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Zeolites in the Neogene Pyroclastic Rocks in the Eastern Part of Tanzawa Mountainland, Central Japan

——Studies on the Alteration of the Green Tuff Formation, 1 ——

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Abstract

Tanzawa group, the Neogene Tertiary system, distributed in the eastern part of Tanzawa mountainland, has been studied from the viewpoint of the alteration of the Tertiary system.

In Karasawa-zawa tuff member, one member composing Tanzawa group, the following five kinds of the zeolites have been ascertained as secondary minerals; laumontite, analcite, heulandite, mordenite and stilbite.

Karasawa-zawa tuff member can be divided into three zones as follows; laumontite zone, heulandite zone and mordenite zone in ascending order.

Introduction

It has been long well known that the cavities or the druses of volcanic rocks are filled with various kinds of zeolites. However, occurrences of zeolite have been confirmed in sedimentary rocks, especially in pyroclastic rocks, by the latest studies on zeolite.

The conception of "zeolite facies", which means the lowest-grade metamorphic facies, was proposed by Coombs et al. (1959), on the basis of their studies made in New Zealand. This proposition was made by Coombs, In Japan also there has been much argument about the alteration or the metamorphic facies of the green tuff formation.

From 1960 to 1961, the writer investigated the Neogene Tertiary strata, distributed in the eastern part of Tanzawa mountainland, with a view to studying the alteration of the green tuff formation. His work is not yet comprehensive enough to discuss the general aspect of the alteration of the green tuff formation in Tanzawa mountainland, but some data on zeolite were obtained, which will be reported on in this paper.

Geological Setting

Stratigraphic studies on the Cenozoic strata, distributed in the eastern part of Tanzawa mountainland, have been carried out by K. Mikami since 1948. By K. Mikami, the Tertiary system was stratigraphically classified into two groups; Tanzawa group and Aikawa group in ascending order. The writer has studied the so-called Tanzawa group. His work consists of the drawing of a detailed geological map and a study of the alteration of Tanzawa group.

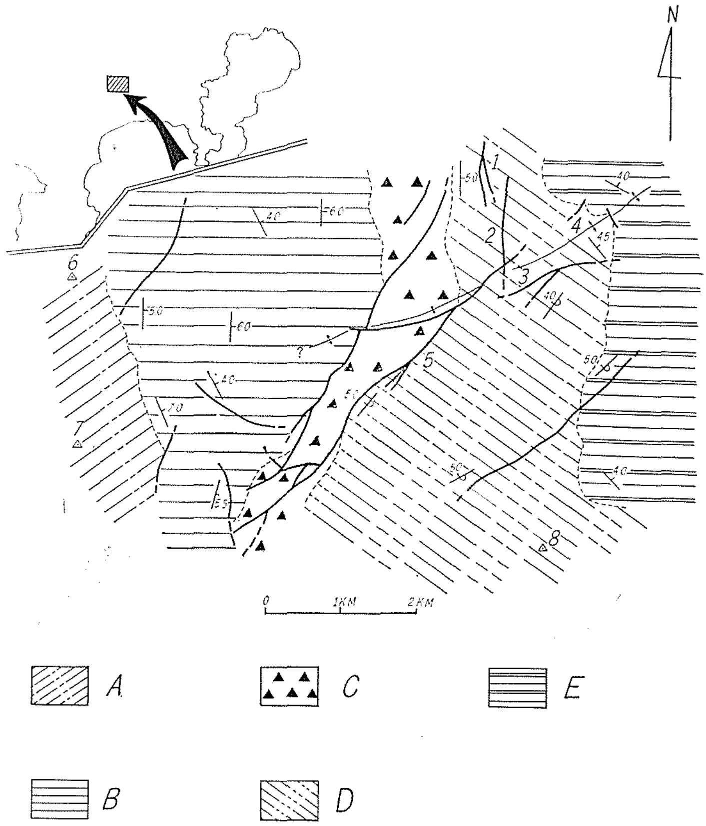
Tanzawa group consists mainly of pyroclastics (tuff-breccia, lapilli-tuff, tuff, etc.). In addition, tuffaceous sediments are sporadically intercalated with the above-mentioned rocks. This group forms a monoclinal structure as a rule; the trend is almost N-S and the dip is 30°-50°E. Furthermore, the gentle folding system having E-W axis is recognized. The geological map is shown in Fig. 1.

