原著論文

Chlorite of Crystalline Schists

by

Akiho MIYASHIRO*

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Abstract

Usually chlorites in crystalline schists are lepto-chlorite. Their optical and X-ray properties are summarized. The chlorite-garnet equilibrium in crystalline schists is discussed. New chemical data regarding the equilibrium are presented.

Introduction

Chlorite is an important rock-forming mineral of low-grade crystalline schists. However, petrologists have paid only a little attention to the composition, properties and stability relations of this mineral. In the present paper I am compiling available data, existing and new, for the purpose of clarifying general characters of chlorite as a rock-forming mineral. Probably such a compilation will be of use at the present state of our knowledge.

Historical Sketch of Studies of Chlorite

TSCHERMAK (1890, 1891) was the first to classify successfully the minerals of the chlorite family on the basis of the chemical compositions. He divided the chlorites into two main groups: orthochlorites and lepto-chlorites. Orthochlorites were regarded as solid solutions having amesite ($H_4Mg_2Al_2SiO_9$) and antigorite ($H_4Mg_3Si_2O_9$) as the end-members. He considered that the solid solution series was discontinuous, consisting of two parts, namely orthochlorites proper and serpentine, as follows:

		Amesite mol. %	Antigorite mol. %
Orthochlorites	Amesite	100~75	0~25
	Corundophilite	75~70	25~30
	Prochlorite (or ripidolite)	70~60	30~40
	Clinochlore	60~50	40~50
	Pennine	50~40	50~60
Serpentine (antigorite)		10~0	90~100

* Geological Institute, Faculty of Science, Tokyo University.
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The chlorites, having chemical compositions different from those of the above series, were called leptochlorites.

Later investigations of ORCEL (1927), WINCHELL (1926, 1936), and HALLIMOND (1939) confirmed the validity of most essential points of TSCHERMAK's work. WINCHELL improved TSCHERMAK's chemical classification by introducing new end-members, especially by taking the Mg-Fe'' and Al-Fe''' substitutions into consideration. Thus, orthochlorites were regarded as solid solutions composed of the following four end-members:

Amesite	$H_4Mg_2Al_2SiO_9$	Antigorite	$H_4Mg_3Si_2O_9$
Daphnite	$H_4Fe_2Al_2SiO_9$	Ferroantigorite	$H_4Fe_3Si_2O_9$

WINCHELL considered that leptochlorites are merely naturally oxidized orthochlorites.

HALLIMOND (1939) devised a useful method of graphical representation of composition relations of the chlorites regardless of theoretical considerations. According to it, the molecular proportions of R_2O_3 ($=Al_2O_3+Fe_2O_3+Cr_2O_3$) and RO ($=MgO+FeO+MnO$) when $SiO_2=200$ are taken as co-ordinates in a rectangular diagram (Fig. 1). In this diagram, the orthochlorites fall on a line, called the orthochlorite line, whereas leptochlorites show outstanding departure from the line.

Recent X-ray studies by HALLIMOND (1939) with BANNISTER, GRUNER (1944), ARUJA (1945), etc. have revealed that amesite, antigorite, cronstedtite and some chamosite, which were formerly regarded as members of the chlorite family, do not have the ordinary chlorite structure, but actually have the kaolin-type structure. Though from a purely chemical point of view amesite and antigorite may be treated as end-members of the orthochlorites, actually the two minerals are not chlorites in the proper sense. Thus, the orthochlorites comprise only the members from corundophilite to pennine. HALLIMOND has pointed out that probably there exist compositional gaps not only between antigorite and pennine, but also between amesite and corundophilite.

There is no unanimous system of division and nomenclature for the members of the chlorite family, but it is not an essential problem how to divide a continuous solid solution field for the sake of nomenclature.

Chemical Compositions

Available chemical data of chlorites from crystalline schists may be divided according to their reliability into three classes as follows:

Class 1, comprising chemical analyses, for which we have no positive reason to doubt the purity of the sample or the quality of analysis,

Class 2, comprising chemical analyses which are evidently inferior in the purity of the sample or the quality of analysis to the data of class 1, and

Class 3, comprising chemical compositions of chlorites calculated from the bulk chemical composition and modes of the host-rocks. The reliability of the data of this class is very limited.

