

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

—Orthohexagonal (Orthorhombic) chlorite from the Hinokami  
mine, Tottori Prefecture—

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(Received September 30, 1972)

## Abstract

Rock specimen composing from chlorite-like mineral in ultrabasic rock at the Hinokami mine was investigated with X-ray, differential thermal and chemical analyses. X-ray, differential thermal and chemical data of the mineral are presented. It was revealed that the specimen is rock formed by ortho-hexagonal chlorites, and consequently the specimen may be called ortho-hexagonal chlorite.

## Introduction

The Hinokami mine is situated at Kawakami, Nitinan-chō Hinogun, Tottori prefecture and the chromite deposits of the mine was famous in Japan. The chromite bodies are occurred mainly in serpentized harzburgite. Orthohexagonal (orthorhombic) chlorite was found near to a chromite body in the Hinokami deposit of Hinokami mine.

Chemical analysis of the specimen shows that it is made up of hydrous aluminium poor magnesian silicate with appreciable amounts of iron. The chlorite is the product of hydrothermal activity of pre-existing ultramafic rock.

As regard to geology of the district, the writer has stated in Journal of the Jap. Assoc. of Min. Pet. and Econ. Geologist. The ultrabasic rock mass in the area occurs in the slightly metamorphosed palaeozoic sediments produced by the Sangun regional metamorphism.

The specimen is characteristically green in color and its streak is pale green.

## Structure of Chlorite

The basic structural feature of the mineral results in a composition for the sheet of  $(\text{Si}_4\text{O}_{10})^{-4}$ ; Al may replace up to half the Si, giving sheets such as  $(\text{AlSi}_3\text{O}_{10})^{-5}$  and  $(\text{Al}_2\text{Si}_2\text{O}_{10})^{-6}$ . These sheets are variously referred to the silica layer, the silica sheet, or the tetrahedral layers. The tetrahedral layer is combined with another sheet-like grouping of cations (usually, Al, Mg, or Fe) of six-coordination with oxygen and hydroxyl anions. Six-coordination means that the anions are arranged around the

cations in an octahedral pattern, one anion at each solid corner of an octahedron and a cation at the center. By the shearing of anions between adjacent octahedron a planar resultant network results and this is often referred to as the octahedral layer. The mineral  $\text{Mg}(\text{OH})_2$  (brucite) have this type of structure, and Mg-OH layer are often known as brucite layer. The brucite layer is trioctahedral, there being three cations for each six OH anions. The dimensions of the tetrahedral and the octahedral layers are closely similar, and consequently, composite tetrahedral-octahedral layers are readily formed, an octahedral layer sandwiched between two tetrahedral layers (a three layer structure) as chlorite.

#### *Structure of Orthohexagonal Chlorite*

A regular sequence of odd layer to form the orthorhombic structure gives an intense 202 reflection at about 2.50 Å. The powder pattern of a regular polytype is usually not distinguishable from that of its related semirandom structure because of the weakness of the diagnostic  $k \approx 3n$  reflections. The semirandom structures occur in more abundance than the regular polytypes. Crystals with regular layer sequences has not been found. The semirandom stacking of adjacent layers has been deduced from the intensity distribution along the  $k \approx 3n$  streaks.

The lattice type of the specimen from general reflection showing  $h+k=2n$  as later described is centered the C-face (001). An orthorhombic crystal gives only the following reflections.  $hkl : h+1=2n$ ,  $okl : (k=2n)$ ,  $hol : h=2n ; (l=2n)$ ,  $hko : (h=2n) ; (k=2n)$ . The reflections of the specimen are  $hkl : h+k=2n$ ,  $okl : (k=2n)$ ,  $hol : (h=2n)$ ,  $okl : (k=2n)$ , 001 : no conditions, so the space group may be explained C 2/m 2/m 2/m. Here, the symbol n is used to represent any integer.

