IRON-RICH CHLORITE FROM SHŌGASÉ, KŌCHI PREFECTURE, JAPAN

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ABSTRACT

Chemical, X-ray, and thermal analyses along with petrographical data are given for a specimen of iron-rich chlorite from Shōgasé, Kōchi Prefecture, Japan. The X-ray data are given also for "chamosite" from the Arakawa mine, Japan. X-ray powder lines, which are indexed on the basis of an ortho-hexagonal cell, together with the thermal data, confirmed that the structure cell of this mineral was similar to that of "chamosite" from Schmiedefeld, Thuringia as suggested by Engelhardt. Some notes on the nomenclature are presented.

Occurrence and general properties

The chlorite was collected during the geologic research for fire-brick silica stone deposits* at Shōgasé, Sanze Village, Agawa County, Kōchi Prefecture**, Japan, in 1952. The deposits are found along a contact between diabasic intrusives and the Palaeozoic sediments as quartzite and schalstein. The chlorite occurs as dark green films either along the outer boundary of the deposits or filling fissures in the wall rocks. Along the chlorite films, the wall rock is dark

* The silica stone is known by the commodity name of "Akashiro keiseki" (red and white silica stone) in Japan. They appear dapple, consisting of the angular fragments of hematite-bearing fine-grained reddish-colored cherty rocks, and the white-colored coarse-grained vein quartz. Some of them look similar to a loin of beef. Substitution of green-colored cherty fragments for the reddish ones is common, and in this case chlorite appears in places of hematite. These iron-containing silica stones have been successfully used in Japan as the raw materials for silica bricks.

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terruginous color and consists of microcrystalline quartz, chlorite and mica (iron-sericite?).

The chlorite is dark green in color, fine scaly in habit, arranged subparallel to the wall rock, vitreous in luster. Pleochroism distinct: X pale greenish yellow, Y and Z green. The refractive indices: $\alpha=1.634$, $\gamma=1.652$, $\gamma-\alpha=0.018$. Apparent optic angle of crystal aggregates is zero to very small; optically negative.

The specific gravity was determined as 3.10 with about 2 grams of sample by means of a picnometer.

Chemical Composition

The results of the chemical analysis are given in Table 1, Column 1, together with some other earlier analyses on chlorite. As written in the later pages "chamosites" in Columns 2 and 3,

Table 1. Chemical analyses of some iron-rich chlorites.

	1	2	3	4	5	6
SiO ₂	24.56%	24.50%	26.65%	24.18%	20.82%	24.78%
TiO ₂	none		tr.		tr.	
Al ₂ O ₃	16.07	16.32	16.14	18.23	17.64	18.69
Fe ₂ O ₃	5.10	7.45	6.69	10.56	8.70	6.45
FeO	34.66	31.46	34.43	29.75	37.96	36.17
MnO	1.42	3.33		0.48		
MgO	6.16	4.59	4.47	5.40	4.15	4.52
CaO	0.30			0.24		
H ₂ O(+)	11.93	11.36	11.42	9.54	10.31	9.09
H ₂ O(-)	0.54		0.08	1.07	0.07	
Total	100.74%	99.01%	99.88%	99.45%	99.65%	99.70%

1. Chlorite from Shōgasé, Kōchi Prefecture, Japan. Analyst: H. Shirozu.
2. "Chamosite" from the Arakawa mine, Akita Prefecture, Japan¹¹⁾.
3. "Chamosite" from Schmiedefeld, Thuringia⁹⁾.
4. Thuringite from Evisa (Corse)¹⁰⁾.
5. Thuringite from Schmiedefeld, Thuringia⁸⁾.
6. Aphrosiderite from Striegau.¹²⁾

have the similar structure cells to this chlorite. Thuringites in Columns 4 and 5, and aphrosiderite in Column 6 are chemically similar to this mineral.

Structural formula and theoretical density

From the chemical analysis in Table 1, column 1, the structural formula is calculated. Assigning O and (OH) ions to the 18 positions in the ideal structure, the formula is:

The discrepancies between the ideal chlorite formula, $(\text{R}_{6-n}\text{Al}_n)(\text{Si}_{4-n}\text{Al}_n)\text{O}_{10}(\text{OH})_8$, are: (i) excess of (OH), (ii) deficiency of octahedral cations, (iii) disparity between tetrahedral and octahedral Al ions. These points need further research.

From the structural formula and the cell dimensions described later, the theoretical density can be calculated. The molecular weight is 665.8. Its volume is $710.1/2 \text{ \AA}^3$. The theoretical density is then 3.11, in excellent agreement with the observed value (Sp. Gr.=3.10).

X-ray powder diagrams

X-ray powder diagrams for Fe $K\alpha$ ($\lambda=1.9373 \text{ \AA}$) radiations were obtained with a 114.6 mm. diameter camera. In addition to the

Figs. 1-2. Powder photographs of ortho-hexagonal iron-rich chlorites.

