Mafic phyllosilicates in low-grade metavolcanic rocks from southern Tanzawa Mountains, central Japan

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The metavolcanics of the Miocene Tanzawa Group of the southern Tanzawa Mountains can clearly be divided into six mineral zones; stilbite, laumontite, prehnite-pumpellyite, epidote, epidote-amphibole and amphibole zones. Four phases of mafic phyllosilicates in the five lower grade zones are identified by systematic X-ray diffraction studies; (1) smectite in the stilbite and laumontite zones, (2) randomly mixed-layer chlorite/smectite mineral which is ubiquitous in the stilbite, laumontite and prehnite-pumpellyite zones, (3) regularly mixed-layer chlorite/smectite in the stilbite zone, (4) chlorite occurs first in the laumontite zone. With increasing metamorphic grade, smectite layers progressively transform to chlorite. Chlorite is the predominant phyllosilicate in the prehnite-pumpellyite zone and is a unique phyllosilicate in the epidote and epidote-amphibole zones.

Variations in $\text{Fe}/(\text{Fe}+\text{Mg})$ of chlorite are positively correlated with $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios of whole-rocks, but the other chemical variations are clearly unrelated to whole-rock compositions. The content of Si decreases with increasing metamorphic grade.

Keywords: Mixed-layer Chlorite/smectite, Chlorite, Low-grade metamorphism, Tanzawa Group

I. Introduction

Metamorphic mineral paragenesis in the Tanzawa Group have been studied by Seki *et al.* (1969), Shimazu *et al.* (1971) and Arai (1987). The correlation between the characterization of phyllosilicates and metamorphic grade, however, has not been revealed in detail.

Phyllosilicates such as smectite, mixed-layer chlorite/smectite, and chlorite concurrently occur with calc-silicate mineral transition from the zeolite throughout prehnite-pumpellyite to greenschist facies. Regularly and randomly mixed-layer chlorite/smectite minerals occur as intermediate products of smectite and chlorite. Mixed-layer mafic

phyllosilicates are particularly interesting because the nature of the interlayering appears to be temperature-sensitive. Therefore, these phases may be useful index minerals to show the grade of low-temperature metamorphic mafic volcanic rocks. In this study we document the mafic phyllosilicate mineralogy from the Tanzawa Group. Detailed X-ray diffraction and electron-microprobe analyses of mafic phyllosilicates and X-ray fluorescence analysis of whole-rock chemical composition have been done in order to make clear the systematic changes in physical and chemical properties of phyllosilicates due to low-grade metamorphism of volcanic rocks. In this study, it will be shown that (1) chemical com-

position and crystal structure of mafic phyllosilicates systematically vary with increasing metamorphic grade and (2) the observed phyllosilicate zonation correlates well with calc-silicate mineral zonation.

II. Geological setting

As shown in Fig. 1, the southern Tanzawa Mountain consists of three geologic units; the early-middle Miocene Tanzawa Group, the late Miocene-early Pliocene Ashigara Group, and the middle Miocene quartz diorite mass intruding into the Tanzawa Group. The Tanzawa Group is composed of andesitic-basaltic volcanic rocks with a total thickness of nearly

10,000 m. The Ashigara Group, separated from the Tanzawa Group by the Kannawa fault, consists of conglomerate, sandstone and mudstone with a small amount of lava and pyroclastic materials of andesite and dacite. The Tanzawa Group has been metamorphosed from the zeolite to amphibole facies which were produced by the intrusion of quartz diorite mass.

III. Analytical methods

The distribution and textural variation of secondary minerals are determined by over 300 thin sections from the Tanzawa Group. Thirty nine Samples were chosen for detail

Fig. 1. Generalized geologic map of the southern part of the Tanzawa Mountains, showing the location of studied samples.

study. Whole-rock chemical analyses of 23 samples were done by the X-ray fluorescence method. Mineral compositions of chlorite were analyzed with a JXA-8600SX/MX electron microprobe using a spot size of $1\text{ }\mu\text{m}$, a beam current of 13 nA and accelerating potential of 15 kv. The clay fraction ($<2\text{ }\mu\text{m}$) was smeared on a glass slide to give an oriented film for X-ray diffraction (XRD). XRD analysis was carried out on air-dried natural, ethylene-glycol-solvated (EG-solvated), K-saturated and heated at 300° , 450° , and 500°C for 1 h prior to the analysis (not showing data on 300° and 450°C). Random powder XRD analysis was also done to identify chlorite polytype.