Tanzawa group is divided into three sub-groups viewed from the lithological standpoint as follows; Togatake sub-group, Oyama sub-group and Susugaya sub-group in ascending order. The stratigraphic succession of Tanzawa group is given in Table 1. Stratigraphical and lithological studies on Tanzawa group will be reported on in another paper in details.

In this paper, the alteration of Karasawa-zawa tuff member belonging to Oyama sub-group will be discussed on the basis of the studies on zeolite.

Generally speaking, Karasawa-zawa tuff member consists mainly of the alternations of dark greenish tuff (fine~coarse) and lapilli-tuff of andesitic and basaltic compositions. Tuffs are dominant in both the upper and the middle horizons, while lapilli-tuffs are predominant in the lower horizon. Volcanic breccias are occasionally intercalated with tuffs and lapilli-tuffs. Light bluish green-colored, dacitic lapilli-tuffs and dacitic pumiceous tuff-breccias are interbedded in the middle and the upper horizons. These dacitic rocks progressively increase in their amount toward the upper horizon, and finally this member, Karasawa-zawa tuff member, gradually changes into Susugaya sub-group. Furthermore, one sheet of basic lava-flow (clinopyroxene andesite) crops out at the river-course of Shimo-Karasawa-zawa.

Fig. 1. Geological Map



A. Shizyuhasse Tuff Member B. Hondani Tuff Member C. Nunokawa Volcanic Breccia Member D. Karasawa-zawa Tuff Member E. Fudoziri Dacitic Tuff Member

1. Kaza-ana Zawa 2. Shimo-karasawa Zawa 3. Naka-karasawa Zawa 4. Ichi-no-miya Zawa 5. Hudakake 6. Tanzawa Yama 7. Togatake 8. Afuri Yama

Judging from mineral composition, andesitic pyroclastics were identified as commonly augite-andesitic and sometimes hypersthene-augite-andesitic ones. (An contents of plagioclase: An 32–An 52). Basaltic pyroclastics also were ascertained as augite-basaltic, hypersthene-augite-basaltic and rarely olivine-basaltic ones. (An contents of plagioclase: An 54–An 62).

The total thickness of the present member is about 1000 M. or more.

Table 1. Stratigraphical Succession

Group	Sub-group	Formation	Member	Description
Tanzawa Group	Susugaya Sub-group	Osawa Formation	Fudoziri Dacitic Tuff Member	? Alternations of well-stratified dacitic tuff and dacitic pumiceous lapilli-tuff.
	Oyama Sub-group	Karasawa-zawa Formation	Karasawa-zawa Tuff Member	Alternations of dark greenish tuff and lapilli-tuff of andesitic and basaltic compositions. (1000 M.).
			Nunokawa Volcanic Breccia Member	Massive volcanic breccia and lapilli-tuff of basaltic and andesitic compositions. (900 M.).
		Hondani-gawa Formation	Hondani Tuff Member	Alternations of tuff and lapilli-tuff of basaltic and andesitic compositions. (1200—1400M.).
	Togatake Sub-group	Shizyuhasse-gawa Formation	Shizyuhasse Tuff Member	Alternations of tuff and lapilli-tuff of basaltic composition. ?

Experimental

The 21 rock specimens were sampled from Karasawa-zawa tuff member and one specimen was sampled from Fudoziri dacitic tuff membr. The geological columns of these members and the geological horizons sampled are shown in Fig. 2. The rock specimens, in the case of the fine grained rocks (cf. tuff), were pulverized in the iron mortar. In the case of the coarse grained rocks (cf. tuff-breccia), matrix of these rocks was selected out and was also pulverized in the iron mortar. And then the powerful magnet freed the powdered rock-specimns of iron filings. The clayey specimens under 2 μ size were procured from these crushed rock samples by means of Stokes' law.

The clayey specimens were examined by the following methods: X-ray powder diffraction and heat treatment. Furthermore, all these rock specimens were observed under the microscope.