The X-ray studies have shown that the structural formula of the chlorites is

where $m=6\sim4$. From a chemical point of view, this formula may be transformed into $(Mg, Al)_m(Si, Al)_4O_{14}\cdot 4H_2O$. Then the collected analyses were recalculated into the above formula on the anhydrous basis of $O=14$. The results of calcu-

Table 1. Chemical compositions of chlorites from crystalline schists (anhydrous basis O=14)

Class	Si	Al	Al	Ti	Fe'''	Fe''	Mn	Mg	H ₂ O ⁺	m	R ₂ O ₃	RO	Fe''/(Mg+Fe'')	Authors
1	2.77	1.23	1.17	0.03	0.28	1.89	0.03	2.51	3.87	5.91	96	320	0.430	HUTTON (1938)
1	2.72	1.28	1.26	—	0.22	1.81	0.04	2.58	3.77	5.91	101	325	0.412	TILLEY (1938)
1	2.66	1.34	1.48	0.03	0.25	1.72	0.01	2.26	3.63	5.75	115	298	0.431	SEITSAARI (1954)
1	2.65	1.35	1.23	0.07	0.31	1.86	0.03	2.35	3.74	5.85	109	320	0.442	HUTTON (1938)
2	2.95	1.05	1.30	0.01	0.06	1.23	0.01	3.23	3.68	5.84	82	304	0.276	MATHIAS (1952)
2	2.85	1.15	1.56	0.04	0.22	1.65	0.01	2.15	3.74	5.63	103	268	0.434	SEITSAARI (1954)
2	2.82	1.18	1.32	0.04	0.26	1.80	0.15	2.19	3.80	5.76	98	294	0.451	This paper, Table 2
3	2.83	1.17	1.79	—	0.01	2.26	—	1.62	3.01	5.68	105	274	0.581	WISEMAN (1934)
3	2.81	1.19	1.15	0.14	0.45	3.15	—	0.73	3.54	5.62	99	275	0.811	BARTH (1936)
3	2.73	1.27	1.10	—	0.60	2.33	0.11	1.65	4.73	5.79	109	299	0.583	GOLDSCHMIDT (1920)
3	2.68	1.32	1.22	0.06	—	1.82	0.03	2.87	3.90	6.00	95	354	0.388	CARSTENS (TILLEY, 1938)
3	2.55	1.45	1.16	—	0.32	1.13	0.03	3.34	3.71	5.98	115	352	0.255	VOGT (1927)
3	2.54	1.46	1.31	—	0.17	1.43	0.01	3.10	3.89	6.02	116	357	0.315	VOGT (1927)

Note. The Al atoms are divided into two groups in this table. The earlier group represents the Al atoms in 4-coordination, whereas the later represents those in 6-coordination. In the compositions of class 3, the total H₂O contents are given instead of H₂O⁺.

lation are shown in Table 1.

In the chlorites of classes 1 and 2, the value of *m* is close to 6, ranging from 5.63 to 5.91, and the value of H₂O⁺ is close to 4, ranging from 3.63 to 3.87. The number of Al atoms replacing Si atoms ranges from 1.05 to 1.35.

The molecular values of R₂O₃ and RO (when SiO₂=200) were also calculated for HALLIMOND's method of graphical representation. The results are plotted in Fig. 1. Most, if not all, of the reliable data fall on the lepto-chlorite field, far to the left of the orthochlorite line. Thus, at least, most of chlorites in crystalline schists can not be regarded as solid

Fig. 1. Compositions of chlorites from crystalline schists after the graphical method of HALLIMOND (1939).

solutions of amesite and antigorite molecules and their iron analogues. It is rather queer that this remarkable fact has been overlooked.

WINCHELL (1926, 1946) has suggested that leptochlorites were probably produced by oxidation of iron in orthochlorites after formation of the crystal. However, even if all the Fe_2O_3 content of the above chlorites is recalculated as 2FeO , the points still fall on the leptochlorite field in many cases. This is an evidence against the view of WINCHELL. Moreover, we have no reason to consider that such oxidation took place after formation of low-grade metamorphic rocks. Thus, probably the leptochlorite compositions of metamorphic chlorites are inherent, and are not due to oxidation after formation of the minerals.

Optical Properties

WISEMAN (1934) showed the range of variation in optical properties of chlorite from low-grade schists of mafic compositions in the Grampian Highlands of Scotland, as follows: The double refraction varies from 0.0045 to a very low value. The refractive index β varies from 1.605 to 1.635 when the chlorite is associated with actinolite. The chlorites having $\beta=1.605\sim1.631$ are optically positive, while those having β greater than 1.632 are negative, and the double refraction increases with increasing divergence of β from 1.632. Chlorites, which are not associated with actinolite, may show higher refractive index β , up to 1.653. He showed graphically that there is a close relation between the refractive index β of chlorite and that of the associated actinolite.