IV. Petrography

Based on the presence or absence of calc-silicates, we delineated metamorphic zones; stilbite (Stb), laumontite (Lmt), prehnite-pumpellyite (Prh-Pmp), epidote (Ep) and epidote-amphibole (Ep-Am) zones.

Primary minerals, including plagioclase, clinopyroxene and Fe-Ti oxides, are fairly well preserved.

The occurrences of secondary phases are described as follows.

1. Stb zone

The Stb zone commonly contains smectite, smectite-rich randomly mixed-layer chlorite/smectite (C/S), regularly mixed-layer C/S and stilbite. Analcime rarely occurs in vesicle and as replacement of plagioclase. Celadonite, which is recognized by its distinctive apple-green color, replaces the matrix and clinopyroxene crystals, and occurs also as a vesicle-filling phase. Other secondary phases are albite, K-feldspar, calcite and quartz in the Stb zone. Some of analcime and celadonite are crosscut by stilbite and/or calcite veins. Stilbite is also intergrown with calcite in some samples.

2. Lmt zone

The phyllosilicates of the Lmt zone are randomly mixed-layer C/S, regularly mixed-layer C/S, chlorite and subordinate amounts of smectite. The phyllosilicates in the Lmt zone are common as replacements of matrix and primary minerals. They also occur as constituents of amygdaloidal assemblages. Vesicles are lined or completely filled by chlorite and/or C/S. Clay minerals grade from fine-grained into more coarsely crystalline. Some of them show platy forms radiating outward from vesicle walls.

Calc-silicate and other metamorphic phases are laumontite, prehnite, pumpellyite, albite, K-feldspar, quartz, hematite, and rarely epidote, calcite and sulfide. Laumontite occurs in vein, vesicle and also as the replacement of plagioclase. Prehnite and pumpellyite occur as a reaction rim of laumontite and replacements of matrix and phenocryst. Epidote, prehnite and pumpellyite are intergrown with laumontite in some samples. Common stable mineral assemblages in the Lmt zone are laumontite + prehnite + pumpellyite + chlorite + C/S, laumontite + pumpellyite + epidote + chlorite + C/S, and pumpellyite + chlorite + C/S.

3. Prh-Pmp zone

Phyllosilicates are composed mostly of chlorites with subordinate amount of randomly mixed-layer C/S in the Prh-Pmp zone. They occur as the replacement products of matrix and phenocryst and vesicle-filling. Epidote, prehnite, pumpellyite and quartz also commonly exist as metamorphic phases. Grandite garnet rarely occurs in matrix and phenocryst (samples of 94112, 9436, 9437, 9439 and 94310). The mineral assemblages of the Prh-Pmp zone are dominated by prehnite + epidote, pumpellyite + epidote, and epidote + prehnite + pumpellyite with excess chlorite (or C/S) + titanite + hematite + quartz + albite.

4. Ep and Ep-Am zones

Chlorite is only one clay mineral occurring in the Ep and Ep-Am zones. The Ep zone is characterized by the assemblage of epidote+chlorite+quartz. In the Ep-Am zone, common assemblages are amphibole+epidote+chlorite+quartz, and amphibole+chlorite+quartz, with excess plagioclase, Fe-oxide, and rarely titanite. Amphibole needles are commonly intergrown with chlorite and epidote except in only one sample (95211) in which amphibole

needles occur around epidote+chlorite.