#### **X-Ray and Thermal Identification**

The X-ray powder diffraction data of the specimen and heated specimens are shown in Table 1. Ni-filtered copper radiation ( $\text{Cu}_K \alpha : 1.5418$ ) was used under the following experimental conditions ; 35 kV, time constant 1.25 seconds, scanning speed  $1^\circ/\text{min.}$ , chart speed 1 cm/min., full scale 1,000 counts and slit 1 mm (divergent) -0.2 mm (receiving). The chlorite rich in magnesia and poor in alumina gives a little weak reflections for 001 and 003 net planes, normal reflection for 004 and the most strong peak for 002. The identification by only X-ray analysis for the various chlorites is very difficult. The 202 reflection at 2.495 Å is characteristic for orthohexagonal lattice as mentioned above. The lattice constants of the specimen computed from the reciprocal lattice are as follows.

$$a=5.308 \text{ \AA}, \quad b=9.222 \text{ \AA}, \quad c=14.676 \text{ \AA}, \quad V=718.9 \text{ \AA}^3, \quad \beta=0^\circ.$$

Each specimen of the fine powder was heated in an electric furnace, and kept at successive temperatures from 200° to 800°C at interval of 100°C. After cooling, the diffractometer patterns of each of the heated specimens were obtained by means of the X-ray apparatus. It appears that Al-poor magnesian chlorite shows a greater shrinkage parallel to c than to the magnesian chlorites. Considerable changes are observed in the reflected intensities, particularly for the 001 reflections. At 450°C, the intensity of 001 is greatly increased and the intensities of 002, 003 and 004 are decrea-

Table 1. X-ray data of orthorhombic chlorite and its heated specimens.

hkl *	Normal temp.		After 450°C	
	d(Å)	I	d(Å)	I
001	14.7	32	14.3 } 14.0 }	86
002	7.35	100	7.34	13
003	4.86	21	4.75	4
020	4.61	6	4.59	11
004	3.67	45	3.661	33
005	2.92	2		
200	2.654	2		
202	2.495	12	2.495	8
025	2.462	3	2.472	3
204	2.161	3		
007	2.101	1		
060	1.538	17	1.536	25
063 } 208 }	1.501	2	1.504	4

hkl\* : Orthorhombic chlorite

Table 1. (continued)

hkl	After 600°C		After 700°C		After 800°C	
	d(Å)	I	d(Å)	I	d(Å)	I
001 *	14.00	37				
020					5.10	3
021	3.910	8	3.909	19	3.900	21
101			3.754 } 3.723 }	2	3.731	3
111			3.507	10	3.507	9
002			2.993	6	3.003	4
160 +			2.894	1	2.894	2
130	2.776	8	2.776	16	2.776	17
131	2.522	10	2.515	20	2.512	26
112	2.462	14	2.462	20	2.465	33
122	2.270	4	2.270	19	2.268	18
220,211			2.163	4	2.163	5
222	1.752	7	1.751	22	1.746	25
123	1.737	4				
241					1.672	4
232					1.638	4
152					1.596	2
004					1.497	5
062			1.484	8	1.480	7
331					1.397	5
261			1.354	4	1.352	10

no symbol : Olivine, 001\* : Chlorite, 160+ : Enstatite

sed. The reflection intensities from 020 and 060 net planes at 450°C are stronger than those at normal temperature. The powder pattern of the specimen could not be seen except 001 reflection at 600°C, at which temperature the basal spacing had diminished still further to 14.0 Å and the pattern of olivine was seen, but at 700°C 001 reflection had disappeared and that of enstatite was faintly observed. In the course of the transformation from chlorite to olivine, silica and water are expelled from the structure. Al-poor Mg-chlorite is supposed to be of polytype ( $\beta=90^\circ$ ). Due to heating in the air, similar to Mg-chlorite, 001 reflection intensifies at the first stage of dehydration (450°) of crystallized water and simultaneously other reflections go down and basal spacings are reduced, but 001 peak of Mg-chlorite is still observed at 800°C.

