# The Occurrence of Calcian Tirodite in the Granite Pegmatite of Kamiotomo, Iwate Prefecture, Japan

By

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Abstract A clinoamphibole from the granite pegmatite of Kamiotomo, Iwaizumimachi, Iwate Prefecture, is found to be a calcian tirodite,  $(Mn_{1.59}Ca_{0.54}Mg_{3.02}Fe_{1.83}Al_{0.10})_{\Sigma_{7.08}}(Si_{7.74}Al_{0.28})_{\Sigma_{8.00}}O_{23}$  on the basis of O=23. This is a rare example of the occurrence of such a high magnesium ferromagnesian mineral in a granite pegmatite. The associated minerals include pyroxmangite  $((Mn_{0.02}Fe_{0.22}Mg_{0.12}Ca_{0.05})_{\Sigma_{1.01}}Si_{0.09}O_3)$ . The assemblage of tirodite and pyroxmangite both compositionally close to above case is also found in a contact metamorphosed manganese ore from Zomeki deposit of the Kusugi mine, Yamaguchi Prefecture. The 2/7 boundary for (Mn+Ca) contents of these Mg-Fe-Mn clinoamphiboles is extant despite the co-existence with pyroxmangite. One of the materials on 2.5/7 boundary of Nambu et al. (1980) occurs as veinlets cutting a wallrock of manganese ore, i.e., in the different mode of occurrence from the present case.

#### Introduction

During the course of mineralogical studies on manganese silicates from granite pegmatites and metamorphosed manganese ore deposits in Japan, a brownish yellow-green fibrous manganese silicates from the granite pegmatite of Kamiotomo, Iwaizumi-machi, Iwate Prefecture, is found to be calcian tirodite with minor pyroxmangite. This is a rare example of the occurrence of such a high magnesium ferromagnesian mineral in an ordinary granite pegmatite, where magnesium contents of ferromagnesian minerals are generally low.

Also, the studies demonstrate the occurrence of tirodite-pyroxmangite assemblage both compositionally very close to above two, respectively, in a contact metamorphosed manganese ore from Zomeki deposit of the Kusugi mine, Yamaguchi Prefecture.

In both tirodites so-called 2/7 boundary of the manganese (precisely manganese plus calcium) content of octahedral cations in Mg-Fe-Mn clinoamphiboles (KLEIN, 1964) is extant, despite the co-existence with pyroxmangites of higher (Mn+Ca)/(Mn+Mg+Fe+Ca) ratios than the associated tirodites. The alternative 2.5/7 boundary of NAMBU *et al.* (1980) is seen in dannemorite from the Moichi mine, Iwate Prefecture, where it occurs as veinlets cutting wallrocks of manganese ore, suggesting that this boundary is for the materials formed under a hydrothermal condition.

### Occurrence and Description of the Studied Material

The granite pegmatite of Kamiotomo, Iwaizumi-machi, Shimohei-gun, Iwate Prefecture, is located about 7 kilometers east of Iwaizumi Station, Iwaizumi Line, Japan National Railway, and was formed for quartz and feldspar down to the middle of 1950's. It is a lenticular body standing with a steep angle in a granodiorite mass, and elongated along N-S direction to more than 20 meters long and flattened to E-W direction less than 5 meters thick (OMORI and HASEGAWA, 1955). At present no trace of pegmatite is left except for a small dump scattered in a granitic debris.

The mineral was firstly noted by NAGASHIMA and NAGASHIMA (1960), who found it as coarse-grained aggregate with pyroxmangite, spessartine and quartz along the southern margin of pegmatite. The studied material was collected by A. K. in 1954 and regarded to be identical with the above reported one by them. It is a small piece of aggregate of greyish yellow-green blady prisms to fibers of tirodite of more than 20 millimeters long and partially coated by a chocolate brown manganese dioxide which is amorphous to X-ray. The mineral is embedded in quartz accompanied by minute grains of pyroxmangite and magnetite.