V. X-ray analysis

1. Clay mineral phases

Four types of phyllosilicates were identified on the basis of systematic XRD study; discrete smectite, discrete chlorite, C/S (random), and corrensite (1:1 regular C/S). Diagnostic XRD data for these phases are presented in Table 1. Peak positions presented in Table 1 represent centroids measured at 1/2 to 2/3 maximum

Table 1. XRD data on $<2\ \mu\text{m}$

Sample Metamorphic zone		d ₀₀ (Å)							Phases identified		
		Air-dred		KCl			500°C				
2102	Prh-Pmp	14.0	7.0	ND						C/S,	Chl
2004	Lmt	14.5	14.0	7.1	14.0	12.4	7.1	14.0		C/S,	Chl
2002	Lmt	14.2	7.1	14.0		7.1		14.2		C/S,	Chl
1513	Lmt	14.6		ND				ND		C/S,	Chl
1507	Lmt	14.6	7.0	ND				ND		C/S,	Chl
1502	Stb	15.8	6.9		12.4	7.1			9.5	S	
1501	Stb	15.8	7.1	ND				ND		S,	C/S
9436	Prh-Pmp	14.8		7.0	ND			ND		C/S,	Chl
9415	Prh-Pmp		14.0	7.1	ND			ND			Chl
3016	Lmt	14.2	7.1	14.2		7.1		14.0			Chl
3102	Stb	29.4	14.2	7.1	14.0		7.1	13.8		C/S,	Co
3517	Lmt	14.2	7.1	ND				ND		C/S,	Chl
3513	Lmt	14.6	6.6	ND				ND		C/S,	Chl
3502	Stb	26.8	14.2	6.9	ND			ND		C/S,	Co, Chl
1804	Lmt	27.8	14.2	6.9	ND			ND		C/S,	Co, Chl
2301	Stb	28.5	14.2	7.1	14.0	12.6	7.1	14.0	8.6		Co, Chl
2202	Stb	28.4	14.5	7.1	13.4		7.0	13.8	9.7	S,	Co
1012	Stb	29.4	14.2	7.2	13.4		7.0	13.8	10.0	S,	Co
2506	Stb	28.5	15.0	7.1	14.0	12.8	7.1	14.0	9.9	S,	Co
d ₀₀ (Å)											
%chlorite											
Ethylene glycol											
2102	Prh-Pmp	14.6	14.0			7.36	7.1	3.50		70-80	
2004	Lmt	14.5	14.0			7.60	7.1	3.45		50-60	
2002	Lmt	14.5	14.0			7.60	7.1	3.55		50-60	
1513	Lmt	15.0	14.0			7.36		3.46		50-80	
1507	Lmt	14.7	14.2			7.82		3.45		40-50	
1502	Stb	17.0		8.40				3.41			
1501	Stb	16.5				7.96		3.43		40-50	
9436	Prh-Pmp	14.5	14.0			7.30		3.45		60-80	
9415	Prh-Pmp		14.0				7.1	3.55		100	
3016	Lmt	14.2					7.1	3.54		100	
3102	Stb	29.4	15.0			7.36		3.48		60-70	
3517	Lmt		14.2			7.89		3.46		40-60	
3513	Lmt	16.7	14.7	14.0		7.75		3.43		40-60	
3502	Stb	29.8	15.8	14.0	8.43	7.85		3.46		40-50	
1804	Lmt	28.9	14.6	14.0		7.55		3.43		40-60	
2301	Stb	29.4	16.0	14.9	14.0	7.68	7.1	3.49		50-70	
2202	Stb	29.4	16.4	15.2		8.38	7.55	7.1	3.44	50-70	
1012	Stb	31.5	16.2	15.2		7.60	7.2	3.45		50-60	
2506	Stb	29.4	16.1	14.5		8.41	7.68	7.1	3.47	50-60	

ND, not determined; Chl, chlorite; C/S, chlorite/smectite (irregular); Co, corrensite; S, smectite.

peak height. According to the measurements of the positions of 002/002 and 004/005 in chlorite/EG-saturated smectite (Reynolds, 1988), the chlorite layer percentage is estimated (Table 1 and Fig. 3).

Smectite; smectites have d_{001} of approximately 15 Å at air-dried state. They expand to about 17 Å with EG-treatment. They also collapse to 12.4–12.8 Å after treatment with KCl, and collapse to 8.6–10.0 Å by heating at 500°C for 1 h (Fig. 2d).

Chlorite; chlorites have d_{001} of approxi-

mately 14.2 Å that show little variation with KCl treatment or heating (Fig. 2a). Chlorite first appears when chlorite layer percentage in C/S is more than 40%.