The mol.% of forsterite generated at 600°~800°C from the specimen may be calculated for d(130) of the forsterite. The value may be computed as 83.4 (Fo. Mol%).

### Differential Thermal Analysis

The D. T. A. curve for the specimen (Fig. 1) was obtained under thermo-couples of C-A, sensitivity of  $\pm 250 \mu V$ , heating rate of 20°C/min. and chart speed of 4 mm/min. The broad and clear endothermic peak on low temperature side at about 139°C is due to loss of absorbed water. The principal well-marked endothermic peak at 679-691°C is considered to be caused by the dehydration of chlorite. The endothermic peak at about 787°C is small and immediately followed by very sharp and comparatively small exothermic peak at about 812-814°C. The high temperature endothermic peak is considered that appeared by the decomposition of chlorite, and

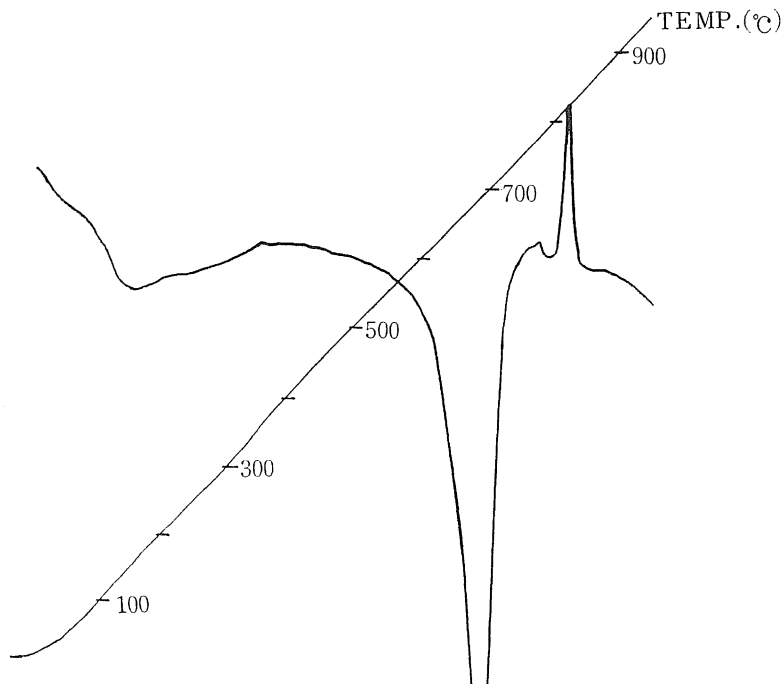


Fig. 1. D. T. A. curve of orthorhombic chlorite from the Hinokami mine.

Minerals	En.	En.	En.	Ex.
Orthorhombic chlorite taken	139°	691°	787°	812° C
Mg-chlorite		620-670°	800-850°	830-880° C
Al-chlorite		610°		900° C
Clinochlore (leuchtenbergite)		615°	840°	850-900° C

major structural changes occur. The sharp exothermic peak is resulted by the crystallization of forsterite. Under the sensitivity condition of  $\pm 500\mu V$ , the D. T. A. curve of the specimen is as shown in Fig. 2. The temperature of decomposition of the silicate layer is not observed in the figure, and the curve is more or less different from the D. T. A. curve (Fig. 1) under  $\pm 250\mu V$  condition. The D. T. A. data (Fig. 1) are compared with the average values of those of Mg-chlorite, Al-chlorite and clinochlore (leuchtenbergite) as the following descriptions.

From the results, it is realized that the principal reaction of the Al-poor Mg-chlorite (orthorhombic chlorite) is taken place at higher temperature than those of clinochlorites and the exothermic reaction of the specimen occurs at lower temperature than those of the other chlorites.

