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STABILITY OF MORDENITE IN ZEOLITE FACIES METAMORPHISM OF THE OYAMA-ISEHARA DISTRICT, EAST TANZAWA MOUNTAINS, CENTRAL JAPAN

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Abstract

In the Oyama-Isehara district where the laumontite subfacies of the zeolite facies is recognized, mordenite-bearing assemblages were stably formed within relatively thin bedded, fine-grained pumice tuff. Bulk chemical compositions of these fine-grained pumice tuffs do not show any difference from those of tuff breccia in which laumontite-bearing mineral assemblages were stably formed. Confined occurrence of mordenite in fine-grained pumice tuff beds must have been chiefly due to the lithological characters of their host rocks which were composed of about 80% of fine-grained fragment of pumice and 20% or less of augite and calcic plagioclase. The fragments of pumice were easily devitrified by reaction with water resulting in mordenite-bearing assemblages. In ordinary tuff or tuff treccia which was chiefly composed of relatively well crystallized pyroclastics, however, hydrothermal reaction of rocks with water was accompanied by the breakdown of moderate amounts of calcic plagioclase to form laumontite (or prehnite-) bearing assemblages.

Preface

The Oyama-Isehara district of the east Tanzawa Mountains mostly consists of early to middle Miocene submarine andesitic pyroclastic rocks with subordinate amounts of dacitic tuff. These volcanic rocks are covered by thick Pleistocene volcanic ashes derived from Hakone and Fuji volcanoes. The geological structure and the zeolite facies metamorphism of the Miocene pyroclastic formation will be described in some detail. The genesis of mordenite-bearing mineral assemblages is also discussed.

Geology of the Oyama-Isehara district

Figure 1 indicates the lithology and geological structure of Miocene pyroclastic rocks and associated dolerite intrusives of the present district.

The pyroclastic rocks are mostly coarse-grained lapilli tuff and tuff breccia frequently overlain by a sequence of doubly graded and fine-grained pumice tuff (FISKE and MATSUDA, 1964; FISKE, 1969). Tuffaceous conglomerates are sometimes intercalated with these tuff breccia and pumice tuff. These volcanic rocks are of andesitic composition with augite as phenocrysts and groundmass-forming minerals. Neither relics of nor pseudomorphs after hypersthene, hornblende and biotite have been found in any specimens collected by the present writers. Chemical compositions and petrographic characters of three augite andesitic tuff breccias are shown in Tables 1 and 2. Tuffaceous conglomerates are composed of subrounded pebbles of andesite, rounded pebbles of chert or sandstone and a matrix of tuffaceous character. Pebbles of chert and sandstone may have been derived from Mesozoic and Paleozoic formations which were exposed at the northern side of the Tanzawa

Table 1. Chemical compositions of altered Miocene andesitic tuff breccias of the Oyama-Isehara district, central Japan.

	HO-11	TO-5	TO-10
SiO_2	59.92	61.29	63.58
TiO_2	0.68	0.65	0.67
Al_2O_3	14.45	13.55	13.56
Fe_2O_3	4.52	3.41	3.48
FeO	3.14	4.03	3.30
MnO	0.15	0.13	0.16
MgO	3.54	2.16	2.38
CaO	5.41	6.63	4.64
Na_2O	2.08	1.96	2.25
K_2O	0.83	0.81	0.86
H_2O+	5.10	3.77	5.12
H_2O-	0.55	1.03	0.45
P_2O_5	0.15	0.13	0.15
Total	100.52	99.55	100.60
Analyst	H. H.	T. T.	H. H.

