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

——Chrysotile and Associated Chlorite from the Wakamatsu Mine, Tottori Prefecture——

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Introduction

Wakamatsu mine is situated in Tari, Nitinan-cho, Hino-gun, Tottori Pref., and the ultrabasic body developed in the district is composed mainly of serpentinized harzburgite.

Chrysotile was found in the 7th level of Wakamatsu mine in small amount, and, in this paper, description will be made on this mineral, and also on chlorite (partial serpentine), forming the surrounding chloritite which is closely related with the former. The associated relation of the minerals is indicated in Fig. 1.

As to the geology and ore deposits of the district the writer has made a description in Journal of the Japanese Association of Mineralogists, Petrologists, and Economic Geologists.

Chrysotile

Physical Properties

Chrysotile in the chloritite (partial serpentinite) is fibrous forms as shown in Fig. 1. It is light yellowish green with silky luster, and its streak is white. Refractive indices are: $N_p=1.546$, $N_g=1.554$, and it shows straight extinction parallel to the direction of a axis.

X-ray Powder Data

Automatically recorded measurement is made, using the X-ray apparatus made by Shimazu Co., on samples pulverized as finely as possible, though the mineral was not easily crushed to very fine powder. The X-ray low angle diffraction chart of the sample is shown in Fig. 2. A small number of reflection shown in Table 1 may be due to the crystallinity of the mineral, and it is perceived that this sample is not of fibrous antigorite, as the marked peak of
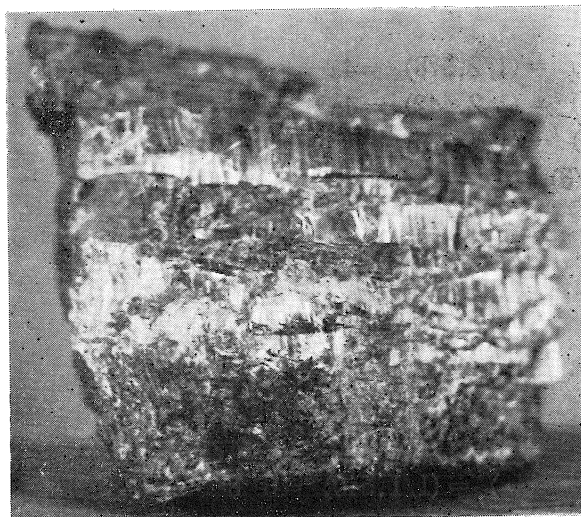
Fig. 1. Chrysotile (fibrous) and chlorite. ($\times 1/3$)
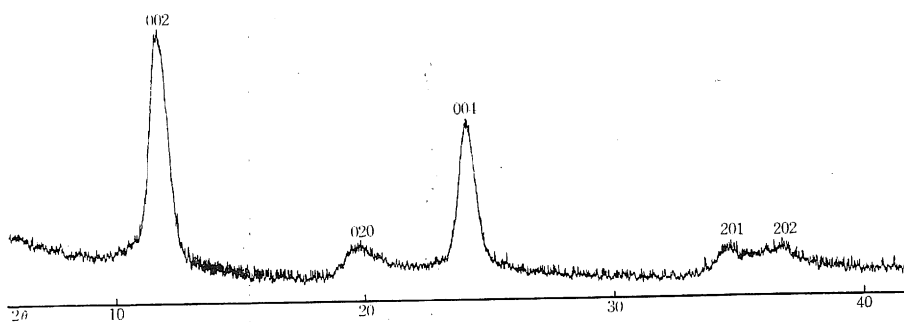7th level of Wakamatsu mine.

Fig. 2. X-ray diffraction diagram of chrysotile from Wakamatsu mine,
Tottori Pref..   (Cu-Kα, Ni filter)

Table 1. X-ray data for chrysotile from Wakamatsu mine.

d (Å)	I/I$_1$	hkl
7.44	100	002
4.48	12	020
3.676	62	004
2.578	4	201
2.442	7	202
1.540	19	060

