greatly by replacement of Mg by Fe^2 than by that of Mg by Fe^3. Moreover, c axis is thought as not warped.

Crystal structure of hornblende has vacancies in each of the two Si_4O_{11}, that can be filled with extra Na atoms. Si in the 4 coordinate can be replaced by Al for continuously from 0 to 4 atoms. Na and K are important components in minerals of tremolite series.

In the both samples, No. 1 and No. 2, Y site is excessive when expressed in the ordinary formula as described previously. Water does not exist in tremolite as a solid solution but exists in each molecules at a certain rate. As O is excessive, $(OH)^-$ must be replaced by excess O^{2-}. With the thought that not only Na and K but Ca exist in lattice openings, chemical formula previously described is corrected as follows. The sample No. 1 is shown as $(Na_{0.17}K_{0.03}Ca_{0.21}\square_{0.59})_{1.00}(Ca_{1.67}Mn_{0.001}Mg_{0.03})_{2.00}(Mg_{4.58}Fe^{2}_{0.07}Fe^{3}_{0.18}Ni_{0.02}Ti_{0.002}Al_{0.15})_{5.00}(Si_{7.67}Al_{0.33})_{8.00}O_{22.00}(OH_{1.37}O_{0.63})_{2.00}$, and the sample No. 2 is noted as $(Na_{0.15}K_{0.02}Ca_{0.13}\square_{0.70})_{1.00}(Ca_{16.8}Mg_{0.32})_{2.00}(Mg_{4.53}Fe^{2}_{0.16}Fe^{3}_{0.31}Ti_{0.003})_{5.00}(Si_{7.82}Al_{0.16}Fe^{3}_{0.02})_{8.00}O_{22.00}(OH_{1.40}O_{0.60})_{2.00}$.

Acknowledgements

The description of the crystal structure of tremolite in the paper is indebted to the studies by Drs. Colville, P. A., Ernst, W. G. and Gilbert, M. C. (1966).

The author is grateful to Mr. Yoshitada Toda, the head of Tari mine, Hirose mining joint stock Co, Mr. Kunio Toda, the department head of the same mine, Mr. Kikuo Hirose, the head of Takase mine of the same company and Mr. Shigenobu Taguma, the department head of the same mine for their aid in investigating ore deposits and gathering samples. The cost of this investigations has been partly defrayed by the Scientific Researches of the Ministry of Education, to which the author wishes to express his thanks.

References

Colville, P. A., Ernst, W. G. and Gilbert, M. C. (1966), Relationships between cell parameters and chemical compositions of monoclinic amphiboles. Am. Mineral., **51**, 1721–1754.

Comeforo, J. E. and Eitel, Wilhelm. (1951), Discussion of "x-ray diffraction patterns of asbestos". Am. Mineral., **36**, 368–369.

Comeforo, J. E. and Kohn. J. A. (1954), Synthetic asbestos investigation. 1. Study of synthetic fluor-tremolite. Am. Mineral. **39**, 537–548.

Deer, W. A., Howie, R. A. and Zussman, J. (1963), Rock forming minerals., **2**, 249–320.

Posnjak, E. and Bowen, N. L. (1931), The role of water in tremolite. Amer. Jour. Sci., 5th ser., **22**, 203–214.

Warren, B. E. (1929), The structure of tremolite $H_2Ca_2Mg_5(SiO_3)_8$. Zeit. Krist., **72**, 42–57.