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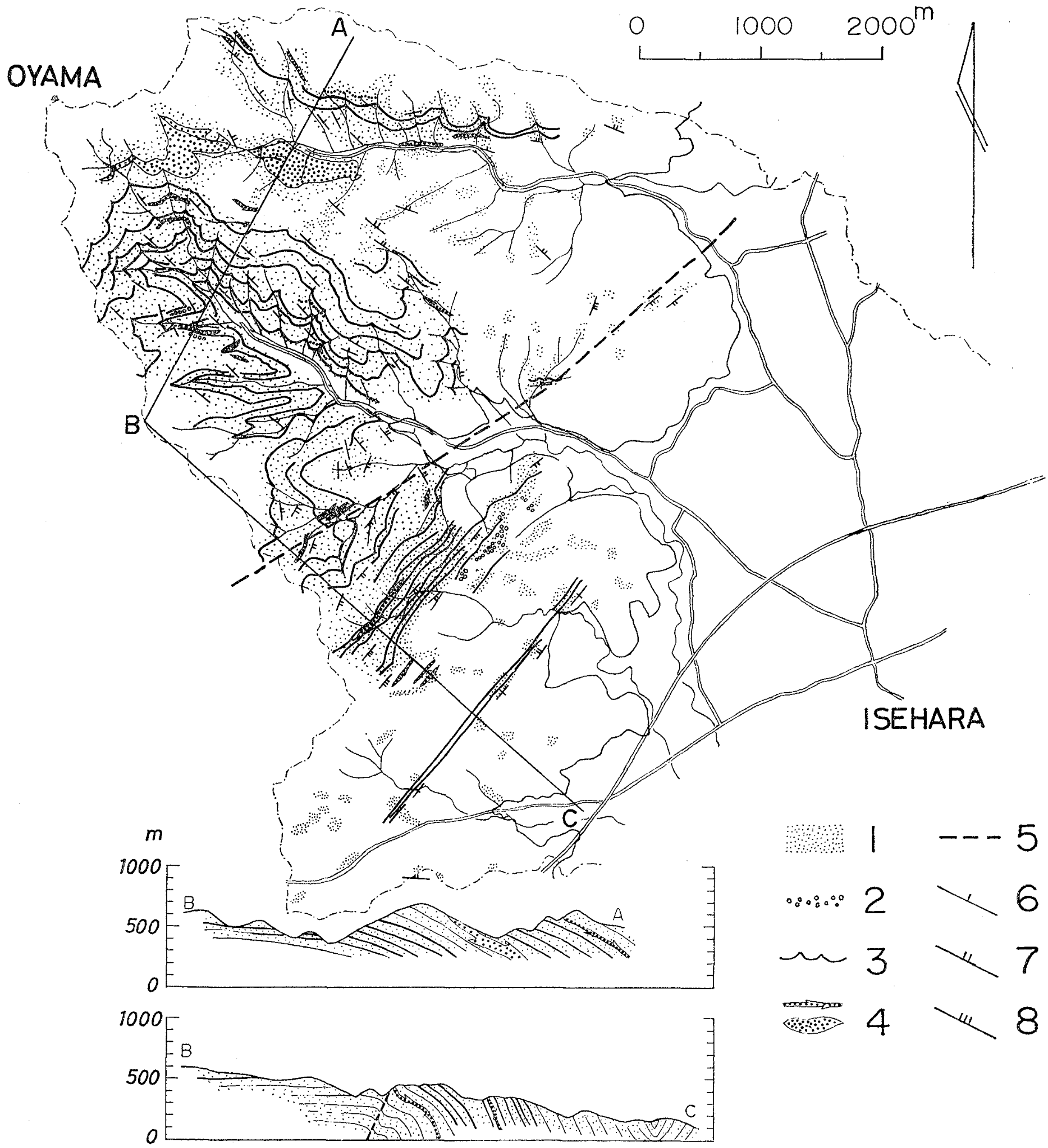

Fig 1. Geological map of Oyama-Isehara district, central Japan.