Corrensite; corrensite (1 : 1 regular C/S) is unambiguously recognized by its 001 superlattice reflections of 26–29 Å (air-dried) and 29–32 Å (EG-solvated) (Fig. 2b). Corrensite occurs only in the Stb and Lmt zones.

C/S (random); the random mixed-layer chlorite/smectite mineral occurs ubiquitously in the Stb and Lmt zones, and persists in the

Fig. 2. X-ray diffraction patterns of clay fraction of some samples from the Tanzawa group (A.D., air-dried; EG, ethylene glycol treatment; KCl, K-saturated treatment; 500°C, heated at 500°C for an hour).

Prh-Pmp zone. As shown in Fig. 2b and 2c, the random interstratification is recognized by broad peak, non-integral spacings of 001 reflections and the systematic response of d_{001} to the following treatments; air-dried=14.3–14.9 Å, KCl=12.4–13.4 Å, EG-solvated=14.5–15.8 Å. Chlorite percentage in C/S is <70%, >40%, >60% in the Stb, Lmt and Prh-Pmp zones respectively. The value of $\Delta 2\theta$ (2θ (004/005)– 2θ (002/002) of chlorite/EG-saturated smectite is decreasing with increase of chlorite percentage in C/S. As shown in Fig. 3 and Table 1, although there is a considerable overlap, smectite transforms to chlorite from Chl 0% ($\Delta 2\theta > 15.7^\circ$) throughout Chl 50–60% ($\Delta 2\theta = 14.0^\circ$ –

14.6°) and Chl 70–80% ($\Delta 2\theta = 13.2^\circ$ – 13.7°) to Chl >90% ($\Delta 2\theta < 12.8^\circ$). The result indicates that the proportion of smectite layers in C/S decreases discontinuously with increasing metamorphic grade.

2. Polytypes of chlorite

Polytypes were identified by diagnostic h0l reflections on random powder patterns (Hayes, 1970) (Fig. 4).

Ib ($\beta = 97^\circ$) type of chlorite can be identified in only two samples of the Lmt zone in which I Ib ($\beta = 97^\circ$) type chlorite is not rare. Chlorite in the Prh-Pmp, Ep and Ep-Am zones are always of I Ib type.

VI. Whole-rock chemical analysis

LOI (loss on ignition) values for the sample studied decrease with increasing metamorphic grade, and their ranges are 5.75–6.80%, 1.21–5.50%, 3.26–4.89% and 2.79–3.61% in the Lmt,

Fig. 3. Changes of $\Delta 2\theta$ in chlorite/ethylene glycol smectite with increasing metamorphic grade.

Fig. 4. Random powder XRD patterns of the <2 μ m fraction of some samples indicating that the chlorite are the Ib and I Ib polytype.

Table 2. Chemical analyses of volcanic rocks from the Tanzawa Group

Sample no.	952011	94730	94728	94724	94723	94312	94311	94310	9439	9438	9437	9433
SiO ₂	48.06	50.75	51.31	50.12	58.14	51.37	49.20	52.66	51.31	52.61	62.05	51.53
TiO ₂	0.29	0.28	0.64	0.71	1.09	0.65	1.10	0.63	0.73	0.65	0.64	0.71
Al ₂ O ₃	7.75	7.21	14.83	15.51	14.47	16.75	17.98	16.03	18.84	15.62	15.30	14.11
Fe ₂ O ₃	10.07	9.34	11.84	9.43	9.80	9.57	10.79	9.80	9.41	9.83	7.09	9.28
MnO	0.16	0.16	0.21	0.15	0.15	0.15	0.15	0.10	0.14	0.16	0.09	0.21
MgO	19.22	17.55	8.57	8.49	4.70	6.96	5.66	7.26	5.87	6.43	2.55	8.34
CaO	10.89	11.84	8.23	8.09	8.49	8.70	8.71	8.99	9.83	9.52	8.76	8.66
Na ₂ O	0.00	0.00	1.10	1.78	0.92	2.70	3.15	1.22	1.96	2.59	2.34	3.75
K ₂ O	0.02	0.03	0.61	1.03	0.00	0.23	1.28	0.31	0.42	0.28	0.64	0.35
P ₂ O ₅	0.03	0.03	0.06	0.10	0.15	0.07	0.16	0.06	0.14	0.09	0.24	0.24
LOI	3.25	2.79	3.61	4.89	3.26	3.42	1.96	3.60	2.93	3.35	1.21	3.05
Total	99.75	99.98	101.01	100.29	101.17	100.59	100.13	100.65	101.56	101.14	100.92	100.23
Fe/(Fe+Mg)	0.21	0.21	0.41	0.36	0.51	0.41	0.49	0.41	0.45	0.44	0.58	0.36

