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Katayamalite, a new Ca-Li-Ti silicate mineral from Iwagi Islet, Southwest Japan

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Abstract

Katayamalite occurs as a fine-grained accessory mineral amounting to 0.3-0.5 percent by volume in the aegirine syenite from Iwagi Islet, Ehime Prefecture, Southwest Japan. It coexists usually with albite, aegirine and pectolite. To the naked eye, katayamalite is white in color and phosphorescent to the ultraviolet rays. Striation white, luster vitreous. Hardness (Mohs) 3.5-4.0. Specific gravity 2.899 (calc.), 2.91 (meas.). (001) cleavage is perfect. In thin section it is colorless with strong absorption. $\alpha = 1.670$, $\beta = 1.671$, $\gamma = 1.677$, $\gamma - \alpha = 0.007$, 2V(+) = ca, 32° .

Chemical analysis shows SiO_2 52.31, TiO_2 10.99, Fe_2O_2 0.29, MnO 0.22, Li_2O 3.25, CaO 28.25, Na₂O 0.22, K₂O 2.89, H₂O 1.21, F 0.34, $-O=F_2$ 0.14, total 99.83%, corresponding ideally to (K, Na) $Li_3Ca_7(Ti, Fe^{+3}, Mn)_2(Si_6O_{18})_2(OH, F)_2$ with Z=4.

Katayamalite is triclinic with $a_0=9.721$, $b_0=16.923$, $c_0=19.942$ Å, $\alpha=91.43^{\circ}$, $\beta=104.15^{\circ}$, $\gamma=89.94^{\circ}$, Space group C1. The strongest lines in X-ray powder data are 3.23 (100) (006.04), 3.06 (30) (243), 2.943 (30) (314.311.153), 2.898 (30) (244.242), 2.417 (30) (008), 1.933 (40) (00.10).

Katayamalite resembles baratovite (Dusmatov *et al.*, 1975) both structurally and also chemically, but it is distinguished from the latter by the difference in crystal system and unit cell parameters. Dominance of OH over F and lacking of Zr replacing Ti are another chemical features of katayamalite.

The name katayamalite is given for the mineralogist, Emeritus Professor Nobuo Katayama.

Introduction

We detected a peculiar colorless mineral showing distinct deep bluish interference color in thin section in the course of studying a new mineral sugilite (Murakami *et al.*, 1976), in the aegirine syenite from Iwagi Islet, Ehime Prefecture, Southwest Japan. This mineral was described as clinozoisite by Sugi and Kutsuna (1944) and Taneda (1952), but this is fairly low in double refraction comparing with typical clinozoisite and phosphorescent to the ultraviolet rays. Because of its tiny size and very small amount, laborious purification was necessary to obtain some milligrams of purified specimen from powdered rocks for taking the X-ray powder data. The X-ray powder pattern was quite different from that of clinozoisite, and no similar pattern could be found in ASTM cards. We investigated this mineral chemically and structurally for about six years, and finally reached the conclusion that this is a new triclinic ring silicate characterized by high Ca and Ti contents and by the presence of Li.

Occurrence

Katavamalite* occurs as a fine-grained accessory mineral in the aegirine svenite from Iwagi Islet, Ehime Prefecture, Southwest Japan. This syenite has a small stock-like form of 0.20×0.15 km in the coarse-grained biotite granite belonging to the Cretaceous Hiroshima granite (Kojima, 1954; Ichikawa et al., 1968; Murakami, 1974). The syenite grades into the surrounding granite through quartz syenite and alkali granite as already described (Murakami et al., 1976). This occurrence and textural feature lead to the conception of the metasomatic formation of the svenite from biotite granite (Murakami and Matsunaga, 1966; Murakami, 1977). Modally the syenite is fairly heterogeneous, especially in color index, leucocratic and melanocratic parts showing patchy lenticular or irregular form. Syenite pegmatite and syenite aplite often occur as a small dike-like mass in the syenite. The syenite is coarse-grained, hypidiomorphic in texture. Constituent minerals are albite, aggirine, pectolite and sugilite with minor amounts of katayamalite, titanite, allanite, andradite, zircon and apatite. In the marginal part of the syenite mass, quartz and microcline are also contained. They tend to increase towards the granite in amount.

As described above, katayamalite occurs only as an accessory mineral amounting to 0.3-0.5 percent by volume. It is poorer in amount in the leucocratic part than in the melanocratic one. With increases of quartz and microcline, it has a tendency of decrease. On the other hand, katayamalite is not found in the sygnite pegmatite nor in the sygnite aplite.