1 : Andesitic tuff breccia
2 : Tuffaceous conglomerate
3 : Andesitic fine-grained pumice tuff
4 : Dolerite dyke
(middle (?) Miocene)
5 : Koyasu fault
6 : Dip of bedding plane=0—30°
7 : Dip of bedding plane=30°—60°
8 : Dip of bedding plane=60°—90°

Table 2. Petrographical descriptions of altered Miocene andesitic tuff breccias in the Oyama-Isehara district, central Japan (see Table 1)

	HO-10	HO-11	TO-5
Metamorphic zone	Zone Ⅱ	Zone Ⅱ	Zone Ⅱ
Relic minerals	Augite………… 3 % Plagioclase (An_{53})………… 4 % Magnetite …… 1 %	Augite………… 1 % Plagioclase (An_{57})………… 9 % Magnetite …… 2 %	Augite………… 3 % Plagioclase (An_{53})………… 4 % Magnetite …… 3 %
Alterations	Phenocrysts of augite were partly replaced by brownish green clay. Plagioclases were altered into laumontite, quartz and albite. Matrix which was originally composed of fine-grained pyroclastics was wholly replaced by laumontite, albite, quartz and dark brownish green clay minerals with very small amounts of epidote.		Plagioclase was partly altered into albite, prehnite and laumontite along cleavage planes and cracks. Augite was partly replaced by yellowish green clay minerals. Matrix parts were wholly replaced by prehnite, albite, clay and quartz with subordinate amounts of epidote, hematite and laumontite.

Table 3. Chemical compositions of altered fine-grained pumice tuffs of the Oyama-Isehara district, east Tanzawa Mountains, central Japan.

	E-1	E-3	C-1	C-2	HO-13	TO-4
SiO_2	54.52	57.92	58.32	58.87	61.56	62.44
TiO_2	0.70	0.74	0.74	0.76	0.59	0.62
Al_2O_3	13.43	13.81	12.72	13.28	12.57	13.55
Fe_2O_3	4.72	3.68	2.99	3.29	2.58	2.89
FeO	4.43	3.71	4.43	4.36	3.76	4.25
MnO	0.17	0.15	0.17	0.13	0.13	0.19
MgO	3.89	3.05	2.36	1.96	2.95	2.35
CaO	5.40	5.99	5.76	6.35	4.43	4.16
Na_2O	2.22	2.33	1.85	1.39	1.77	2.42
K_2O	0.45	1.00	0.79	0.77	0.67	1.19
H_2O+	4.35	3.95	5.90	5.68	4.20	1.80
H_2O-	5.85	3.17	3.95	3.27	4.96	4.13
P_2O_5	0.06	0.23	0.12	0.17	0.08	0.08
Total	100.19	99.73	100.10	100.28	100.25	100.07
Analyst	H. H.	T. T.	T. T.	T. T.	H. H.	H. H.

Note: H. H. Hiroshi HARAMURA
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geosynclinal basin.

The thickness of fine-grained pumice tuff varies from 4 cm to several meters. The color in the field of unweathered pumice tuff is usually light bluish green, but when weathered, it shows always a characteristic dark brown or dark greysh brown color. Lateral extent of the pumice tuff is far wider than any other kinds of Miocene volcanic rocks of this district. Consequently, the thin pumice tuffs can be used as good marker beds for the study of geologic structure. The grading of grain-size within a bed of this kind of tuffaceous rocks has been very useful to determine the right-side up nature of the Miocene volcanic formation. Microscopic observations indicate that these pumice tuffs were originally composed of augite, calcic plagioclase and pumice fragment. Clastic grains or phenocrysts of quartz are very rare. Neither relics of nor pseudomorphs after hypersthene, hornblende and biotite have been found. The vitroclastic texture is well preserved in these pumice tuffs even when most of pumice fragments were already replaced by zeolites, chlorite-clay and quartz. Chemical compositions and petrographic characters of fine-grained pumice tuffs are represented in Table 3 and Table 4.

Some sheets of augite dolerite are intruded concordantly or subconcordantly into the Miocene volcanic formation. Contact metamorphism of the surrounding pyroclastic rocks by these intru-

Table 4. Petrographic descriptions of analysed Miocene fine-grained pumice tuffs of the Oyama-isehara district, central Japan (see Table 3).