Under the microscope, the prisms form subparallel aggregates in coarse-grained quartz and small grains of pyroxmangite and magnetite occur in direct contact with tirodite (Fig. 1). It is colourless in thin section. Between crossed polars a lamellar twinning with a twinning plane  $\{100\}$  is very common. The maximum extinction angle is about  $18^{\circ}$  for Z'. The refractive indices measured by the immersion method are:  $\alpha=1.652(2), \ \beta=1.664(2), \ \gamma=1.676(2)$ . Observed 2V is nearly 90°, which is essentially equal to the calculated value,  $(-)2V=88.54^{\circ}$ . Dispersion is indiscernible. Besides above stated minerals, very minute colourless flakes of chlorite are found as interstitial aggregates to tirodite prisms. Some of prisms are partially coated by orange brown clayey material.

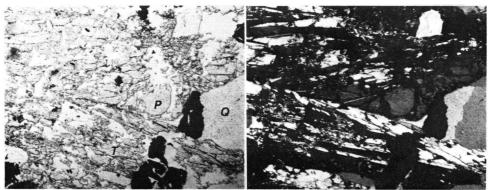


Fig. 1. Photomicrographs of calcian tirodite(T) in association with pyroxmangite (P), quartz (Q) and magnetite (opaque). Field view: approximately 1.9×1.5 mm. Left: one polar. Right: crossed polars.

Table 1. X-ray powder diffraction patterns of calcian tirodite and manganoan cummingtonite.

20   9.09   9.09   0.09   0.00   80b   9.034   0.00   0.00   8.296   110   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.			1.			2.				1.			2.	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$							hkl	I	d(obs.)	d(calc.)	hkl	I	d(obs.)	hkl
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	20			020	80Ь	9.034	020					30	1.6768	551
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	100	8.32	8.32	110	90vb	8.296	110	2	1.672	1.671	391			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					vf	5.179	001	15	1.658	1.660	550	60	1.6494	461
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	5.10	5.08	130	20Ь	5.040	130			1.656	461			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	4.84	4.84	111	20	4.834	111	15	1.627	1.628	$48\overline{1}$	40	1.6189	1.11.0
30 4.16	5	4.71	4.68	200						1.627	1.11.0			
Vf	12	4.54	4.54	040	50	4.516	040	2	1.595	1.594	601	30	1.5877	531
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	30	4.16	4.16	220	40	4.150	220	1	1.579	1.580	133			
vf 3,602 221 10 1,5139 570   40 3,437 3,432 131 60b 3,426 131 60b 3,251 240 1 1,504 1,504 641 1 1,508 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,5068 0,12,0 40 1,508 392 1 4885 481,6 133 1,508 392 1 4885 481,6 1 4 1,502 551 1 4 1,484 372 1 4 1,484 372 1 4 1,4541 3,11,0 30 1,4541 3,11,0 30 1,4541 3,11,0 30 1,4541					vf	4.054	111	9	1.561	1.561	600	25	1.5566	600
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	3.877	3.866	$13\bar{1}$	35	3.856	131					v f	1.5311	620
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					vf	3.602	221					10	1.5139	570
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	5	3.437	3.432	131	60b	3.426	131	6	1.514	1.514	0.12.0	40	1.5068	0.12.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40	3.262	3.260	240	806	3.251	240	1	1.504	1.504	641			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	100	3.081	3.077	310	100Ь	3.071	310			1.503	392			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	2.984	2.976	221	30	2.968	221			1.502	551			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					15	2.932	151					30	1.4885	481,602
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			2.774	330	40	2.766	330	3	1.484	1.484	372			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12	2.739	2.739	151	70	2.726	151	5	1.460	1.460	3.11.0	30	1.4541	3.11.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2.673	331	20	2.661	331					10	1.4277	4.10.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9	2.618	2.614	061	50	2.6027	061	15	1.410	1.411	$66\bar{1}$	75	1.4063	$66\overline{1}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10	2.536	2.542	260	50	2.5111	$20\bar{2}$	5	1.381	1.382	1.13.0			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	2.425			5	2.4205	311,222					30		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$												vf	1.3495	1.11.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				350	20	2.3575	350	5	1.335	1.336	662	20	1.3333	662
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6	2.306			40	2.2959	171			1.336	$73\bar{1}$			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$										1.334	710			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	2.262	2.261	421						1.344	4.10.2			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$												v f		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	2.205			20	2.1925	$24\bar{2}$	3	1.297	1.298	0.14.0	35	1.2921	0.14.0,
$\begin{array}{cccccccccccccccccccccccccccccccccccc$											353			2.12.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$								2	1.281			25	1.2789	751
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						100								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$								2	1.271			10	1.2671	4.12.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	2.083			20	2.0799	202							
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$										1.270	4.12.1			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	_	0 0				221 0000000000								
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	7	2.033			30	2.0255	351							
4 1.979 1.978 401 $\underline{c} = 5.315$ $\underline{d} = 102.63^\circ$ 4 1.864 1.863 510 50 1.8600 510 1.853 1.855 17 $\underline{c} = 1.852$ 460	0	1 00			0.0									
30 1.9606 $40\bar{2}$ , $28\bar{1}$ $\beta = 102.63^{\circ}$ $\beta = 102.63^{\circ}$ $\beta = 102.63^{\circ}$ 1.853 1.855 17 $\bar{2}$ 1.852 460					20	1.9850	370		-				_	
4 1.864 1.863 510 50 1.8600 510 1 1.853 1.855 172 1.852 460	4	1.979	1.978	401			_						_	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$									$\beta = 102.$	63°			$\beta = 1$	02.63°
1.852 460					50	1.8600	510							
	1	1.853												
10bb 1,8023 312,0,10,0			1.852	460	40		040 -							
					10bb	1.8023	312,0.1	0.0						