In the electric oven some clayey specimens were heated at (500±10)°C for 2 hours in the air. (thermal gradient 240°C /hour). All 22 clayey specimens

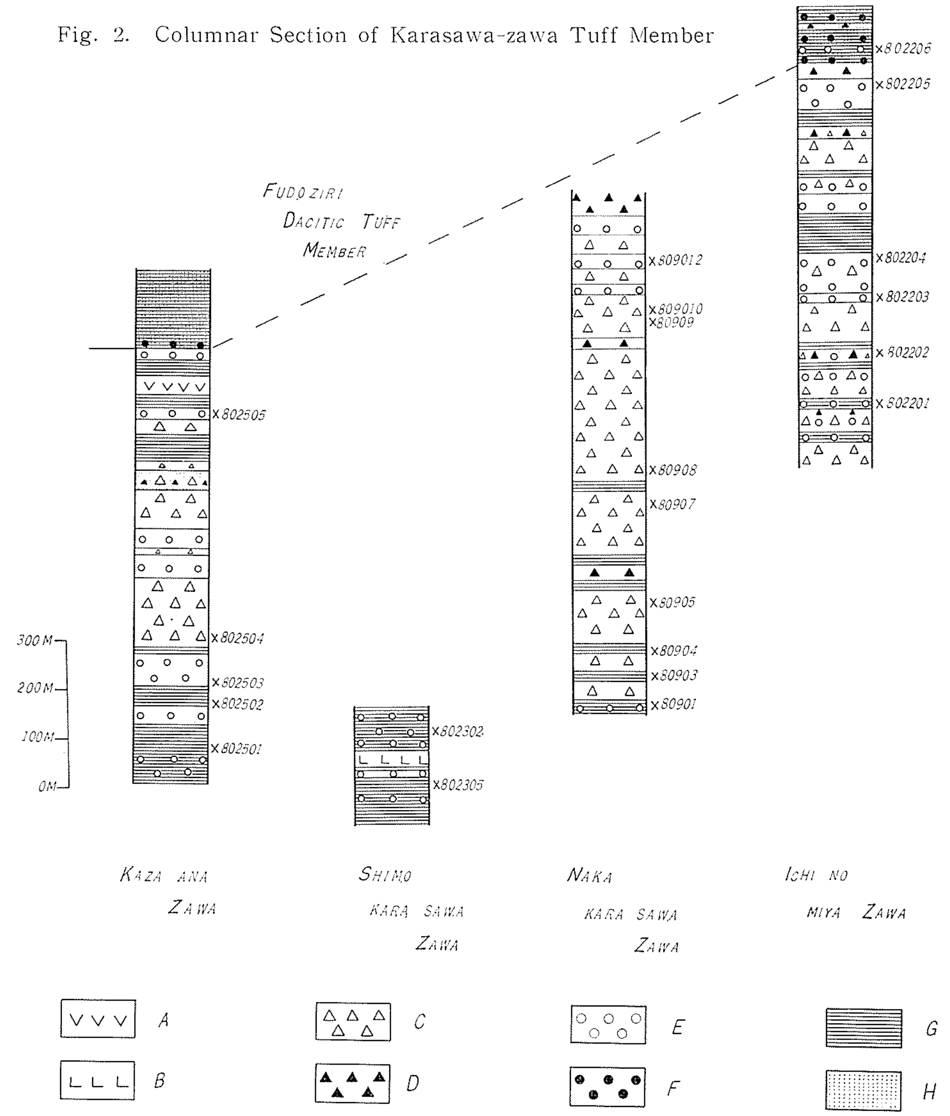
Table 2. Zeolites in rock specimens from Karasawa-zawa tuff member

Sample	Zeolite	
80901	Laumontite	Andesitic fine tuff
80903	Laumontite Stilbite	Basaltic fine lapilli-tuff
80904	Stilbite	Basaltic fine tuff
80905	Laumontite Heulandite Mordenite	Basic andesitic lapilli-tuff
80907	Laumontite Heulandite	Andesitic lapilli-tuff
80908	Laumontite Analcite	Basaltic tuff-breccia
80909	Laumontite Analcite Heulandite	Andesitic lapilli-tuff
809010	Analcite Heulandite	Andesitic fine tuff
809012	Analcite Stilbite Heulandite	Andestic lapilli-tuff
802201	Laumontite	Basaltic fine lapilli-tuff
802202	Heulandite Mordenite	Andesitic lapilli-tuff
802203	Analcite Heulandite	Basaltic lapilli-tuff
802204	Analcite Heulandite	Andesitic fine lapilli-tuff
802205	Heulandite Mordenite	Andesitic fine lapilli-tuff
802206*	Mordenite	Dacitic lapilli-tuff
802302	Laumontite Analcite	Andesitic fine lapilli-tuff
802305	Analcite	Dacitic tuff
802501	Laumontite Heulandite	Basic andesitic tuff
802502	Laumontite Heulandite	Basaltic fine tuff
802503	Laumontite Analcite Heulandite Mordenite	Basaltic lapilli-tuff
802504	Laumontite Heulandite Stilbite	Basic andesitic lapilli-tuff
802505	Laumontite Analcite	Basic andesitic lapilli-tuff