Sample	Zone	Relic minerals	Alteration
E-1	Zone I	Augite………… 5 % Plagioclase……11% (An_{76}) Magnetite …… 5 %	Augite and calcic plagioclase are generally very fresh and unaltered. Glass shards were completely replaced by the assemblage of mordenite, pale green clay minerals and analcime. Some irregular form druses (1.1—1.4 mm in diameter) filled with laumontite and mordenite are observed. Inthese druses, mordenite is always grown from the wall of the druses and laumontite fills the central interstitial part. Veinlets of 0.3 or less mm thickness composed of laumontite with or without quartz are also observed.
E-3	Zone I	Augite………… 3 % Plagioclase……21% (An_{57}) Quartz……… 0.5% Magnetite …… 4 %	Phenocrysts of augite, plagioclase and quartz were generally unaltered and fresh. Glass shards were unaltered and fresh. Glass shards were generally replaced by quartz, mordenite, pale green clay and hematite. Some druses (0.6 mm in diameter) filled with laumontite and quartz are observed.
C-1	Zone II	Augite………… 3 % Plagioclase……10% (An_{60}) Magnetite …… 3 %	Augite and plagioclase are generally unaltered except partial replacement of plagioclase by mordenite and celadonite along the cleavage planes. Glassy matrix was completely replaced by pale green clay, mordenite, hematite and quartz.
C-2	Zone II	Augite………… 4 % Plagioclase……12% (An_{60}) Magnetite …… 4 %	
HO-13	Zone II	Augite………… 3 % Plagioclase……11% (An_{57}) Magnetite …… 3 %	Plagioclase was partly altered into mordenite along crystal margin and cleavage planes. Augite phenocrysts were partly replaced by yellowish green clay minerals. Glass shards were wholly replaced by mordenite, clay and quartz with very small amounts of prehnite and laumontite.
TO-4	Zone II	Augite………… 2 % Plagioclase…… 6 % (An_{60}) Magnetite …… 2 %	Plagioclase was partly replaced by mordenite and quartz. Glass shards were wholly altered into the assemblage of mordenite, yellowish green clay, hematite and quartz.

sions is not clear. Probably, if the contact metamorphism had occurred by the intrusions of the dolerite sheets, the metamorphic features were erased during the low-grade metamorphism by which almost whole rocks of the present area were altered into zeolite facies mineral assemblages.

The Miocene volcanic formation of this district shows a folded screen structure gently inclined to northwest with an anticlinal axis and a synclinal axis (Figure 2).

Low-grade metamorphism of the Oyama-Isehara district

The present district can be divided into two parts (Zone I and Zone II) by the presence or absence of prehnite as a metamorphic mineral formed in Miocene andesitic pyroclastic rocks (Figure 3). Epidote also occurs, though very rarely, replacing tuffaceous matrix parts of the pyroclastic rocks of Zone II. No pumpellyite has been identified in either Zone I or Zone II.

The distributions of chlorite (almost colorless or pale green under the microscope and with low double refraction of γ-α<0.010) and clay(vermiculite or celadonite, pale green-pale brown-green under the microscope and moderately high double refraction of γ-α=0.010−0.025) found in low-grade metamorphosed volcanic rocks are shown in Figure 4. The east boundary of the distribution of chlorite almost coincides with the boundary between Zone I and Zone II defined by the first appearance of prehnite.