$d = 1.56$ Å $(hkl = 24.3.0)$ is absent. Its lattice constants computed from the reciprocal lattice are as the following description:

$$(1/d_{201})^2 = (1/2.578)^2 = 4a^{*2} + c^{*2} + 4c^* a^* \cos\beta^* \qquad (1)$$
$$(1/d_{202})^2 = (1/2.442)^2 = 4a^{*2} + 4c^{*2} + 8c^* a^* \cos\beta^* \qquad (2)$$
$$(1/d_{004})^2 = (1/3.676)^2 = 4^2 c^{*2} \qquad (3)$$

From (1), (2) and (3),

$$a^* = 0.18877,$$
$$c^* = 0.06801,$$
$$\cos\beta^* = 0.06445$$
$$\beta^* = 86°18'$$
$$\beta = 93°42'.$$
$$a = 1/(a^* \sin\beta^*) = 5.309 \text{ Å},$$
$$c = 1/(c^* \sin\beta^*) = 14.731 \text{ Å}.$$
$$(1/d_{060})^2 = (1/1.540)^2 = 6^2 b^{*2}$$
$$b^* = 0.10826$$
$$b = 9.237 \text{ Å},$$
$$d_{100} = a\sin\beta = 5.297 \text{ Å},$$
$$V = abc\sqrt{1-\cos^2\beta} = 721.3 \text{ Å}^3.$$

The unit cell dimensions resulting from the transformation can now be assembled as follows:

$a = 5.309$ Å, $b = 9.237$ Å, $c = 14.734$ Å, $\beta = 93°42'$, $a\sin\beta = 5.297$ Å, $V = 721.3 \text{Å}^3$.

Chemical Composition

Hydrochloric acid solution of chrysotile was used for analyses of SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, etc.. The results of the analysis, atomic ratio and structural formula are as shown in Table 2.

As seen from the analysis table, the number of (OH) ions is more than its ideal value of 4, and the number of ions in the four and six co-ordinates is less than their respective ideal value of 2 and 3. Such values taken by the mineral are distinctive for chrysotile, and are differed from those of other serpentine minerals, such as antigorite or lizardite.

McConnell (1954) argued that (OH) ions may replace some O atoms in the four co-ordinate net work. For some cases an interpretation may be that certain (OH) ions might combine with O in the form of H_2O that is strongly absorbed.

Crystal Chemistry

In serpentine minerals, Si can replaced by Al, and Mg by Al, Fe^2, Fe^3. In the present sample, though Al that will apparently replace Si may exist, the one that replace Mg does not exist. In cases when chlorite and (or) serpentine are formed from peridotites, iron that is contained in peridotites (olivine,

pyroxene) is separated as magnetite, and does not enter the chlorite or serpentine structure. Formation of chrysotile instead of antigorite may be due to the action of lateral pressure and longitudinal tension, in addition to the chemical environment.

Chrysotille and chlorite (Table 4, mentioned after) have similar chemical composition and are in associated relation, but, as the latter contains a little more Al_2O_3 than the former, they differ in their layer components.

Table 2. Analysis and structural formula of chrysotile from the
Wakamatsu mine, Tottori Pref..

	Wt. %	Mols		Atom. ratios	Ditto when (O, OH) = 9
SiO_2	41.32	688	Si	688	1.910
TiO_2	0.02	0.3	Ti	0.3	0.001
Al_2O_3	1.35	13	Al	26	0.072
Fe_2O_3	0.61	4	Fe^3	8	0.022
FeO	0.90	13	Fe^2	13	0.036
MnO	0.05	1	Mn	1	0.003
MgO	41.26	1032	Mg	1032	2.865
CaO	0.14	3	Ca	3	0.008
Na_2O	0.03	0.5	Na	1	0.003
K_2O	0.01	0.1	K	0.2	0.001
H_2O_+	13.77	765	H_+	1530	OH 4.247
H_2O_-	0.62		O	3242.2	
	100.08				

Numbers of atoms when (O, OH) = 9

Si	1.910	
Al	0.072	} 1.98
Al	—	
Ti	0.001	
Fe^3	0.022	
Fe^2	0.036	
Mn	0.003	2.94
Mg	2.865	
Ca	0.008	
Na	0.003	
K	0.001	
(OH)	4.247	

Structural formula

$[(Mg_{2.865}, Fe^2_{0.036}, Fe^3_{0.022}, Ca_{0.008}, Na_{0.003}, K_{0.001}, Ti_{0.001})_{2.94}]^{VI}$
$[(Si_{1.910}, Al_{0.072})_{1.98}]^{VI} O_{4.75}(OH)_{4.25}$

(Analyst : J. Kitahara)

Ion numbers of tetrahedron and octahedron, calculated from 9 (O, OH) in the chemical formula of chrysotile, are less than the respective ideal value 2 and 3.