Sugilite is an important component mineral in the syenite, but it is not always accompanied by katayamalite, lacking in some katayamalite-bearing rocks. Where it coexists with katayamalite, it tends to decompose to a micaceous mineral in many cases. This seems to mean the disequilibrium relation between them. Accordingly, the main constituents equilibrated with katayamalite are albite, aegirine and pectolite whose chemistry and optical properties are already described in detail by Murakami *et al.* (1976).

^{*} The name katayamalite has been approved by the Commission on New Mineral Names of the International Mineralogical Association (March 15, 1982).

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FIG. 1. Microphotograph of katayamalite. K: Katayamalite. Pl: Albite. Px: Aegirine. Pc: Pectolite.

Besides these minerals, there is another polymorph of katayamalite. According to the single crystal study, this polymorph shows monoclinic symmetry and has a large unit cell composed of $a_0=3\times9.721$, $b_0=2\times16.923$, $c_0=19.942$ Å, $\beta=$ 104.15° , Z=24. Space group is P2/m, P2, or Pm. Because of its resemblance to katayamalite, it is difficult to discriminate these two under the microscope, and any discernible difference in chemical composition and specific gravity between them has not been recognized, although the details will be described in another paper. The monoclinic polymorph with large cell is small in amount and seems to coexist with katayamalite, although its exact occurrence has not been made clear.

Chemistry

Katayamalite was separated from the host rock by means of magnetic separator and heavy liquid for chemical analysis. Semi-quantitative analyses by the spectrographic and solid mass spectrometric methods were done for the separated specimen, leading to detect nine elements, Si, Ti, Fe, Mn, Ca, Na, K, Li, and F, as major elements. Al, Mg, Sn, Ba, Be and P are very small or negligible in quantity.

Quantitative analysis for these major elements was also made. Si, Ti, Fe, Mn, Ca, Na and K were determined with an electron probe microanalyzer with takeoff angle of 40°, using natural minerals (hematite for Fe, manganosite for Mn, albite for Na, and adularia for K) and synthetic materials (CaSiO₃ for Si and Ca, TiO₂ for Ti) as the standard samples. Li was determined by the flame photometry. H_2O by the gravimetry through the dehydration technique using high frequency induction heating, and F with a specific ion electrode.

 Fe_2O_3 was checked by the KMnO₄ titration. The analytical result and atomic ratios calculated on the basis of Si=12.000 are shown in Table 1. As shown in this table, katayamalite is characterized by high Ca and Ti contents and by the presence of Li. Relatively high ratio of K/Na is curious in contrast with the very low value of K_2O/Na_2O in host rocks.

Table 1.	Chemical	composition	and	atomic	ratios	of	katayamalite.
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SiO	52.31	Si	12.00
TiO_2	10.99	Тi	1.90
$\mathrm{Fe}_{2}\mathrm{O}_{3}$	0.29	Fe	$0.05^{\int 1.95}$
MnO	0.22	Ca	6.94 6 08
CaO	28.25	Mn	0.04^{\int} 0.98
Na_2O	0.22	Na	0.10 0.05
K_2O	2.89	Κ	0.85°
Li ₂ O	3.25	Li	3.00
H_2O	1.21	0	35.78
F	0.34	OH	1.85 2 10
0=	F 0.14	F	$0.25^{\int 2.10}$
Total	99.83		

X-ray data

X-ray single crystal study indicates that katayamalite is triclinic, the cell parameters being determined by using Philips PW 1100 single crystal diffractometer as $a_0=9.721$, $b_0=16.923$, $c_0=19.942$ Å, $\alpha=91.43^\circ$, $\beta=104.15^\circ$, $\gamma=89.94^\circ$, space group C1, Z=4. If we adopt P lattice cell, the cell dimensions are $a_0=9.763$, $b_0=9.721$, $c_0=19.942$ Å, $\alpha=104.15^\circ$, $\beta=81.76^\circ$, $\gamma=119.92^\circ$, space group P1, Z=2, $h_c=k_p$, $k_c=-2h_p-k_p$, $l_c=l_p$. However, structure analysis and indexing of X-ray powder data are based on C lattice cell. The strong lines in the powder pattern are 3.48 (20)(025.205.203), 3.30 (20) ($\overline{135}.1\overline{34}$), 3.23 (100) ($006.0\overline{44}$), 3.06 (30) ($\overline{243}.2\overline{41}$), 2.943 (30) ($\overline{314}.3\overline{11}.\overline{153}$), 2.898 (30) ($\overline{244}.\overline{136}$), 2.790 (20) ($\overline{315}.3\overline{12}$), 2.417 (30) (008), 1.933 (40) (00.10), 1.841 (25) (190.\overline{46}2.\overline{191}), 1.382 (25) (00.14). The detail of the powder data is listed in Table 2*. According to the result of structural analysis, katayamalite is a ring silicate and its structure is topologically similar to that of baratovite determined by Sandomirskii *et al.* (1976) and Menchetti and