Sodic plagioclase is very common in altered andesitic tuff breccias in stable association with

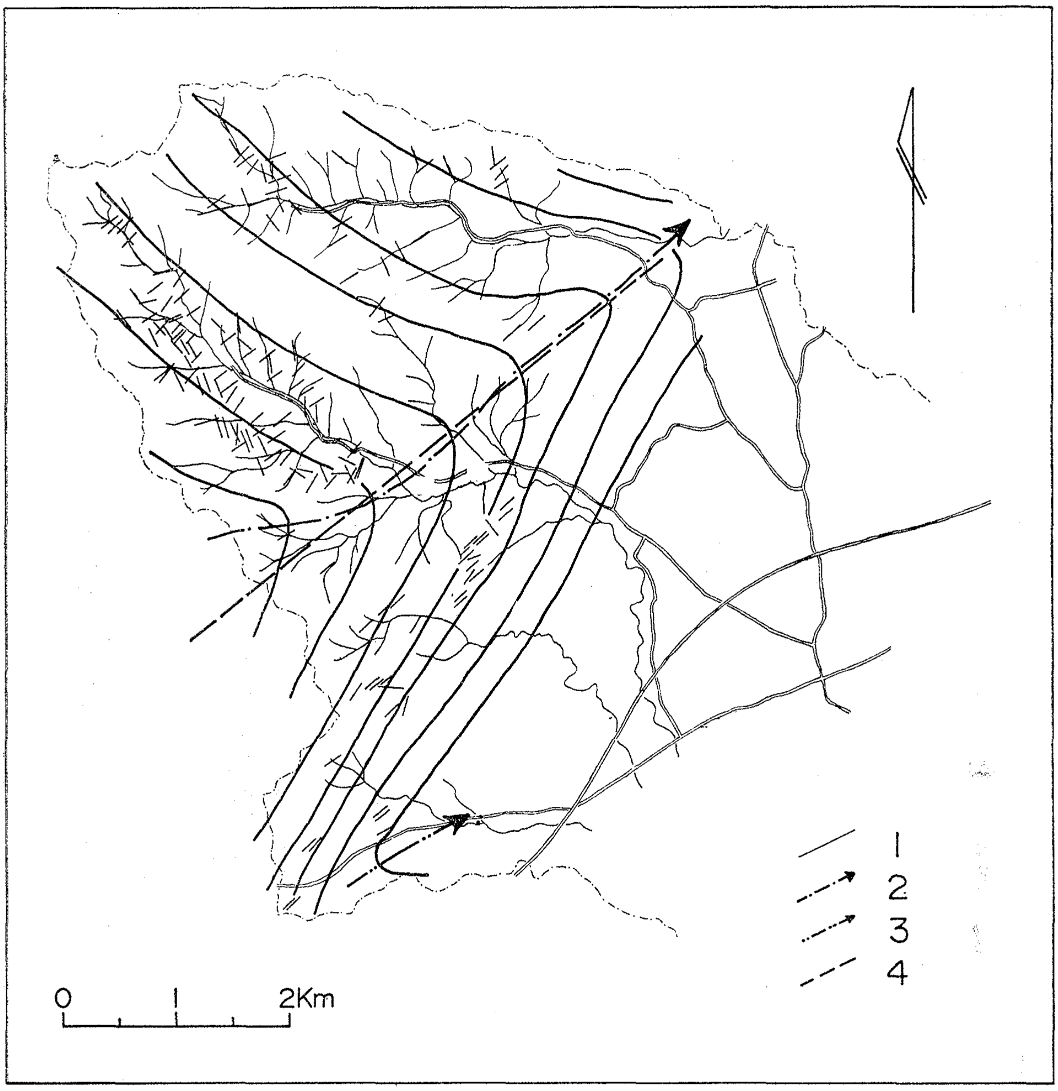

Fig 2. Folded screen structure of Miocene pyroclastic formation in Oyama-Isehara district, central Japan.
1 : Minor fault, 2 : Anticlinal axis, 3 : Synclinal axis, 4 : Koyasu fault

prehnite, chlorite or clay, laumontite and quartz. In fine-grained pumice tuffs intercalated with tuff breccia, however, mordenite-chlorite (or clay)-quartz association is common and the occurrence of sodic plagioclase is rare. Compositions of sodic plagioclases inferred from their index of refraction range from An_{02}–An_{10}. Analcime associated with laumontite and quartz is also present in some rocks of this district (Figure 5). Analcime showing no cleavage and very low refractive indices is generally isotropic but rarely shows very weak double refraction.