* marked rock specimen was sampled from Fudoziri dacitic tuff member.

were examined by X-ray powder diffraction under the following condition; Radiation 35 KVP 15 mA, Target Cu, Filter Ni, Scanning Speed 1° or 2°/min., Scale Factor 16, Multiplier 1, Time Constant 1 sec, Div. slit 1°, Scatt. Slit 1°, Rec. Slit 0.4mm. (Apparatus: Geigerflex).

Fig. 2. Columnar Section of Karasawa-zawa Tuff Member



A. Dike Rock B. Lava-flow C. Basaltic & Andesitic Tuff-breccias D. Dacitic Tuff-breccia E. Basaltic & Andesitic Lapilli-tuff F. Dacitic Lapilli-tuff G. Tuff & Tuffaceous Mud H. Dacitic Pumiceous Pyroclastics

Result and Identification of zeolite

Judging from the results thus obtained, it has been confirmed that all 22 rock specimens have at least one kind of zeolite; laumontite, analcite, heulandite, mordenite and stilbite. (Table 2).

The distinctive features of their X-ray powder diffraction patterns will be described respectively as follows.

Laumontite

The existence of laumontite can be easily recognized, owing to its characteristic diffraction peaks, i. e. 9.5Å, 6.9Å, 41.1Å, 3.5Å and so on, as showh in Fig. 3 and Table 3.

Analcite

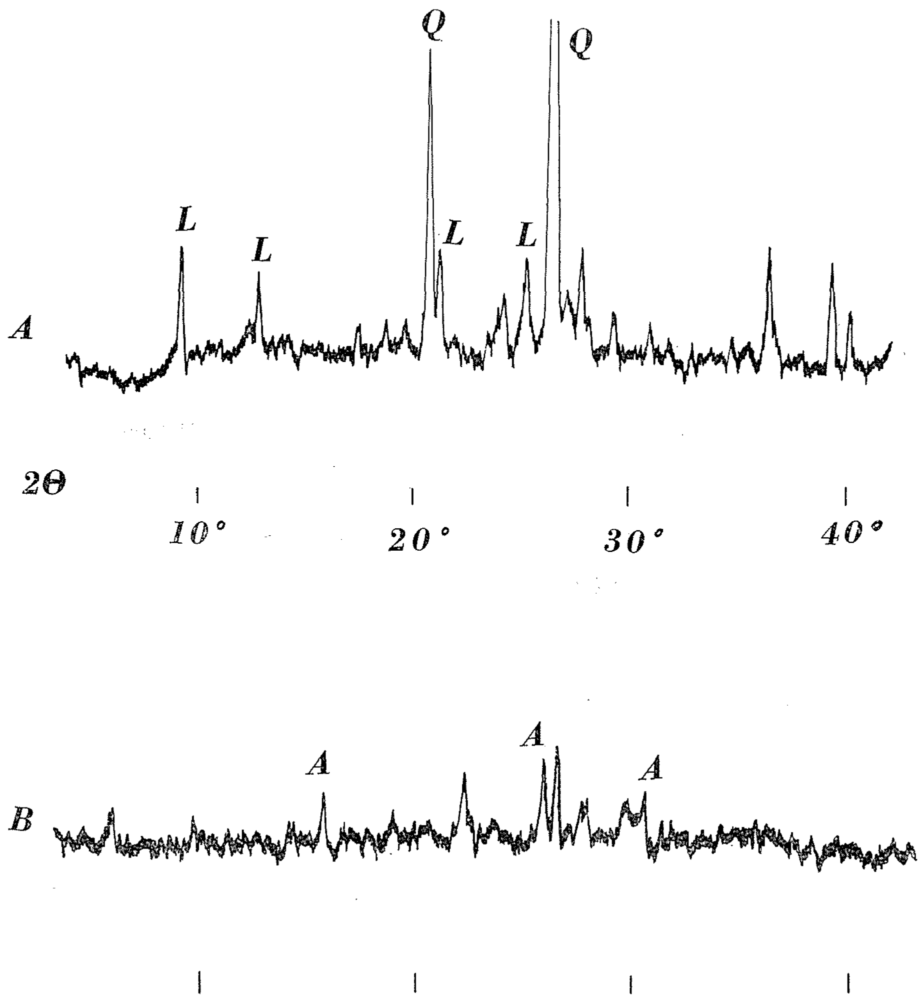
In general, analcite is indistinguishable from wairakite by their diffraction patterns. However the zeolite having analcite-structure in Karasawa-zawa tuff member has been determined to be analcite by micro-scopic observation. Both analcite and wairakite exhibit slight birefringence, but there are distinguishable difference between them; birefringence of analcite is usually 0.001 or less, and that of wairakite is approximatery 0.004. (Rock Forming Minerals Vol. 4, pp. 344-345). Analcite shows its original X-ray powder diffraction patterns. (5.6Å, 3.4Å, 2.9Å, 1.7Å etc. as given in Fig. 3 and Table 3).