Sample no.	94112	94110	9417	9415	9413	9411	2113	2108	2102	1513	3513
SiO ₂	54.86	53.91	50.05	45.05	50.81	49.96	49.94	51.87	51.34	47.39	54.84
TiO ₂	0.64	0.65	0.92	0.77	0.92	0.70	1.06	1.11	1.01	0.81	0.90
Al ₂ O ₃	16.72	17.13	17.13	18.23	17.35	16.65	18.38	14.03	14.11	16.08	14.01
Fe ₂ O ₃	8.96	9.01	9.56	10.34	9.56	9.56	9.88	12.77	12.97	9.21	11.20
MnO	0.11	0.12	0.14	0.14	0.16	0.22	0.18	0.19	0.19	0.13	0.17
MgO	6.06	5.14	7.66	8.30	5.53	4.88	6.14	4.94	5.13	7.88	4.53
CaO	7.96	9.78	7.26	8.72	6.56	10.22	4.72	7.48	8.19	9.71	5.89
Na ₂ O	1.98	2.51	3.24	1.29	4.37	4.17	4.94	2.32	1.82	1.72	2.81
K ₂ O	0.06	0.13	0.92	1.96	1.12	0.40	0.86	0.30	0.42	0.61	0.04
P ₂ O ₅	0.15	0.12	0.12	0.10	0.14	0.11	0.28	0.09	0.09	0.13	0.09
LOI	3.10	2.39	5.50	4.93	3.88	3.44	4.22	4.78	5.11	6.80	5.72
Total	100.59	100.89	102.49	99.84	100.40	100.30	100.61	99.87	100.38	100.47	100.20
Fe/(Fe+Mg)	0.43	0.47	0.39	0.39	0.47	0.50	0.45	0.57	0.56	0.37	0.56

LOI, Loss on ignition.

Fe/(Fe+Mg) are calculated without volatiles

Prh-Pmp, Ep and Ep-Am zones respectively (Table 2.). Fe/(Fe+Mg) in whole-rocks commonly ranges from 0.36 to 0.57 except 2 samples of 95211 and 94730 Fe/(Fe+Mg) of which is 0.21.

VII. Electron microprobe analysis

There has much difficulty in obtaining chemical data about smectite and C/S. The difficulty has arisen from polishing the minerals. Therefore, chemical compositions of only 27 chlorites are presented in Table 3.

The Fe/(Fe+Mg) ratio of chlorites ranges widely from 0.20 to 0.50. This ratio for chlorites and whole-rocks were plotted on Fig. 5, in which a positive correlation between these two

variables, though roughly, is present. As shown in Fig. 5, the Al/Si ratio of chlorites in the Ep and Ep-Am zones is higher than that in the Lmt and Prh-Pmp zones.

Compositions of chlorite fall mostly in the pynochlorite field of Hey's (1954) chlorite classification (Fig. 6). It is likely that silicon decreases with increasing metamorphic grade (Si/28 oxygens: Lmt zone, 6.12–6.70, Prh-Pmp zone, 5.62–6.62, Ep zone, 5.72–6.14, Ep-Am zone, 5.65–6.14). Si is more than 6.19 in some garnet-bearing samples.

Chemical differences in respect of tetrahedral and octahedral Al, octahedral vacancy and interlayer cations (Ca+Na+K) versus Fe/(Fe+Mg) ratio of chlorites are plotted on Fig.