Laumontite and mordenite as rock-forming minerals are widely found in rocks of the present district (Figure 5). Laumontite mostly occurs in altered andesitic tuff breccia, but the occurrence of mordenite is confined to altered fine-grained pumice tuffs.

The occurrence of calcite in low-grade metamorphic rocks of the present district is not common. Calcite-bearing rocks constitute only 7% of the specimens collected from this district.

From Figures 3, 4 and 5, it is clear that the Oyama-Isehara district can be divided into two Zones characterized by the following mineral associations:

Zone II: Prehnite-chlorite (or clay)-albite-laumontite (or mordenite)-quartz

Zone I: Clay-albite-laumontite (or mordenite)-quartz

The assemblages of low-grade metamorphic minerals observed in rocks of these Zones are shown in Table 5.

The boundary between these two Zones does not coincide to any geological structures such as

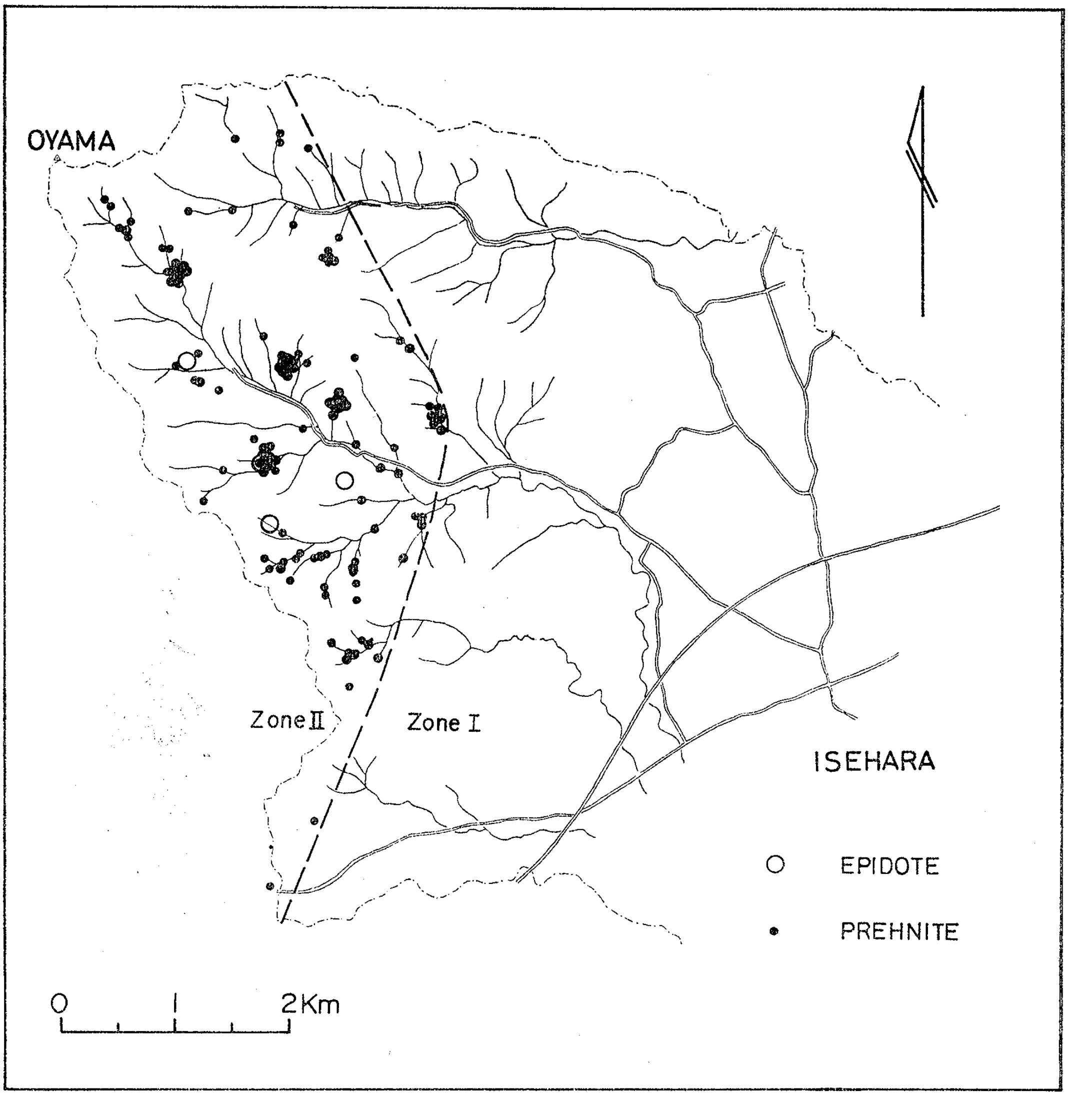

Fig 3. Distribution of prehnite-bearing and epidote-bearing altered rocks in Oyama-Isehara district, central Japan.

a stratigraphic horizon or tectonic break. Probably the boundary between Zone I and Zone II dips steeply to the east.

Pumpellyite has not been found in any of rock-specimens collected by the present authors. Zone I and Zone II must have been formed by metamorphism under the conditions of laumontite subfacies of the zeolite facies. It has been reported from many fields of the world that prehnite is stably formed in rocks of the higher-grade part of the area where laumontite was stably formed (SEKI, 1969).

The clear oblique relation between the metamorphic zone boundary and stratigraphic horizons suggests that the metamorphism in the present district must have caused not by simple diagenetic process but by an other geological process such as the intrusion of quartz diorite magma from which most of heat energy to cause metamorphic reactions came (SEKI and others, 1969a; SEKI and others, 1971).

Veins composed of prehnite and quartz are developed in some prehnite-bearing rocks of Zone II. No prehnite-bearing vein have been found in Zone I. Seggregation veins chiefly composed of Ca-zeolites such as laumontite and stilbite widely occur along joints or fissures of rocks in Zone I and Zone II. The thickness of these veins varies from 0.3 mm to 1.3 cm. Mineral associations of these zeolite veins are as follows: laumontite, laumontite-quartz, laumontite-stilbite, laumontite-stilbite-quartz, laumontite-stilbite-chabazite, stilbite, and stilbite-quartz. It is commonly observed that when veins are composed