Heulandite

It is also very difficult to distinguish between heulandite and clinoptilolite by their X-ray powder diffraction patterns. Mumpton (1960), however, described the relationship between heulandite and clinoptilolite. According to his paper, heulandite becomes amorphous at 350°C, on the other hand, clinoptilolite is stable below 750°C. Consequently, heulandite is distinguishable from clinoptilolite by heat treatment.

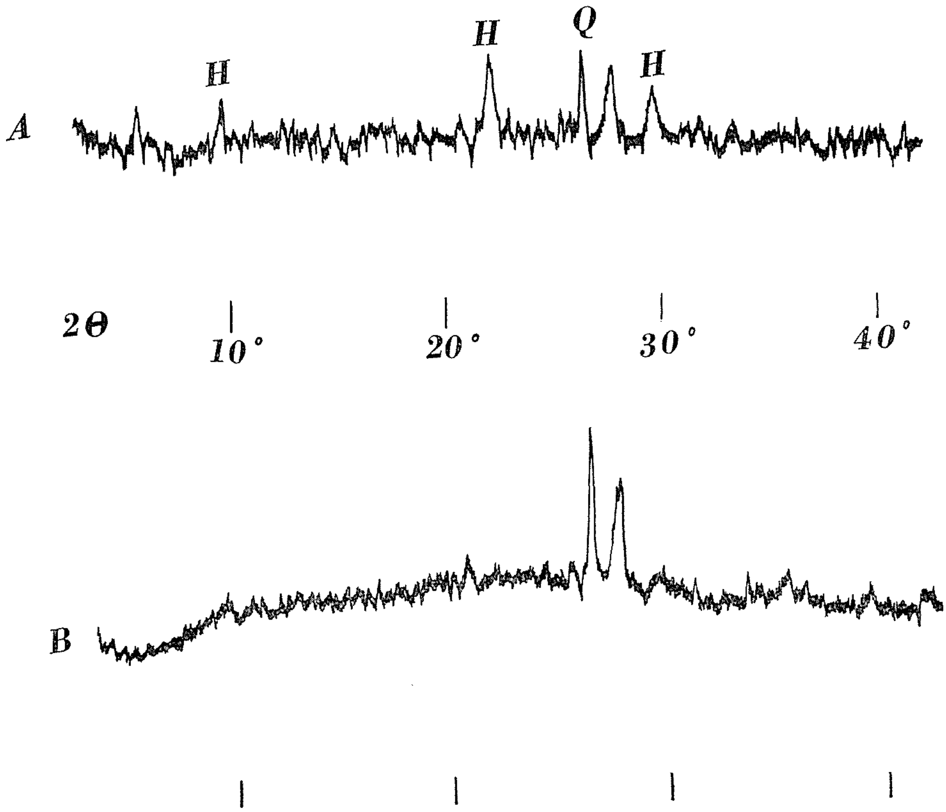
Each zeolite having heulandite-structures in Karasawa-zawa tuff member was examined by heating at 500°C for 2 hours. After heating their original X-ray powder diffraction patterns (8.9Å, 4.7Å, 3.96Å, 2.99Å etc. as shown in Fig. 4) all disappeared. So it has been ascertained that all of the zeolite having heulandite-structures in the present member are heulandites.