D. T. A. data of chlorites indicate endothermic dehydration reactions in two stages followed by an exothermic recrystallization. The X-ray data show that the first reaction corresponds to the decomposition of the brucite layers with only minor changes in

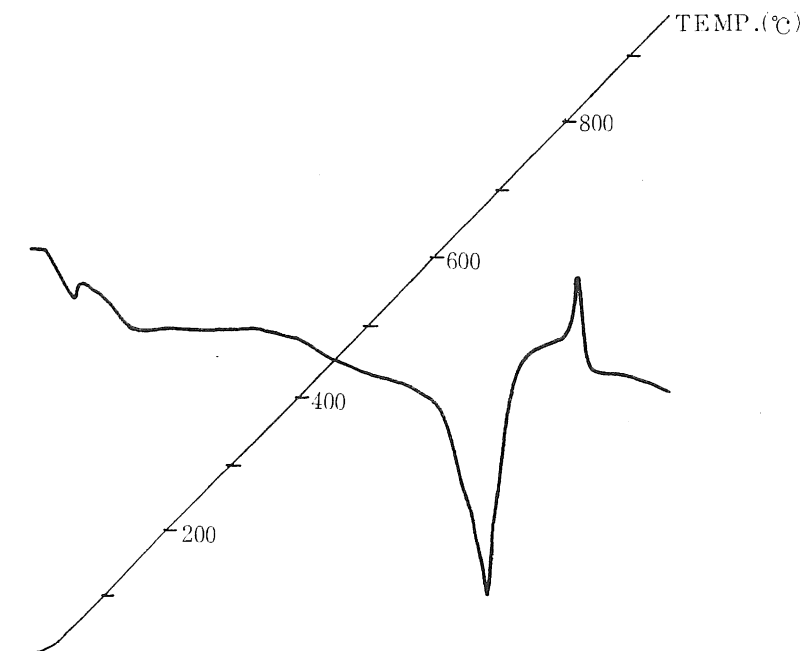


Fig. 2. D. T. A. curve of ditto

unit-cell parameters. However, considerable rearrangement of the structure take places, as is shown by the changes in the X-ray reflection intensities. It will be seen that the intensity changes are of important discriminative value. The second reaction corresponds to loss of water from the talc layer, and this is followed by a recrystallization forming new products, predominantly olivine  $(\text{Mg, Fe})_2\text{SiO}_4$ .

The temperatures of the dehydration reactions and the extent to which they are clearly separated depend on the composition, crystallinity and particle size of the chlorite, and on the thermal conditions. Chlorites that are low in iron and notably high in magnesian in character, the two dehydrations take place at temperatures very approximately  $600^\circ$  and  $820^\circ\text{C}$ .

### Chemistry

Hydrochloric acid solution of the specimen fused with carbonate mixture was used for analyses of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{MgO}$ , etc.. The results of chemical analysis and its atomic ratios are shown in Table 2. As seen from the table 2, the number (OH) ions is more than its ideal value of 8 and the number of ions in six coordination is considerably less than the ideal value of 6. The values taken by the mineral are distinctive for orthorhombic chlorite, and are different from monoclinic chlorite. (OH) ions may replace some O atoms in the four coordinate network. As seen from above cited analysis, the deviation from the ideal structure is due to the more strong hydrogen combination between (OH) in the brucite layer and in the talc layer.

Chlorite was formed by the primary alteration of enstatite and  $\text{Fe}_2\text{O}_3$  component in the specimen is supposed to have become a chemical constituent of the chlorite through this alteration. In chlorite minerals, Si can be replaced by Al, and Mg by Al,  $\text{Fe}^3$ ,  $\text{Fe}^2$ , etc.. In the specimen, though Al that will replace Si may exist, the one that replace Mg does not present. The specimen contains lesser  $\text{Al}_2\text{O}_3$  than normal clinoclchlorite.