Table 3. Representative electron microprobe analyses and atomic

Sample. *	952011 l	94730 l	94728 m-l	94724 v-l	94723 m-l	2113 v-l	2112 c-l	2108 v-l	2102 v-l	94312 c-l	94311 c-l	94310 c-l	9439 c-l
SiO ₂	29.25	28.44	27.71	29.33	28.05	30.14	30.42	28.52	26.99	29.91	28.79	29.98	31.32
TiO ₂	0.04	0.04	0.13	0.03	0.04	0.00	0.02	0.03	0.18	0.00	0.00	0.00	0.03
Al ₂ O ₃	20.44	20.05	19.18	17.86	17.69	18.10	17.48	15.62	15.11	16.43	16.43	14.94	16.47
Cr ₂ O ₃	0.27	0.09	0.06	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.01	0.03
FeO**	12.47	11.92	22.41	18.39	19.65	18.13	17.69	26.66	27.12	22.73	26.83	21.95	17.76
MnO	0.10	0.12	0.40	0.40	0.44	0.36	0.35	0.42	0.35	0.41	0.37	0.22	0.33
MgO	21.34	24.62	16.87	20.88	19.23	20.96	21.22	15.30	13.49	20.06	16.29	20.46	22.43
CaO	0.18	0.03	0.49	0.10	0.11	0.08	0.12	0.21	0.38	0.20	0.21	0.14	0.22
Na ₂ O	0.02	0.00	0.03	0.01	0.00	0.02	0.02	0.02	0.01	0.00	0.02	0.01	0.02
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.04	0.06	0.05	0.00	0.00	0.00	0.00	0.00
NiO	0.02	0.07	0.06	0.04	0.00	0.02	0.04	0.05	0.00	0.00	0.00	0.00	0.03
Total	84.13	85.39	87.34	87.06	85.20	87.83	87.42	86.91	83.64	89.76	88.94	87.72	88.64
Si	5.95	5.72	5.77	5.98	5.90	6.07	6.14	6.12	6.07	6.05	6.02	6.19	6.23
Al IV	2.05	2.28	2.23	2.02	2.10	1.93	1.86	1.88	1.93	1.95	1.98	1.81	1.77
Al VI	2.86	2.46	2.48	2.28	2.29	2.36	2.30	2.07	2.08	1.97	2.07	1.83	2.10
Ti	0.01	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
Cr	0.04	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Fe	1.91	1.80	3.51	2.82	3.11	2.75	2.69	4.30	4.59	3.46	4.22	3.41	2.66
Mn	0.02	0.02	0.07	0.07	0.08	0.06	0.06	0.08	0.07	0.07	0.06	0.04	0.05
Mg	6.47	7.37	5.24	6.35	6.03	6.29	6.39	4.89	4.52	6.05	5.08	6.30	6.65
Ni	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Total	11.31	11.69	11.34	11.53	11.52	11.46	11.44	11.36	11.29	11.56	11.43	11.58	11.48
Ca	0.04	0.01	0.11	0.02	0.03	0.02	0.03	0.05	0.09	0.04	0.05	0.03	0.05
Na	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.01
K	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Total	0.05	0.01	0.12	0.03	0.03	0.03	0.05	0.07	0.10	0.04	0.06	0.04	0.06
Cation total	19.36	19.70	19.46	19.56	19.55	19.49	19.49	19.43	19.39	19.60	19.49	19.61	19.53
Fe/(Fe+Mg)	0.23	0.20	0.40	0.31	0.34	0.30	0.30	0.47	0.50	0.36	0.45	0.35	0.29
Temperature #	267	306	297	263	275	249	238	241	249	252	257	229	222

* Abbreviations of rock type and occurrence of chlorite: l, lava; t, tuff; b, breccia;

m, matrix; p, replacing plagioclase; c, replacing clinopyroxene; v, vesicle or vein filling.

** FeO as total iron. # The temperatures are derived from $T(^{\circ}\text{C}) = 321.98(\text{Al IV}) - 61.92$ (Cathelineau, 1988).