Fig. 3. X-ray powder diffraction patterns of laumontite and analcite



A. Analcite L. Laumontite Q. Quartz

Fig. 4. X-ray powder diffraction pattern of heulandite



A; at room temperature. B; after heating at (500±10)°C for 2 hours.
H. Heulandite Q. Quartz

Mordenite

The existence of mordenite can be easily recognized by its characteristic X-ray powder diffraction patterns, i. e. 9. 2Å, 6. 6Å, 4. 5Å, 4. 0Å, 3. 4Å, 3. 3Å. 3. 2Å etc.. (Table 3)

Stilbite

The zeolite showing the following X-ray powder diffraction patterns has been determined to be stilbite, that is 9. 0Å, 4. 6Å, 4. 0Å, 3. 2Å, 3. 03Å, 3. 00Å etc. as in Table 3.

Table 3. X-ray powder diffraction data for mordenite, stilbite and laumontite + analcite. (Cu-K_{α_1}; λ=1.54050Å)

Mordenite			Stilbite			Lauumontite		
2θ	d (Å)	(I/Io) × 100	2θ	d (Å)	(I/Io)×100	2θ	d (Å)	(I/Io)×100
6.44	13,798	17	8.71	10,155	5	9.26	9,501	100
7.00	12,617	11	9.76	9,017	100	12.83	6,910	60
7.38	11,936	11	16.43	5,400	5	13.51	6,553	13
9.63	9,205	46	16.70	5,304	6	14.35	6,146	19
12.75	6,910	28	19.05	4,643	18	§ 15.78	5,604	
13.38	6,602	46	19.41	4,572	7	17.55	5,035	19
13.69	6,458	33	19.89	4,458	5	18.33	4,844	24
14.50	6,104	28	20.74	4,287	11	18.83	4,716	25
15.19	5,824	28	21.89	4,055	60	19.80	4,480	25
17.75	4,979	17	23.74	3,751	8	20.74	4,287	13
18.06	4,897	14	25.04	3,559	4	21.35	4,149	74
19.56	4,525	41	25.52	3,490	8	§ 21.93	4,055	
* 20.88	4,247	(34)	26.17	3,398	14	§ 23.37	3,798	
22.13	4,019	53	27.05	3,288	4	23.59	3,767	13
22.81	3,897	29	27.94	3,195	16	** 24.30	3,660	37
23.06	3,847	30	28.60	3,118	6	25.28	3,517	55
23.56	3,767	41	28.87	3,087	7	** 25.94	3,437	(120)
25.63	3,477	100	29.35	3,035	44	26.55	3,348	21
26.38	3,373	96	29.67	3,005	17	27.20	3,276	33
* 27.63	3,229	(111)	31.04	2,882	5	27.88	3,195	37
29.81	3,000	30	32.19	2,778	20	28.26	3,151	22
30.81	2,901	34	32.82	2,728	5	** 29.40	3,035	37
31.94	2,803	9	34.35	2,605	5	** 30.60	2.919	63
34.94	2,569	20	34.91	2,569	9	31.10	2,873	27
35.56	2,520	28	35.66	2,513	5	** 31.95	2,795	21
36.56	2,453	14	36.08	2,486	5	§ 33.30	2,688	
38.06	2,360	7	36.49	2,460	4	34.78	2,576	19
39.44	2,285	11	36.63	2,453	4	35.57	2,520	15
40.50	2,225	8	38.20	2,354	5	§ 35.80	2,506	
41.75	2,159	5	38.78	2,319	3	36.75	2,440	21
43.38	2,083	3	39.70	2,268	3	38.00	2,366	13
44.06	2,052	8	40.52	2,225	4	39.57	2,274	9
44.88	2,017	9	40.98	2,199	3	40.20	2,241	8
46.50	1,951	8	42.50	2,125	4	40.60	2,220	17
48.38	1,879	12	43.04	2,102	4	41.40	2,179	10
50.25	1,812	11	43.82	2,065	6	41.90	2,154	19