It is to be noted that analyses of chlysotile, hitherto been reported, also give the less ion number than the ideal ones, as given by the above sample.

Structure of antigorite is such one that the octahedron layer of kaolinite is replaced by Mg, and chrysotile is a clay mineral having the double chain lattice. Chrysotile is fibrous, but of a layered type as kaolin group. The tetrahedron of one side layer is conected the brucite layer, and two of all OH replace O at the apex of the SiO_4 tetrahedron. Chrysotile has twisted layers only around a axis, forming either hollow cylinders or curves elongated to a axis. Chrysotile cell, consisting of two layers, is arranged in the alternate superposition.

Chlorite

Harzburgite altered primarily to chloritite, and in small portion of it chrysotile was formed. Chlorite, composing the chloritite, consists of portions that somewhat differ in the greenish tint.

X-ray data

The X-ray pattern of the chlorite which seems to be homogeneous is shown in Fig. 3, and the X-ray data are indicated in Table 3.

In montmorillonite and vermiculite, the reflection of the 7 Å line, corresponding to (002) is generally weak, but it is strongly expressed by chlorite. It is, therefore, perceived that the sample is not montmorillonite nor vermiculite in its X-ray nature and it is also valid from the chemical analysis table, of later insertion that it is none of these two minerals.

In this sample, the reflection ray is few in number, and any high angle reflection is hardly observed, so that, it must be of low crystallininity. The value of d (001) has a close relation with the amount of Al^{IV}. As shown in the chemical analysis table of later page, Al^{IV} is so abnormally small as 0.045, and this small value reflected to the high value of d (001) = 14.68 Å.
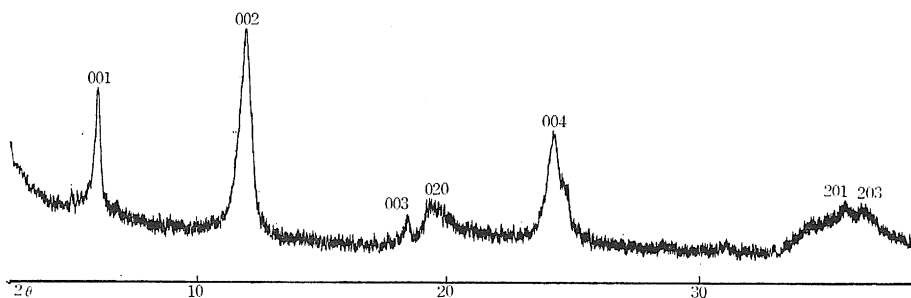

Fig. 3. X-ray powder diffraction diagram of chlorite from Wakamatsu
mine, Tottori Pref.. (Cu-Kα, Ni filter)

Table 3. X-ray data for chlorite from Wakamatsu mine.

d (Å)	I/I$_1$	hkl	
14.68	30	001	
7.36	100	002	
4.86	8	003	
4.60	15	020	
3.669	84	004	
2.505	1	$13\bar{2}$,	201
2.454	8	132,	$20\bar{3}$
2.098	3	007	
1.749	1	136,	$20\bar{7}$
1.537	31	060,	$33\bar{1}$
1.503	1	062,	331
1.331	1	262,	$2.0.\overline{10}$

The direct-cell constants are functions of the reciprocal cell equation and are computed as follows.

$$(1/d_{201})^2 = (1/2.505)^2 = 4a^{*2} + c^{*2} + 4c^* a^* \cos \beta^* \qquad (1)$$

$$(1/d_{20\bar{3}})^2 = (1/2.454)^2 = 4a^{*2} + 9c^{*2} - 12c^* a^* \cos \beta^* \qquad (2)$$