Chemistry of chlorite minerals may be described in relation to chlorite, having the assumed composition of  $\text{Mg}_3\text{Si}_5\text{O}_{20}(\text{OH})_4 + \text{Mg}_6(\text{OH})_{12}$  that represents, as its structure, the equal number of talc and brucite layers. 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  $\text{Si}_7\text{Al} - \text{Si}_4\text{Al}_4$ . Chlorite consists of talc layer and brucite layer as described above, and this structure is constructed by the combination of ion between the two layers. Decrease of the base distance with the amount of  $\text{Al} + \text{Fe}^3$  is explained by the fact that the electric charge of talc layer is changed by the replacement of the octahedral site by  $\text{Fe}^3$ , which is compensated by the insufficient charge caused by the corresponding replacement of Si in the tetrahedral site by  $\text{Al} + \text{Fe}^3$ , and the charge equilibrium is maintained. Opposite surfaces of the two layer have opposite charges, and the attraction between the layers becomes stronger as  $\text{Al} + \text{Fe}^3$  content increases. As the chlorite specimen contains small amounts of  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  in tetrahedral site, it is considered that the sample is unstable. Atomic ratio of  $\text{Fe}^3$  in the six coordination is 0.37 and  $\text{Al} + \text{Fe}^3$  in the four coordination is 0.50. As this  $\text{Al} + \text{Fe}^3$  amount is comparatively small, the base distance increases. In the chlorite analysis, small amounts of calcium and alkalies are included. They are regarded as structural ions.

Table 2. Chemical analysis of orthorhombic chlorite.

	Wt. %	Atom. ratios when O(OH) = 18	
SiO <sub>2</sub>	36.87	Si	3.50
TiO <sub>2</sub>	0.01	Ti	0
Al <sub>2</sub> O <sub>3</sub>	3.43	Al	0.38
Fe <sub>2</sub> O <sub>3</sub>	6.94	Fe <sup>3</sup>	0.49
FeO	0.59	Fe <sup>2</sup>	0.05
NiO	0.43	Ni	0.03
MnO	0.10	Mn	0.006
MgO	36.91	Mg	5.26
CaO	0.03	Ca	0.006
Na <sub>2</sub> O	0.04	Na	0.006
K <sub>2</sub> O	0.03	K	0.002
H <sub>2</sub> O <sub>+</sub>	13.77	OH	8.71
H <sub>2</sub> O <sub>-</sub>	0.79	O	9.29
	99.94		
Tetrahedral ions		Octahedral ions	
Si	3.50	Fe <sup>3</sup>	0.37
Al	0.38	Fe <sup>2</sup>	0.05
Fe <sup>3</sup>	0.12	Ni	0.03
	4.00	Mn	0.01
		Mg	5.26
		Ca	0.01
		Na	0.01
		K	0
			5.74

(Analyst : J. Kitahara)

In oxygen-containing minerals, the amount of oxygen on a volume basis far exceeds all other elements. Thus in oxygen compounds the structure is generally determined by the arrangement of the oxygen ions, but ions of the other elements fitting in the interstice between these large ions, the sum of positive and negative charges on the ions must balance.

Chlorite forms an extensive isomorphous series with a high degree of atomic or ionic substitution. Fe<sup>3</sup> in six coordination replace Mg, and it is supposed that Fe<sup>3</sup> may be presented in four coordination from the ionic radius (0.64 Å). Radius ratio (R/R<sub>0</sub><sup>-2</sup>) of Al lies near the theoretical boundary between four (R/R<sub>0</sub><sup>-2</sup>=0.22-0.40) and six (R/R<sub>0</sub><sup>-2</sup>=0.41-0.73) coordinations, so may occur on both. Al tends to assume four coordination and substitute for Si, and also it occurs more often in six coordination. As radius ratio of Al is 0.46, it favours six coordination. Radius ratio of Fe<sup>3</sup> also lies near the limit of four coordination, then it is expected that Fe<sup>3</sup> may assume four coordination as shown in Table 2.

### Acknowledgement

The writer is grateful to late B. Sc. Kazuhiro Takigawa of a respective friend, the chief staff of mining section of Hinokami mining station, Nitetsu Kōgyo K. K., for his aid in surveying the chromite deposits.

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