50.75	1,796	12	44.58	2,030	5	43.30	2,088	9
52.63	1,739	7	47.82	1,901	5	45.45	1,992	7
53.25	1,717	7	48.60	1,872	3	46.30	1,959	12
55.50	1,654	4	49.99	1,823	11	§ 47.84	1,901	
56.69	1,622	4	50.37	1,809	4	48.80	1,865	17
57.50	1,601	4	51.28	1,779	5	49.87	1,826	8
58.75	1,569	3	52.95	1,726	4	50.66	1,799	7
59.69	1,548	9	56.10	1,638	4	51.84	1,763	8
			57.22	1,609	3	§ 52.55	1,739	
			57.78	1,594	7	53.45	1,711	11
			58.20	1,584	5	§ 54.30	1,688	
			59.39	1,555	5	§ 55.25	1,660	
						56.29	1,633	9
						56.70	1,622	10
						§ 57.90	1,591	
						58.90	1,567	10

The powdered specimen of mordenite contains a small quantity of plagioclase. * marked peaks; mordenite + plagioclase

In the X-ray powder diffracton data for laumontite + analcite, § marked peaks are diffraction peaks of analcite; ** marked peaks are those of laumontite + analcite.

Occurrences of the zeolites

Occurrences of the zeolites were studied by micro-scopic observation. The results are summarized as follows.

Laumontite

Laumontite is commonly yielded in basic andesitic or andesitic pyroclastics. Ca-rich plagioclase (An contents of plagioclase : An32—An64) in the lower horizon of Karasawa-zawa tuff member is generally replaced by laumontite. Namely, the micro- and large-grained plagioclase in matrix of tuff-breccias or lapilli-tuffs are more or less replaced by laumontite, the former almost entirely, and the latter partly. No Ca-rich plagioclase (An contents of plagioclase: An32—An56) in the upper horizon is replaced by laumontite.

It is also commonly noticed that matrix-material, mainly composed of glass, is replaced by laumontite. Laumontite usually assumes a net-work in texture, but sometimes shows congregated block towards the upper horizon. The veinlet of laumontite is rather rarely observed.

The felsic-menerals paragenetic with laumontite are commonly analcite, heulandite and prehnite. In the case of laumontite-prehnite assemblage, augite is often altered more or less to aegirin-augite. In some cases, furthermore, laumontite co-exisits with mordenite or stilbite. Only in the pyroclastics including some dacitic fragments, the mineral assemblage, laumontite-mordenite, is recognized.

Analcite

Analcite occurs commonly in matrix of pyroclastic rocks basaltic or andesitic in composition. Furthermore, it is sometimes observed that analcite exists in dacitic pyroclastics.

It is comparatively difficult to observe its occurrence, for it is smaller than the other zeolites in amount. The present zeolite is generally needle-shaped or columnar-shaped in form.

In the lower horizon of the present member, Ca-rich plagioclase (An:An40 - An60) is often replaced partly by analcite.

Laumontite is the zeolite paragenetic with analcite in the lower horizon; heulandite in the upper horizon. Besides, carbonates often co-exist with analcite in the upper horizon.

Heulandite

Heulandite is the most common zeolite observed in Karasawa-zawa tuff member. Heulandite replaces glass in matrix of pyroclastic rocks of andesitic composition. Glassy parts of pumiceous rock-fragments are selectively replaced by heulandite and the pumiceous structures still remain.

Heulandite takes needle-shaped or short columnar-shaped crystal form, and shows radial or trappered arrangements.

Ca-rich plagioclase (An contents: An50 - An62) in the rock specimens are rarely altered to heulandite in slight degree.

Of the secondary minerals co-existing with heulandite, analcite is the most common; laumontite, stilbite, prehnite and carbonates are sometimes found in the lower horizon. Mordenite is the zeolite paragenetic with heulandite found in the upper horizon.

Mordenite

Mordenite is mostly observed in dacitic pyroclastics, although it is sometimes recognized in andesitic ones. Mordenite selectively replaces glass in matrix or in the pumiceous rock-fragments of these pyroclastics.

No Ca-rich plagioclase is altered to mordenite. Mordenite commonly co-exists with heulandite. It increases in its quantities towards the upper horizon. In the uppermost horizon, mordenite is the only kind of zeolites observed.

Stilbite

Stilbite is found in basaltic or andesitic pyroclastics. It mainly replaces glass and sometimes Ca-rich plagioclase partly. (An contents of plagioclase An32-An50) (ex. 80904).

Stilbite shows generally short columnar-shaped form and trappered arrangement. Veins, consisting of stilbite alone or stilbite + heulandite, are often recognized.