<sup>1.</sup> Calcian tirodite. Kamiotomo, Iwaizumi-machi, Iwate Prefecture, Japan. Diffractometer method. Cu/Ni radiation.

<sup>2.</sup> Manganoan cummingtonite. Wabash Iron Formation, Labrador, Newfoundland, Canada. Powder camera method. Fe/Mn radiation. After Klein (1964). b=broad. f=faint. v=very.

# X-Ray Powder Study

X-ray powder diffraction pattern was obtained using Cu/Ni radiation by the diffractometer method as given in Table 1, where it is compared with that of manganoan cummingtonite from Newfoundland (KLEIN, 1964). From the indexing after the reference to the indices of compared pattern, the unit cell parameters are calculated as: a=9.598, b=18.168, c=5.315Å,  $\beta=102.63$ °.

## **Chemical Composition**

The chemical composition of tirodite is determined by Link Energy Dispersion system, together with that of the associated pyroxmangite as given in Table 2. The empirical formula of tirodite calculated on the basis of O=23 has a slight excess of cations, which may be due to the presence of ferric iron. If the analysis is corrected in terms of this interpretation and of addition of H<sub>2</sub>O provided that all the non-silicate anions are occupied by (OH) only, it requires Fe<sub>2</sub>O<sub>3</sub> 2.12, FeO 12.57, H<sub>2</sub>O 1.98, total 99.06%. Since the calcium content in the empirical formula exceeds 0.50, the material is termed as calcian tirodite (HAWTHORNE, 1983). The chemical composition of the associated pyroxmangite has slightly higher content of manganese and lower one of iron than those of pyroxmangite from the same pegmatite (OMORI and HASEGAWA, 1955). The co-existence of calcian tirodite and pyroxmangite suggests that them anganese content in the former reaches the upper limit of diadochic capacity under the condition of pegmatite formation. Along with the calcium content, all the known calcian tirodites in Japan are in association with calcic amphiboles, *i.e.*, the materials from Wakasugi, Osaka Prefecture (CaO 4.40% in weight) (AIKAWA *et al.*, 1978), the

		1.	2.			
	wt. %	number of atoms (O=23)	wt. %	number of atoms (O=3)		
SiO <sub>2</sub>	51.24	7.74	45.42	0.99		
$Al_2O_3$	2.02	0.36	0.00			
FeO*	14.50	1.83	11.86	0.22		
MgO	13.40	3.02	3.69	0.12		
MnO	12.39	1.59	33.29	0.62		
CaO	3.34	0.54	2.33	0.55		
Total	96.89		99.92			

Table 2. Chemical analyses of calcian tirodite and pyroxmangite from Kamiotomo, Iwate Prefecture.