1. Chlorite from Shōgasé.
2. "Chamosite" from the Arakawa mine.

chlorite from Shōgasé, a specimen of "chamosite" from a quartz vein of the Arakawa mine, recently described by T. Sudo¹¹⁾ was also examined.

The diagrams are shown in Figs. 1 and 2. The measured lattice

Table 2. X-ray powder data for ortho-hexagonal iron-rich chlorites.

	1			2			3	4
<i>hkl</i>	<i>I</i>	<i>d</i> _{obs.} (Å)	<i>d</i> _{calc.} (Å)	<i>I</i>	<i>d</i> _{obs.} (Å)	<i>d</i> _{calc.} (Å)	<i>I d</i> (kX)	<i>I d</i> (kX)
001	2	14.1	14.16	4	14.1	14.17		3 14
002	10	7.05	7.08	10	7.05	7.09	10 6.62	10 6.93
003	2B	4.46	{4.72	4	4.71	{4.72	5 4.54	5 4.63
020			4.66			4.68		
022				$\frac{1}{2}$	3.92	3.90		
004	8	3.53	3.54	8	3.53	3.54	8 3.47	9 3.50
005	$\frac{1}{2}$	2.83	2.832	3	2.84	2.834	2 2.78	3 2.779*
024			2.818			2.823		
200	3	2.67	2.691	1	2.70	2.699		1 2.689
201	$\frac{1}{2}$	2.63	2.640	$\frac{1}{2}$	2.67	2.651		
202	5§	2.50	2.515	5	2.52	2.522	5 2.50	7 2.507
025	$\frac{1}{2}$	2.42	2.420					$\frac{1}{2}$ 2.330
204	2§	2.14	2.142	4	2.15	2.147	5 2.14	3 2.134
007	$\frac{1}{2}$	2.02	2.023	1	2.023	2.024		
206	1	1.76	{1.775	3	1.778	{1.777	5 1.77	2 1.767
240			1.761			1.768		
207				$\frac{1}{2}$	1.63	1.619		
060	5	1.553	1.553	4	1.558	1.558	2 1.56	5 1.556
062	3	1.517	1.517	2	1.522	1.522	5 1.52	2 1.524
208	$\frac{1}{2}$	1.477	{1.479	3	1.479	{1.481	2 1.48	1 1.473
063			1.475			1.480		
064	1B	1.419	{1.422	1	1.424	1.426	2 1.42	1 1.425
0010			1.416	2	1.417	1.417		
209				$\frac{1}{2}$	1.359	1.360		
401	$\frac{1}{2}$	1.340	1.339	$\frac{1}{2}$	1.344	1.343		
402	1	1.319	1.321	1	1.325	1.326		
066	$\frac{1}{2}$	1.299	1.298	$\frac{1}{2}$	1.300	1.301		

Table 2.—*Continued*

404				$\frac{1}{2}$	1.259	1.261		
2010	$\frac{1}{2}$	1.255	$\left\{ \begin{array}{l} 1.257 \\ 1.253 \end{array} \right.$	$\frac{1}{2}$	1.255	1.255	2	1.26
0012	$\frac{1}{2}$	1.180	1.180	1	1.181	1.181	2	1.18
				$\frac{1}{2}$	1.171			
				$\frac{1}{2}$	1.081			
				$\frac{1}{2}$	1.074			
	$\frac{1}{2}$	1.045		1	1.047		1	1.05
	$\frac{1}{2}$	1.010		2	1.011		1	1.01

Equivalent indices: 02/ $\equiv$ 11/; 20/ $\equiv$ 13/; 24/ $\equiv$ 15/ $\equiv$ 31/; 06/ $\equiv$ 33/; 40/ $\equiv$ 26/.

1. Chlorite from Shōgasé. Fe $K\alpha$, $\lambda=1.9373\text{\AA}$. Camera radius 57.3 mm. B: an unusually broad line. § The head of a diffused band extending to the side of smaller spacings.
2. "Chamosite" from the Arakawa mine. Fe $K\alpha$, $\lambda=1.9373\text{\AA}$. Camera radius 57.3 mm..
3. "Chamosite" from the Arakawa mine. Data by Sudo¹¹⁾. Co K. Camera radius 28.65 mm.. The readings were not calibrated. The 14 Å line was not recorded owing to the small radius of the camera.
4. "Chamosite" from Schmiedefeld, Thuringia. Data by Engelhardt⁵⁾ Fe $K\alpha$. Camera radius 57.5 mm.. * Line possibly due to siderite.

spacings and visually estimated intensities are given in Table 2 (Columns 1 and 2). Column 3 gives the data by Sudo¹¹⁾, and Column 4, the data by Engelhardt⁵⁾. The reflections of chlorite from Shōgasé (Fig. 1 and Table 1, Column 1) are fairly diffuse and some bands are shading on the side of smaller spacings. These characteristics may indicate a rather irregular structure. On the other hand, the reflections of "chamosite" from the Arakawa mine are moderately sharp. There is high similarity not only between the diagrams of chlorites from Shōgasé and from Arakawa, but also among them and those of "chamosite" from Schmiedefeld, Thuringia. These data bear some resemblances to those of ortho-hexagonal kaolin-type chamosite described by Brindley¹⁾, but some discrepancies are found between them.