^{*} In indexing of X-ray powder reflections, the results of intensity measurement of single crystal diffractometry were referred to. The intensity data were converted to those in powder diffractometry, and strong reflections were selected. These were compared with X-ray powder reflections and indexing was carried out.

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C la	attice ce	-11	P la	ttice c	ell	1(1-) 8	d (
h	k	l	h	k	l	<i>a</i> (calc.) A	<i>a</i> (meas.) A	1
$ \begin{array}{c} 0 \\ -2 \\ -2 \\ 1 \\ 1 \end{array} $	$-\frac{4}{2}$	$ \begin{array}{c} 0 \\ 1 \\ 2 \\ 2 \end{array} $	$-2 \\ 2 \\ 0 \\ -2 \\ 1$	$^{0}_{-2}$ $^{-2}_{1}$	$ \begin{array}{c} 0 \\ 1 \\ 2 \\ 2 \end{array} $	$\begin{array}{c} 4.229 \\ 4.216 \\ 4.216 \\ 4.085 \\ 4.085 \end{array}$	4.14 ^b	15
-1 -1 1	-3 -3	$\frac{3}{4}$	-1 2 1	-1 -1 1	3 4 3	4. 085) 3. 698) 3. 695∫	3.66	15
$-{2 \atop 2}$	$ \begin{array}{c} 2\\ 0\\ 0 \end{array} $	5 5 3	$-1 \\ 1 \\ -1$	$-\frac{0}{2}$	5 5 3	3.483 3.428 3.426	3.48	20
-1 1	3 3	5 4		$-1 \\ 1 \\ 0$	5	3. 261 j 3. 258∫	3.30	20
$\begin{array}{c} 0\\ 0\\ 1\end{array}$	$-4 \\ 0 \\ 5$	$\begin{array}{c} 4 \\ 6 \\ 1 \end{array}$		0	$\begin{array}{c} 4 \\ 6 \\ 1 \end{array}$	3.224 3.222 3.085	3. 23	100
$-1 \\ -2 \\ 2 \\ -2 \\ 2 \\ 2 \\ 2 \\ -2 \\ 2 \\ 2 $		2 3 1 6	$ \begin{array}{c} -2 \\ 3 \\ 1 \\ 1 \end{array} $	-1 -2 -2 -2	2 3 1 6	$\begin{array}{c} 3.085 \\ 3.049 \\ 3.045 \\ 3.027 \\ 2.025 \end{array}$	3.06 ^b	30
$-\frac{2}{3}$ $-\frac{1}{-1}$	$-1 \\ -1 \\ 5 \\ 5$	$ \frac{4}{4} 1 2 3 $	-1 -3 -2	$-\frac{3}{3}$ -1 -1	4 1 2 3	2. 949 2. 947 2. 929 2. 928	2.943	30
$-2 \\ -1 \\ 1 \\ 2 \\ -3$	$ \begin{array}{r} -4 \\ -3 \\ -4 \\ -1 \end{array} $	46525	$ \begin{array}{c} 3 \\ 2 \\ 1 \\ 1 \\ 2 \end{array} $	$-2 \\ -1 \\ 1 \\ -3 \\ -3 \\ -2 \\ -3 \\ -3 \\ -2 \\ -3 \\ -3$		2. 883 2. 883 2. 881 2. 881 2. 880 2. 764	2.898	30
3	-1	2	$-1 \\ -3 \\ 2$	31	234	2.762	2.730	20
-1^{-1}	0	7	-2	-1 -2	$\frac{4}{7}$	2.686	2.702	15
3	-1	6	2	3	6	2.564)	2.558	15
3 0	$-1 \\ 0$	3	-1	3 0	3 8	2. 361)	2.417	30
-3	$-1 \\ -1 \\ -1 \\ -1 \\ -1 \\ -1 \\ -1 \\ -1 \\$	7 4	$-\frac{2}{1}$	3 3	$\overline{7}$	2. 366 2. 364	2.357	10
-1^{1}	5 5	5 6	$-3 \\ -2$	-1^{1}	5 6	2.337	2.333	15
$-2 \\ 2 \\ 3$	-4 - 4	7 5	3 1 - 3	$-\frac{2}{2}$	7 5 4	2. 290) 2. 288∫ 2. 181)	2.288	15
$-3 \\ -3 \\ -3 \\ 3$	$3 \\ -1 \\ -1$	⁺ 7 85		$-3 \\ -3 \\ 3$	7 8 5	2. 101 2. 181 2. 179 2. 177	2. 185	15
$-\frac{1}{2}$	5	6 7	$-3 \\ -2$	$\frac{1}{-1}$	6 7	2. 151) 2. 151)	2.146	10
$-2 \\ 2 \\ 1$	-4 - 4	8 6		$-2 \\ 2 \\ 1$	8 6 5	2.109	2.108	10
$-1 \\ -3 \\ -3$	$-7 \\ -5 \\ -1$	5 6 9	$\begin{array}{c} 4\\4\\2\end{array}$	$-1 \\ -3 \\ -3$	5 6 9	2.080	2.085	10
3 1 _1	1 5	6 7 8	$-1 \\ -3 \\ -2$	3 1 1	6 7 8	1.998 1.983 1.983	1.999 ^ь	10
0	ŏ	10	-2	- 1	10	1.933	1.933	40
$^{-1}_{1}$	-7 -7	7 6	$\frac{4}{3}$	$^{-1}_{1}$	7 6	1.865 1.864	1.863	15