<sup>(\*</sup> total Fe)

<sup>1.</sup> Calcian tirodite. Empirical formula:  $(Mn_{1.59}Ca_{0.54}Mg_{3.02}Fe_{1.83}Al_{0.10})_{\Sigma_{7.08}}(Si_{7.74}Al_{0.28})_{\Sigma_{8.00}}O_{23}$ .

<sup>2.</sup> Pyroxmangite. Empirical formula:  $(Mn_{0.02}Fe_{0.22}Mg_{0.12}Ca_{0.05})_{\Sigma_{1.01}}Si_{0.09}O_3$ .

		1.	2.			
	wt. %	number of atoms (O=23)	wt. %	number of atoms (O=3)		
$SiO_2$	51.26	7.89	46.48	0.99		
$Al_2O_3$	0.10	0.02	0.00			
FeO*	16.86	2.17	13.99	0.25		
MgO	12.71	2.92	3.44	0.11		
MnO	12.54	1.63	33.76	0.61		
CaO	2.86	0.47	2.68	0.06		
Total	96.33		100.35			

Table 3. Chemical analyses of tirodite and pyroxmangite from Zomeki deposit of the Kusugi mine, Yamaguchi Prefecture.

- 1. Tirodite. Empirical formula:  $(Mn_{1.63}Ca_{0.47}Mg_{2.92}Fe_{2.08})_{\Sigma 7.10}(Si_{7.89}Fe_{0.09}Al_{0.02})_{\Sigma 8.00}O_{23}$ .
- 2. Pyroxmangite. Empirical formula:  $(Mn_{0.61}Fe_{0.25}Mg_{0.11}Ca_{0.06})_{\Sigma_{1.03}}Si_{0.99}O_3$ .

Shimozuru mine, Miyazaki Prefecture (CaO 5.31% in weight) and the Osotari mine, Miyazaki Prefecture (CaO 6.29% in weight) (ISHIDA, 1985).

Also, the authors' chemical survey of tirodite disclosed the occurrence of pyrox-mangite-tirodite assemblage both compositionally very close to the described materials in an ore from Zomeki deposit of the Kusugi mine, Yamaguchi Prefecture. The manganese ore deposit of the mine is of contact metamorphosed bedded type and the material was collected by S.M. from the dump. It is a massive grey ore composed of visible light cream grey tirodite fibers of millimeter order, grey yellow spessartine grains of 0.n millimeter order with minor pyroxmangite of light pinkish grey colour. In Table 3 their chemical compositions are demonstrated with their empirical formulae to indicate the compositional proximity to above materials, respectively, despite the entirely different mode of occurrence. The latter tirodite has a slightly lower calcium content than the former, but both of them keep the 2/7 boundary (KLEIN, 1964).

In 1980, Nambu et al. advocated an alternative 2.5/7 boundary from the occurrence of some high manganese Mg-Fe-Mn clinoamphiboles. Among the materials employed for the presentation of this boundary, dannemorite from the Moichi mine, Iwate Prefecture (Nambu et al., 1974) is best described, and this is also observed by one of the present authors (A.K.). Obviously it forms fracture-filling veinlet in chert forming the footwall of manganese ores, and the X-ray powder diffraction peaks are all weak with broader profile as compared with those of ordinary Mg-Fe-Mn clinoamphiboles, as expected from the asbestiform feature. Nambu et al. (1974) consider this mineral to be the product under a hydrothermal condition. A part of 2.5/7 boundary keepers would be occupied by products under such a condition as distinct from those currently described.

<sup>(\*</sup> total Fe)

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