I determined optical properties of many chlorites in low-grade mafic schists of the Gosaisyo-Takanuki district in Abukuma Plateau, northeastern Japan. The results are similar to those of WISEMAN. A close relation between the refractive indices of chlorite and those of the associated actinolite was found in this case, too. The larger the $\text{Fe}''/(\text{Mg}+\text{Fe}'')$ ratio of the host-rock, the higher the refractive indices of the chlorite and associated actinolite, as shown in Fig. 2. Thus, the relation is controlled mainly by the Mg- Fe'' substitution of the minerals.

Fig. 2. The relation between the β index of chlorite and the γ index of the associated actinolite in actinolite-chlorite-schists of the Gosaisyo-Takanuki district, Abukuma Plateau. The numbers attached to three points represent the $\text{Fe}''/(\text{Mg}+\text{Fe}'')$ ratio of the host-rocks.

orthochlorites. As the leptochlorite composition of metamorphic chlorites is essential, his diagrams are not satisfactory for petrological purposes.

Fig. 3 shows one of WINCHELL's diagrams. In order to plot the compositions of leptochlorite into this diagram, we must make some artificial modification of the compositions so that the compositions conform to the orthochlorite formula.

One of such modifications is acquired by regarding the abscissa of the diagram as representing the total number of Al atoms in the structural formula and by regarding the ordinate as representing the value of $(\text{Fe}'' + \text{Fe}''') / (\text{Mg} + \text{Fe}'' + \text{Fe}''')$. Through this procedure, the compositions of classes 1 and 2 are plotted in the diagram for comparison of the actual analyses with the optical properties. It is found that most analyses fall on the "ripidolite" field just as is suggested by the optical properties.

X-ray Properties

Kaolin-type minerals such as amesite, antigorite and some chamosite, give the first-order basal reflection with $d \approx$ about 7 Å. On the other hand, chlorite proper usually gives the first-order basal reflection with $d \approx$ about 14 Å. This is an important diagnostic feature. Chlorites rich in iron, however, give the weak (001) and (003) reflections and strong (002) and (004). If the (001) and (003) reflections be overlooked, the (002) and (004) reflections may be mistaken for the (001) and (002) reflections, respectively, of a kaolin-type mineral.

So far as I have examined, chlorites from low-grade schists of the Gosaisyo-Takanuki district and of the Sanbagawa zone give a clear basal reflection with $d \approx$ about 14 Å in all cases. Therefore, these chlorites probably have the ordinary chlorite structure. The observed value of the basal spacing d was nearly constant, ranging from 14.14 to 14.17 Å (true Å). If we take the intensity of the (004) reflection as a constant value, the relative intensities of the (001), (002), and (003) reflections tend to decrease with the increase of the β index.

Chlorite-Garnet Equilibrium

Chlorite and pyralspite garnet (i. e. Ca-poor garnet) are resembling each other in chemical composition and occur in association in some low-grade metamorphic rocks. Their composition and stability relations are of some petrological interest*. It is well known that chlorite is stable only at low temperatures, while pyralspite garnet is stable through a much wider range, up to a very high temperature.

New data on the equilibrium relation between chlorite and pyralspite in a low-grade schist are given below. The host-rock of the analyzed minerals is pyralspite-bearing sericite-chlorite-schist from Oyahana at Minano-mati, Titibugun, Saitama Prefecture (Specimen No. AM461020-15). It is composed of quartz

Fig. 3. The optical properties of chlorite and related minerals after WINCHELL (1936, 1951). Rip, Pro, Rump, and Aph mean the fields of "ripidolite", "prochlorite", "rumpfite" and "aphrosiderite", respectively, in his nomenclature. The compositions of chlorites of classes 1 and 2 are shown as dots.

* This problem has been discussed by RAMBERG (1945).

(48%), albite (19%), chlorite (15%), sericite (13%), pyralspite (1.2%), opaque minerals (3%) and negligible quantities of apatite, calcite, epidote and stilpnomelane (MIYASHIRO, 1955). The schists of the area did not reach the metamorphic grade at which biotite is formed.