TABLE 2. X-ray powder data of katayamalite.

(continued to be next page)

C la	ttice o	ell	P la	ttice o	cell	d(1-) Å	1() Å	T
h	k	l	h	k	l	a (caic.) A	a (meas.) A	1
-1	-9	1	5	-1	1	1.846)		
-1	9	0	-4	$^{-1}$	0	1.845		
. 1	9	0	-5	1	0	1.842		
-4	-6	2	5	-4	2	1.842		
-1	9	1	-4	-1	1	1.841		
-4	6	2	[-4	z	1.840	1 0 (1	05
-5	-3	3	4	-5	3	1.837	1.841	25
4	-0	3	3	-4	3	1,830		
_5		2	4		42	1,030		
	_9	2	5	-1	2	1.835		
-5^{-1}	3	3	1	-5	วั	1 835		
-4	ĕ	ĭ	-1	-4	1	1.834		
ō	4	$1\overline{0}$	$-\hat{2}$	ō	$1\overline{0}$	1.741)	1 5 10	10
-1	9	4	-4	-1	4	1.737	1.740	10
-3	3	11	0	3	11	1.638)	1 6/1	10
3	3	8	-3	3	8	1.638∫	1.041	10
4	0	11	2	-4	11	1.611	1 612	15
4	0	7	-2	4	.7	1.609)	1.012	10
2	-6	11	4	-2	11	1.532	1 500	
	0	9		2	9	1.531	1.532	15
-2	-10	5 14	6	-2	14	1, 529]	1 202	25
<u> </u>		14	ι υ	0	14	1, 300	1.302	40

TABLE	2^{-1}	(continued)
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CuKa, 35 kV, 15 mA.

Sabelli (1979). The structure consists of sheets of Si_6O_{18} rings connected by Ca-octahedral sheets and by Ti-octahedra, Li-tetrahedra and 12-fold K-polyhedra. OH and F are coordinated to only Ca. Accordingly, the structural formula of katayamalite is written as $(K_{0.85}Na_{0.10})_{0.95}Li_{3.00}(Ca_{6.94}Mn_{0.04})_{6.98}(Ti_{1.90}Fe^{+3}_{0.05})_{1.95}Si_{12.00}O_{35.78}((OH)_{1.85}F_{0.25})_{2.10}$, corresponding ideally to $(K, Na)Li_3(Ca, Mn)_7(Ti, Fe^{+3})_2$ [Si₆O₁₈]₂(OH, F)₂. The detailed description of the structure will be given in another paper (Kato and Murakami, in preparation).

Optical and physical properties

To the naked eye, katayamalite is white in color, but brilliant bluish white to the ultraviolet of short wave. Striation is white and luster is vitreous. Hardness (Mohs) is 3.5-4.0. Specific gravity measured by the suspension method using Clerici solution is 2.91 ± 0.02 , while the calculated value is 2.899.