Discussion and Conclusion

As shown in Table 2. and Fig. 2, from the viewpoint of zeolite, Karasawa-zawa tuff member can be divided into three zones as follows; laumontite zone, heulandite zone and mordenite zone in ascending order. Each of these zones is comparatively discordant with the stratigraphic structure. Moreover, it is presumed, on the basis of the data obtained, that clinoptilolite zone may be instituted in a member upper than Karasawa-zawa tuff member.

Mordenite, one of the Na-zeolites in Karasawa-zawa tuff member, will be discussed. From both theoretical and experimental data, it is already known that the present zeolite is stable under lower temperature than in the case of analcite. On the other hand, mordenite is stable under higher temperature than in the case of clinoptilolite. Mordenite zone has therefore been expected to lie between clinoptilolite zone and analcite zone in the green tuff formation.

It may be justifiable that the uppermost Karasawa-zawa tuff member is equivalent to mordenite zone. According to K. Koizumi and R. Roy (1961), mordenite co-exists with laumontite under Ca-rich condition. In the lower horizon of Karasawa-zawa tuff member, mordenite, co-existing with laumontite, may have been generated under Ca-rich circumstance, judging from the chemical composition of pyroclastic rocks.

As for the alteration of Ca-rich plagioclase, mostly labradorite, it is commonly noticed that Ca-rich plagioclase is more or less altered to the following mineral assemblage, viz., laumontite + prehnite + epidote, in the lower horizon of the present member. In the case where SiO_2 and H_2O are in excess, Ca-rich plagioclase may be capable of being altered to the above-mentioned mineral assemblage.

It is assumed that the alteration of the present member is largely controlled by the chemical composition of starting materials. Namely, in Karasawazawa tuff member, the ratio, (Na, K)/Ca, increases towards the upper horizon, judging from the chemical composition of pyroclastics composing the present member, and Na-zeolite occurs and increases in amount towards the upper horizon.

The other secondary minerals, like mafic clay minerals, will be reported in detail in the near future, from the viewpoint of the relationships between these mafic clay minerals and zeolite.

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References

BOWEN, N. L. and J. F. SCHAIRER: Amer. Jour. Sci., Vol. 29, pp. 151-217 (1935)

COATS, R. R.: Econ. Geol., Vol. 35, pp. 1-16 (1940)

COOMBS, D. S., Ellils, A. J., FYFE, W. S. and TAYLOR, A. M.: Geochim. et Cosmochim. Acta, Vol. 17, pp. 53-107 (1959)

CREASY, S. C.: Econ. Geol., Vol. 54, pp. 351-375 (1959)

FYFE, W. S., TURNER, F. J. and VERHOOGEN, J.: Geol. Soc. Amer. Mem. 73, Chap. 4 (1958)

INABA, A.: The Earth Science, no. 43, pp. 11-22 (1959) (in Japanese)

ISHIHARA, H.: The Earth Science: no. 70, pp. 1-14 (1964)

KOBAYASHI, K. and OINUMA, K.: Jour. Geol. Soc. Japan, Vol. 66, pp. 506-516 (1960) (in Japanese)

KOIZUMI, M. and R. ROY: Jour. Geol., Vol. 68, pp. 41-53. (1961)

MIKAMI, K.: Science Reports of the Yokohama National Univ., Sec. 2, no. 8, pp. 57-106 (1962)

MUMPTON, F. A. : Amer. Min., Vol. 45, pp. 351-369 (1960)

NAKAZIMA, W. and KOIZUMI, K. : The Earth Science, no. 58, pp. 26-31 (1962)(in Japanese)

SCHWARTZ, M. G. : Econ. Geol., Vol. 54, pp. 161-183 (1959)

SUDO, T. et al. : Jour. Geol. Soc. Japan, Vol. 69, pp. 1-14 (1963)

WILSHIRE, H. G. : Univ. Calif. Publ. Geol. Sci., Vol. 32, pp. 243-272 (1957)

WILSHIRE, H. G. : Jour. Proc. Royal Soc. N. S. W., Vol. 93, pp. 105-120 (1959)

YAMAGISHI, I. : Jub. Pub. in the Comm. Prof. H. Fujimoto 60th Birthday, pp. 245-254 (1958) (in Japanese)

YOSHIMURA, T. : The Earth Science, no. 52, pp. 19-29 (1960) (in Japanese)

ZEN, E-An: Amer. Jour. Sci. , Vol. 259, pp. 401-409 (1961)