Engelhardt interpreted his "chamosite" data as a layer structure of chlorite cell with orthorhombic (ortho-hexagonal) instead of

monoclinic axes. Although the evidences for his interpretation were not satisfactory, the data described here can be thoroughly interpreted according to his idea of the "chamosite" cell. Thermal behaviours given in the next section are also in agreement with his idea.

The lattice parameters were estimated as follows: Basal reflections at 14.1, 7.05 and 3.53Å and their higher orders were used to obtain the c-parameters. The b-parameters were obtained by taking the strong 1.55Å reflections as the 060. The bases of the cells were assumed to be centred and ortho-hexagonal in shape, so that $a = b/\sqrt{3}$. The calculated spacings, with their hkl indices, are compared with the measured spacings in Table 2, Columns 1 and 2. The agreement is everywhere close. Some basal reflections with an odd number for l index are recorded. The cell dimensions obtained here are shown in Table 3, where they are compared with those given by Engelhardt⁵⁾.

Table 3. Cell dimensions of ortho-hexagonal iron-rich chlorites.

	1	2	3
a	$b/\sqrt{3}=5.38\text{\AA}$	$b/\sqrt{3}=5.40\text{\AA}$	5.393 kX
b	9.32	9.35	9.341
c	14.16	14.17	14.00

1. Chlorite from Shōgasé.
2. "Chamosite" from the Arakawa mine.
3. "Chamosite" from Schmiedefeld, Thuringia. Data by Engelhardt⁵⁾.

Thermal properties

Fig. 3. Differential thermal analysis curve of chlorite from Shōgasé.

Differential thermal analysis curve of chlorite from Shōgasé is given in Fig. 3. It has two endothermic peaks; at about 600°C, and about 730°C.

The X-ray diagrams of the material heated up to 670°C, the end of the first endothermic curve, show a strengthening of 14Å line and considerable weakening of the higher order lines.

These thermal behaviours are characteristic to chlorite-type structure.

Note on the nomenclature

There are a number of mineral species belonging to the iron-rich chlorite; thuringite, chamosite, daphnite, bavalite, aphrosiderite, metachlorite, etc., and their nomenclatures are confused. But it has been shown that most of them except chamosite have similar structure.

The minerals hitherto called chamosite are generally found in the iron-rich sedimentary formations, and have been shown by Brindley¹⁾ and others⁴⁾ to include kaolin-type and chlorite-type minerals; the common chamosite has kaolin-type layers, consisting of a mixture of monoclinic and ortho-hexagonal cells in varying proportions; several chamosites including the specimen of type locality have probably monoclinic cells like most of other chlorites; "chamosite" from Schmiedefeld, Thuringia already mentioned has been considered as to have an orthorhombic (ortho-hexagonal) cell based on the chlorite-type layer. The chlorites described here belong to the latter category. It has been stated by Brindley¹⁾ and Hey⁷⁾ that these complex relations need a new nomenclature.

The chemical compositions of the Shōgasé chlorite and also "chamosites" from the Arakawa mine and Schmiedefeld are alike to earlier analyses of some of thuringites, chamosites as well as to some of aphrosiderites (Table 1). Chemically these three chlorites belong to thuringite, and the "chamosite", having the above-mentioned difficulties in nomenclature, must be abandoned*. Aphroside-

* After Dana's System 6th edition (1914, p. 658), chamosite is a variety of thuringite. The original sample of chamosite included siderite. It was reexamined later and shown to have a composition approximating thuringite.##

rite is used for more magnesia-rich members.

These chlorites have ortho-hexagonal cells, and their structural relation to thuringite is similar to that of ortho-antigorite to antigorite as studied by Brindley and Knorring³⁾.

For the reasons, these chlorites may be named "ortho-thuringite". But then, there arises a confusion with the term "orthochlorite". The writer prefers to leave this question of nomenclature unsettled at present.

In this sense, it is not reasonable to use the name "chamosite" as a mineral name. As suggested by Hey⁷⁾, it must be used as an inclusive term like limonite or wad.

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#The analyses of chamosite generally inform us of rather smaller Fe_2O_3 contents than thuringite. But the writer considers that the disparities are small and it is not necessary to distinguish these two species referred to their chemical composition.

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