In thin section, katayamalite occurs as single crystals, twinned or granular aggregates, individual grain being $0.01-0.2 \times 0.1-0.5$ mm in size. They have a tabular form with perfect (001) cleavage, gently bent in part. Parallel twinning with composition plane (001) is common. It is colorless and clear without alteration product and dusty inclusion. Fine granular inclusions such as aegirine, pectolite, wollastonite and albite are often scattered in the core as well as in

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marginal parts. Rarely weak zonation is recognized around the albite inclusions. Dispersion is strong r > v. Strong absorption and weak double refraction are also characteristic. $\alpha = 1.270$, $\beta = 1.671$, $\gamma = 1.677$, $\gamma - \alpha = 0.007$, $2V(+) = about 32^{\circ}$, and b is near Y. Z is about 36° from the normal to (001).

Comparison of katayamalite with baratovite

As described above, katayamalite reveals a resemblance to baratovite (Dusmatov *et al.*, 1975) in structural properties, although the crystal system is different. Besides, they have a close affinity also in physical and optical properties such as density and refractive indices. Lately, we detected in baratovite the phosphorescence similar to katayamalite. In chemistry too, there are several similarities despite the following differences. The difference in chemical composition between them is that katayamalite is OH dominant and contains no Zr, while baratovite is F dominant and contains Zr replacing Ti. However, there is a quite essential divergency in crystal system and accordingly unit cell parameters between them. The dominant properties of two minerals are compared in Table 3.

	Katayamalite	Baratovite
Crystal system	Triclinic	Monoclinic
Space group	<i>C</i> 1	C2/c
Ζ	4	4
Unit cell dimensions	$\begin{array}{c} -a = & 9.721 \text{\AA} \\ b = & 16.923 \\ c = & 19.942 \\ \alpha = & 91.43^{\circ} \\ \beta = & 104.15 \\ -\gamma = & 89.94 \end{array}$	$ \begin{array}{c} -a = 16.941 \text{\AA} \\ b = 9.746 \\ c = 20.907 \\ -\beta = 112.50^{\circ} \end{array} $
D_{m}	2.91 g/cm ³	2. 92 g/cm ³
$D_{\mathbf{x}}$	2.899 g/cm ³	2. 912 g/cm ³
Chemical formula	$(K, Na) Li_{3} (Ca, Mn) {}_{7} (Ti, Fe^{+3}) {}_{2} [Si_{6}O_{18}]_{2} (OH, F) {}_{2}$	$\begin{array}{c} \operatorname{KLi}_{3}\operatorname{Ca}_{7}(\operatorname{Ti},\operatorname{Zr})_{2}\\ [\operatorname{Si}_{6}\operatorname{O}_{18}]_{2}\operatorname{F}_{2}\end{array}$
Optical properties	$ \begin{array}{c c} -\alpha = 1.670 \\ \beta = 1.671 \\ \gamma = 1.677 \\ \gamma - \alpha = 0.007 \\ -2V(+) = 32^{\circ} \end{array} $	$\beta = 1.672$ $\gamma = 1.673$ $-2V(+) = 60^{\circ}$
X-ray powder data	$\begin{array}{c} 3.\ 23\ (100)\ (006\cdot 0\overline{4}4)\ ,1.\ 934\ (40)\\ (0.\ 0.\ 10)\ ,\ 2.\ 943\ (30)\ (\overline{3}\overline{1}4\\ \cdot 3\overline{1}1)\ ,\ 2.\ 898\ (30)\ \overline{2}\overline{4}4\cdot\overline{1}\overline{3}6)\ ,\\ 2.\ 419\ (30)\ (008)\end{array}$	3. 22 (100) (006) , 2. 41 (20) (008) 1. 92 (17) (0. 0. 10)

TABLE 3. Comparison of katayamalite with baratovite.

In occurrence also, katayamalite resembles the baratovite. According to Dusmatov *et al.* (1975), baratovite occurs in quartz-albite-aegirine pegmatitic veinlet

and albitite associated with quartz-aegirine syenite, and katayamalite is found in albite-pectolite-aegirine syenite.

Name and type specimen

The name katayamalite is given for Emeritus Professor Nobuo Katayama, an eminent mineralogist of Japan.

The type specimen will be deposited at Yamaguchi University, National Science Museum, Tokyo and Sakurai Museum, Tokyo.

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