Fig. 5. The ratios of Al/Si and Fe/(Fe+Mg) in chlorites from the Tanzawa Group plotted against whole rock values (structural formula calculated on the basis 28 oxygens).

proportions (basis 28 oxygens) of chlorite from the Tanzawa group

UNK No.	9438	9437	9436	9433	9417	9415	9413	9411	94112	94110	1513	3517	3513	3502
*	m-l	p-l	c-l	c-l	m-t	m-l	c-l	mb	c-l	c-l	v-t	m-b	m-t	v-l
SiO ₂	31.09	29.43	31.05	31.73	29.53	29.84	29.47	30.89	31.53	29.51	31.42	29.03	28.445	29.19
TiO ₂	0.02	0.00	0.00	0.02	0.00	0.02	0.05	0.01	0.02	0.00	0.05	0.07	0.082	0.02
Al ₂ O ₃	16.04	16.80	14.63	16.40	14.77	18.95	17.36	15.98	15.45	17.03	14.83	15.64	16.429	14.90
Cr ₂ O ₃	0.02	0.04	0.14	0.02	0.02	0.04	0.03	0.07	0.00	0.00	0.00	0.00	0.012	0.00
FeO**	20.23	22.61	17.80	16.10	23.21	19.00	23.57	22.18	17.73	21.08	15.44	26.25	25.652	25.20
MnO	0.27	0.22	0.04	0.34	1.10	0.28	0.33	0.34	0.29	0.31	0.33	0.52	0.329	0.48
MgO	19.80	20.01	21.73	22.40	16.31	21.99	18.47	19.72	21.65	19.80	22.47	14.27	14.186	17.10
CaO	0.35	0.15	0.26	0.29	0.42	0.10	0.18	0.31	0.32	0.16	0.39	0.24	0.519	0.11
Na ₂ O	0.00	0.00	0.04	0.00	0.00	0.03	0.02	0.01	0.02	0.02	0.00	0.02	0.011	0.01
K ₂ O	0.03	0.00	0.05	0.01	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.00	0	0.00
NiO	0.16	0.02	0.00	0.09	0.17	0.03	0.09	0.03	0.08	0.06	0.05	0.00	0	0.01
Total	88.03	89.26	85.73	87.40	85.53	90.29	89.56	89.56	87.12	87.95	84.97	86.04	85.665	87.04
Si	6.32	5.98	6.40	6.34	6.34	5.87	6.00	6.23	6.39	6.04	6.46	6.26	6.15	6.20
Al IV	1.68	2.02	1.60	1.66	1.66	2.13	2.00	1.77	1.61	1.96	1.54	1.74	1.85	1.80
Al VI	2.16	2.01	1.96	2.21	2.08	2.26	2.16	2.04	2.08	2.15	2.05	2.24	2.34	1.93
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00
Cr	0.00	0.01	0.02	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Fe	3.09	3.46	2.76	2.42	3.75	2.81	3.61	3.37	2.70	3.25	2.39	4.26	4.17	4.03
Mn	0.05	0.04	0.01	0.06	0.20	0.05	0.06	0.06	0.05	0.05	0.06	0.10	0.06	0.09
Mg	6.00	6.07	6.68	6.68	5.22	6.45	5.60	5.93	6.54	6.04	6.88	4.59	4.57	5.41
Ni	0.03	0.00	0.00	0.01	0.03	0.00	0.02	0.00	0.01	0.01	0.01	0.00	0.00	0.00
Total	11.33	11.58	11.43	11.38	11.28	11.59	11.46	11.41	11.39	11.50	11.39	11.20	11.16	11.46
Ca	0.08	0.03	0.06	0.06	0.10	0.02	0.04	0.07	0.07	0.03	0.08	0.06	0.12	0.03
Na	0.00	0.00	0.02	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.01
K	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Total	0.09	0.03	0.09	0.07	0.10	0.03	0.05	0.08	0.09	0.04	0.09	0.06	0.12	0.03
Cation total	19.42	19.61	19.52	19.45	19.37	19.62	19.51	19.49	19.47	19.55	19.47	19.27	19.28	19.49
Fe/(Fe+Mg)	0.34	0.36	0.29	0.27	0.42	0.30	0.39	0.36	0.29	0.35	0.26	0.48	0.48	0.43
Temperature#209	263	195	205	205	281	260	222	198	253	187	217	236	228

Fig. 6. Fe/(Fe+Mg) versus Si compositional variations of chlorites (modified after Hey (1954)).

Fig. 7. Plots of Al^{IV} , Al^{VI} , $Ca + Na + K$, VI vacancy versus $Fe/(Fe + Mg)$ for chlorites (structural formulae calculated on the basis 28 oxygens).