From (1) and (2),

$$a^* = 0.1925,$$
$$c^* = 0.0681,$$
$$\cos \beta^* = 0.14506$$
$$\beta^* = 81°20'$$

or

$$\cos \beta^* = (\cos \gamma \cdot \cos \alpha - \cos \beta) / (\sin \gamma \cdot \sin \alpha)$$
$$\cos \beta = -0.14506$$
$$\beta = 98°40',$$
$$a = 1/(a^* \sin \beta^*) = 5.254 \text{ Å},$$
$$c = 1/(c^* \sin \beta^*) = 14.845 \text{ Å}.$$
$$d_{060} = 1.538$$
$$d_{010} = b = 9.226 \text{ Å},$$
$$d_{100} = a\sin \beta = 5.194 \text{ Å},$$
$$d_{001} = c\sin \beta = 14.675 \text{ Å},$$
$$V = abc\sqrt{1 - \cos^2 \beta} = 711.9 \text{ Å}^3.$$

The unit cell may be denoted in the following manner.

a = 5.254 Å, b = 9.226 Å, c = 14.845 Å, β = 98°40', asin β = 5.194 Å,

V = 711.9 Å^3.

Crystal Chemistry of Chlorite

Chlorite consists of talc layer and brucite layer, and this structure is maintained by the ionic combination between the two layers, Si being replaced by Al. Diminution of the base distance with the amount of Al is explained by

the fact that the electric charge of serpentine layer is changed by the replacement of Al. The excessive charge caused by the replacement of the octahedral site of the serpentine layer by Al is compensated by the insufficient charge caused by the corresponding replcement of Si in the tetrahedral site by Al, and the charge equilibrium is maintained. Thus, the octahedral site needs positive charge and the tetrahedral site negative charge, and the layer becomes neutral as a whole. Confronted surfaces of the coupled layer have opposite charges, and the attraction between them becomes larger as Al content increases.

It seems that a slight difference of temperature may have a deciding effect on the formation of either chlorite or serpentine, but serpentine of the chlorite composition is in an equilibrium condition which is easily broken. Even if chlorite is formed in the same manner as the formation of the serpentine structure, serpentine instead of chlorite will be formed, if it is not in a stable condition. Since the chlorite sample contains small amounts of Al_2O_3 in tetrahedral site, it is considered that the sample is unstable and altered easily to serpentine. For a fixed formation it takes several days, even above 600°C, and more times are needed below 500°C. Thus, serpentine of the chlorite composition seems to be stable below 500°C, but chlorite itself is very stable, and this coincides with the rarity of those serpentines in nature which contain a considerable amount of Al. The result of analyses of chlorite and serpentine indicates that those chemical compositions are rarely partially overlapped. The limiting amount of Al, capable of replacing Si atoms, is about 0.5 atoms, corresponding to about 10% of Al_2O_3.

The position occupied by Si and Al of the tetrahedron site is regular, and that taken by Fe, Mg, and Al of the octahedron site is also not irregular. One site in the talc layer is almost occupied by iron. It seems that Mg ion in the brucite layer was replaced by Al ion, and no replacement has taken place at the octahedral site of the talc layer. The base distance d_{001} is affccted, as noted above, mostly by the replacement of Si by Al ions.

Chemical Composition of Chlorite

The results of chemical analysis and structural formula of the chlorite sample are as listed in Table 4.

Atomic ratio of Al in the six co-ordinate is 0.192, and that in the four co-ordinate is 0.045. This Al^{IV} amount is small, being corresponding to the chemical composition of the chlorite. It is known that with the increasing amount of Al^{IV} the base distance decreases, and with that of Fe^2, replacing Mg, b axis elongates. Base distance of chlorite is twice as that of serpentine, and in both structures of chlorite and serpentine, the relation between base distance and chemical composition can be treated in the same manner. Recently, Nelson

and others have synthesized 14 Å chlorite of continuous composition, with exception of serpentine composition, and also obtained septechlorite of the same composition and of serpentine structure.

If trivalent ions that enter the four and six co-ordinates are equal in amount, total sum of positive ions in the six co-ordinate amounts to six. As trivalent Al ions are contained more in the six than four co-ordinate, as indicated in the chemical analysis of Table 4, total sum of ions in the six co-ordinate becomes less than six in order to keep balance of the electric charge.
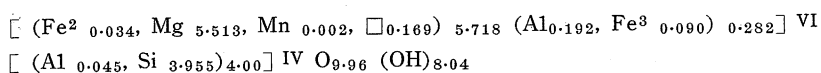
Chlorite was formed by the primary alteration of enstatite, and Fe_2O_3

Table 4. Analysis and structural formula of chlorite from the
Wakamatsu mine, Tottori Pref..