The chlorite and pyralspite garnet were separated by means of the electromagnetic separator and Clerici solution. The pyralspite sample was sufficiently purified, whereas the chlorite sample contained about 7% of sericite. The results of chemical analysis by H. HARAMURA are shown in columns I and II of Table 2. From the values of column II, the composition of pure chlorite was calculated as shown in column III.

The analyzed minerals show the following properties:

Pyralspite $a_0 = 11.63 \text{ \AA}$ (true $\text{\AA}$)

Chlorite $\beta_D = 1.628$, $\gamma - \alpha = 0.001$. Biaxial positive with $2V = 10^\circ$.

$d_{001} = 14.16 \text{ \AA}$ (true $\text{\AA}$). $I_{001} : I_{002} : I_{003} : I_{004} : I_{005} : I_{006} : I_{007}$
 $= 16 : 85 : 40 : 100 : 26 : 0 : 8$.

The relative intensities of the basal reflections of the chlorite were assumed to be proportional to the relative heights of the peaks in a Geiger-counter X-ray diffractogram for $\text{CuK}\alpha$ radiation.

Table 2. Pyralspite and chlorite from a pyralspite-bearing sericite-chlorite schist at Oyahana, Titibu.

	I	II	III
SiO_2	36.68	28.42	27.4
Al_2O_3	18.53	21.49	20.6
TiO_2	0.85	0.44	0.5
Fe_2O_3	7.85	3.15	3.4
FeO	10.78	19.18	20.9
MnO	18.03	1.52	1.7
MgO	trace	13.12	14.3
CaO	5.71	trace	trace
Na_2O	n.d.	0.20	0.1
K_2O	n.d.	0.72	0.0
H_2O_+	0.8	10.57	11.1
H_2O_-	0.1	0.70	—
Total	99.33	99.51	100.0

I: Pyralspite ($\text{Mn} : \text{Fe}'' : \text{Mg} = 62.8 : 37.2 : 0.0$).

II: Mixture of chlorite (93%) and sericite (7%).

III: Calculated composition of pure chlorite ($\text{Mn} : \text{Fe}'' : \text{Mg} = 3.6 : 43.5 : 52.9$).

Fig. 4. Composition relations between chlorites (crosses) and associated pyralspite (dots) in schists from Oyahana and Kangasala.

The pyralspite is much higher in Fe''/Mg and $\text{Mn}/(\text{Mg} + \text{Fe}'')$ ratios than the associated chlorite. The composition relation is diagrammatically shown in Fig. 4

Mn plays an important role in the formation and stability of pyralspite in metamorphic rocks. If the Mn content of a schist is very small, practically all the Mn may be contained in chlorite. The increase in the Mn content of the rock should cause an increase in the Mn content of chlorite, until the upper limit of the Mn content of the chlorite is reached. A further increase of the Mn content of the rock will cause the formation of a more manganiferous mineral,

which is usually pyraispite. The compositional variation of pyraispite with metamorphic grade was discussed in another paper (MIYASHIRO, 1953).

SEITSAARI (1954) gave data of the chlorite-pyralspite equilibrium in a pyralspite-bytownite-schist from Kangasala, Finland, as shown in Fig. 4. Pyralspite is higher in Fe''/Mg and $\text{Mn}/(\text{Mg}+\text{Fe}'')$ ratios than the associated chlorite in this case, too. The Kangasala rock represents a higher grade than the Oyahana rock. Pyralspite becomes poorer in Mn with increase of metamorphic grade. Thus, the probable variation in the equilibrium relation with metamorphic grade is similar to that in the biotite-pyralspite equilibrium (MIYASHIRO, 1953), and is schematically shown in Fig. 5. Probably some of the high-grade part of the figure is not realized in ordinary cases, because some other minerals such as cordierite and anthophyllite occur instead.

Not only the grade of metamorphism but also the type of metamorphism have a strong influence on this equilibrium, especially on the compositional variation of pyralspite. However, this problem is outside the scope of the present paper.

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Fig. 5. Variation of the equilibrium relation between chlorite and pyralspite garnet with metamorphic grade. The composition fields of chlorite and pyralspite are indicated by C and P respectively. Pyralspite M_1 is in equilibrium with chlorite M_2 in a rock M.

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結 晶 片 岩 の 緑 泥 石

都 城 秋 穂

(要 旨)

本稿において、私は、結晶片岩のなかの緑泥石の化学組成、光学的性質、およびX線の性質を概観し、さらに、結晶片岩のなかの緑泥石とざくろ石との化学平衡を論じた。