7. It can be seen that tetrahedral Al increases with increasing metamorphic grade. Octahedral Al has not any tendency with metamorphic grade. Octahedral vacancy and interlayer cations can not be correlated with metamorphic grade.

VIII. Summary and conclusions

The characterization of mafic phyllosilicates and calc-silicates are illustrated in Fig. 8.

The results of this study can be summarized as follows:

1) Smectite is transformed to chlorite through C/S or corrensite with increasing metamorphic grade. The proportion of smectite layers in C/S decreases discontinuous-

ly.

2) Kimbara (1973) has observed that Ib ($\beta=90^\circ$) chlorite associated with mixed-layer mineral of chlorite and smectite appears in the Lmt zone and the chlorite seems to convert to IIb ($\beta=97^\circ$) type in the Prh-Pmp zone by the increase of metamorphic grade in the eastern Tanzawa Mountains. This study shows that IIb is the main type, but Ib ($\beta=97^\circ$) is very rare in the Lmt zone. Stilbite transforms to the laumontite at temperatures of about 150°C in low-grade metamorphic terrains (Liou, 1971). Laumontite is present in the geothermal field at temperatures below 200°C (Bird *et al.*, 1984), and occurs in burial metamorphic environments at temperatures of approximately 100°C (Evarts and Schiffman, 1983). The result indicates that

Minerals	Metamorphic zone				
	Stb	Lmt	Prh-Pmp	Ep	Ep-Am
Smectite					
Celadonite	-----				
C/S					
	% S in C/S decreases with increasing metamorphic grade				
Corrensite		-----			
Chlorite (Si/28 oxygens)		(Si > 6.12)	(6.62 > Si > 5.62)	(5.72-6.14)	(5.65- 6.14)
Analcime	-----				
Stilbite					
Laumontite					
Prehnite					
Pumpellyite					
Epidote					
Grandite garnet			-----		
Amphibole					

Fig. 8. Phyllosilicate and calc-silicate mineral zonations of the Tanzawa group from Southern Tanzawa Mountains.

Ilb chlorite may form at temperatures of $\sim 150^\circ$ to 200°C .

3) Fe/(Fe+Mg) ratio of chlorites is positively correlated with those of whole-rocks. Si in chlorites decreases with increasing metamorphic grade.

4) A Cathelineau (1988) expression were used to derive temperatures of chlorite formed (Table 3). The chlorites provide temperatures of about 200° , 200° – 280° , 270° and 300°C in the Lmt, Prh-Pmp, Ep and Ep-Am zones, respectively. Temperatures calculated for chlorites in the Lmt zone (about 200°C) are compatible with the observed mineral paragenesis, from the viewpoint of the appearance of prehnite and pumpellyite as a reaction rim of laumontite with C/S minerals. These temperatures can be taken as the laumontite-disappearing temperature and can be a boundary between the zeolite and prehnite-pumpellyite facies in the Tanzawa group. The chlorite temperatures for other zones, are in agreement with occurrence of Ca-Al silicates and amphibole (Liou, 1979; Bird *et al.*, 1984).

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南部丹沢山地の変質火山岩に産出する粘土鉱物の特徴

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南部丹沢山地の中新世丹沢層群に産出する粘土鉱物の構造的性質と化学組成は変成度に伴って規則的な変化傾向を示す。スメクタイトは束沸石と濁沸石帯に、C/S 不規則混合層鉱物は束沸石、濁沸石とブドウ石ーパンペリー石帯に、C/S 規則混合層鉱物は束沸石帯に分布する。C/S 不規則混合層鉱物中のスメクタイトの割合は変成度の高まりに伴って、70-100%, 40-50%, 20-30% と 0-10% という段階的に変化する。緑泥石は最初に濁沸石帯に産出し、ブドウ石ーパンペリー石帯に卓越し、緑れん石と緑れん石ーアクチノ閃石帯に唯一の粘土鉱物になる。緑泥石の $\text{Fe}/(\text{Fe}+\text{Mg})$ は全岩組成に支配される。Si 含有量は変成度が高くなるにつれて低くなる。