	Wt. %	Mols		Atom ratios	Ditto when (O, OH) = 18
SiO_2	42.10	701	Si	701	3.955
TiO_2	0.02	0.3	Ti	0.3	0.002
Al_2O_3	2.62	26	Al	42	0.237
Fe_2O_3	1.22	8	Fe^3	16	0.090
FeO	0.46	6	Fe^2	6	0.034
MnO	0.02	0.3	Mn	0.3	0.002
MgO	39.08	977	Mg	977	5.513
CaO	0.21	4	Ca	4	0.023
Na_2O	0.05	1	Na	2	0.011
K_2O	0.02	0.2	K	0.4	0.002
H_2O_+	12.82	712	H_+	1424	OH 8.035
H_2O_-	1.19		O	3190.1	
	99.71				

$$
\begin{array}{ll}
\text{Si} & 3.955 \\
\text{Al} & 0.045
\end{array} \Bigg\} 4.00
$$

$$
\begin{array}{ll}
\text{Al} & 0.192 \\
\text{Ti} & 0.002 \\
\text{Fe}^3 & 0.090 \\
\text{Fe}^2 & 0.034 \\
\text{Mn} & 0.002 \\
\text{Mg} & 5.513 \\
\text{Ca} & 0.023 \\
\text{Na} & 0.011 \\
\text{K} & 0.002
\end{array} \Bigg\} 5.87
$$

$$
\text{(OH)} \quad 8.04
$$

Structural formula

$[(Fe^2{}_{0.034}, Mg_{5.513}, Mn_{0.002}, \square_{0.169})_{5.718} (Al_{0.192}, Fe^3{}_{0.090})_{0.282}]$ VI
$[(Al_{0.045}, Si_{3.955})_{4.00}]$ IV $O_{9.96}$ $(OH)_{8.04}$

(Analyst : J. Kitahara)

component of chlorite in the chemical analysis table is supposed to have become a chemical constituent of chlorite through this alteration, and was not produced by secondary oxidation of chlorite.

Chemistry of chlorite minerals may be described in relation to chlorite, having the assumed composition of $Mg_6Si_8O_{20}(OH)_4 + Mg_6(OH)_{12}$ that represents, as its structure, the equal number of talc and brucite layer. It has been regarded that for chlorite a wide range of replacement in both layers is possible, thus the replacement of Si by Al is in a range of $Si_7Al - Si_4Al_4$. $Mg_{12}Si_3O_{20}(OH)_{16}$ and $(Mg_8Al_4)(Si_4Al_4)O_{20}(OH)_{16}$ are the ideal formulae of serpentine and amesite respectively, and no serpentine of such composition has been reported, and these two are related structurally to kaolin group. Existence of chlorite having the composition beyond the range of Si_{4-7} is very scarce in example. When the effect of the Al-Si replacement is compensated by the Al-Mg replacement in brucite rather than talc layer, the largest electrical charge occurs in the brucite layer of the chlorite structure. As seen from the above-cited analysis, the deviation from the ideal structure is due to the more strong hydrogen combination between OH in the brucite layer and O in the talc layer.

In a number of chlorite analyses, small amount of Ca and/or alkalies are included. As these elements have almost no effect on the calculation formula, they have been regarded as structural ions, but it seems that they exist as impurities or absorbed superficial or internal layer ions.

Origin of Chlorite and Chrysotile

Ultrabasic rock body of this district consists mainly of altered harzburgite, which is the product of post-magmatic action (autometamorphism by magmatic water) acted upon the igneous body intruded in a state of half-melting. Thus, in some part it turned out serpentinite body, while in another part it altered to chlorite rock. It is regarded that some part of this chloritite, which is consisted of chrysotile, was formed by additional hydration to chlorite. That is to say, the chemical environment may have a serious effect on the formation of chlorite or chrysotile. Chlorite was primarily formed mainly from enstatite. Though the formation of chrysotile from olivine has been a fixed theory, it may be sure that, in the present case, it was formed from enstatite, in some changed chemical environment, as explained above.

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