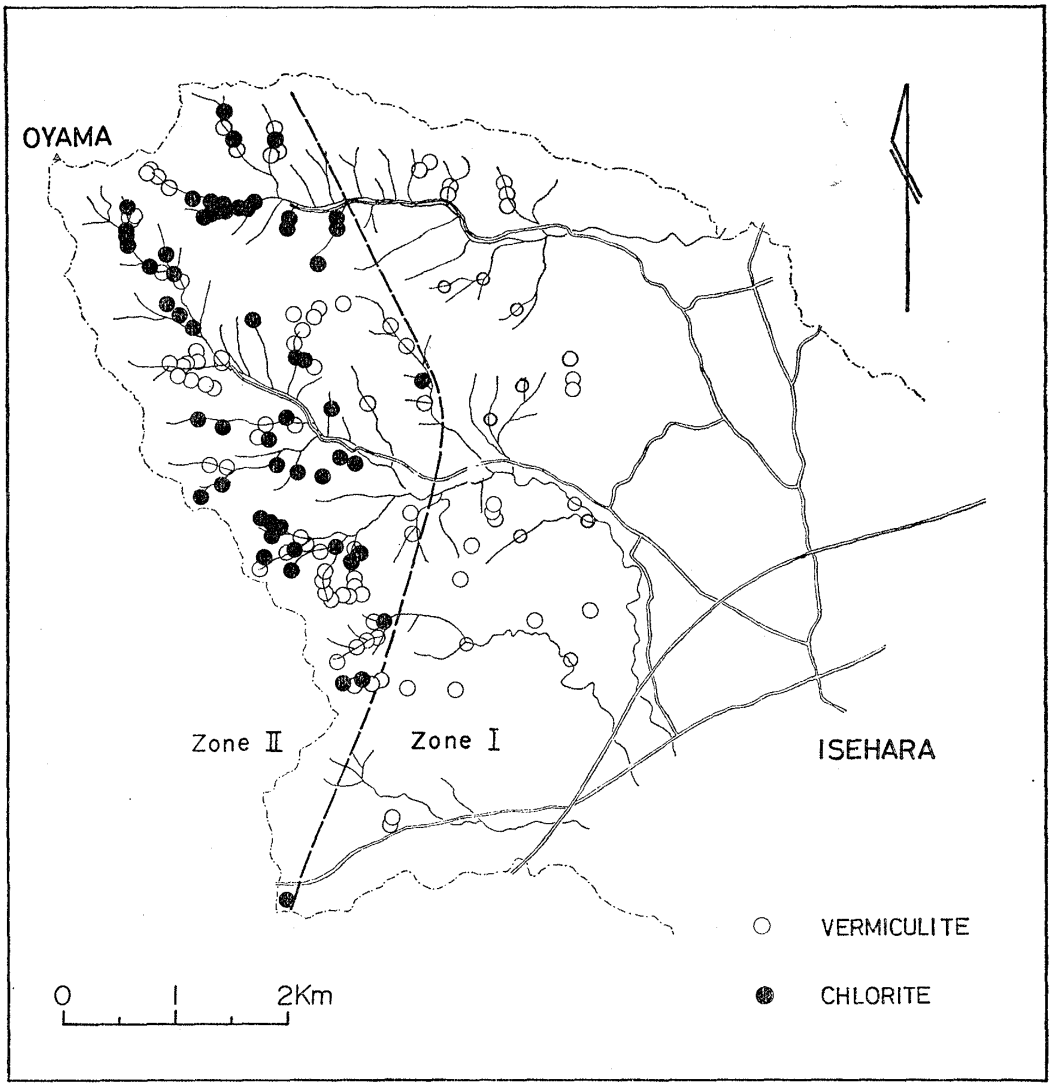

Fig 4. Distribution of chlorite and clay (vermiculite-celadonite) formed in altered rocks of Oyama-Isehara district, central Japan.

of laumontite and stilbite the milky chalk-like laumontite constitutes the marginal part and the clear semi-transparent stilbite fills the central interstitial part of veins. It can also be observed in the field that minor faults which cut the veins composed of laumontite or laumontite-stilbite are filled with stilbite and quartz. Probably laumontite in veins was formed during zeolite facies metamorphism of Zone I and Zone II but stilbite in veins must have been formed during the time of retrogressive fall of temperature from the laumontite subfacies to lower-grade. No wairakite-, mordenite-and calcite-bearing veins have been found.

Stability of mordenite in the laumontite subfacies of the zeolite facies

It has been said previously in this paper that, in the Oyama-Isehara district, laumontite mostly occurs in altered tuff breccias but the occurrence of mordenite is confined to thin beds of altered fine-grained pumice tuff. In this chapter the stability of mordenite in the zeolite facies metamorphism will be discussed in some detail.

(a) Stable association of mordenite with laumontite and prehnite in the Oyama-Isehara district.

In some altered fine-grained pumice tuffs, both mordenite and laumontite can be observed. In these cases, mordenite forming characteristic radial aggregates seems to be stably associated with well crystallized tabular crystals of laumontite.

The mordenite-bearing altered fine-grained pumice tuffs are usually cut by veins which are chifly composed of laumontite or laumontite-

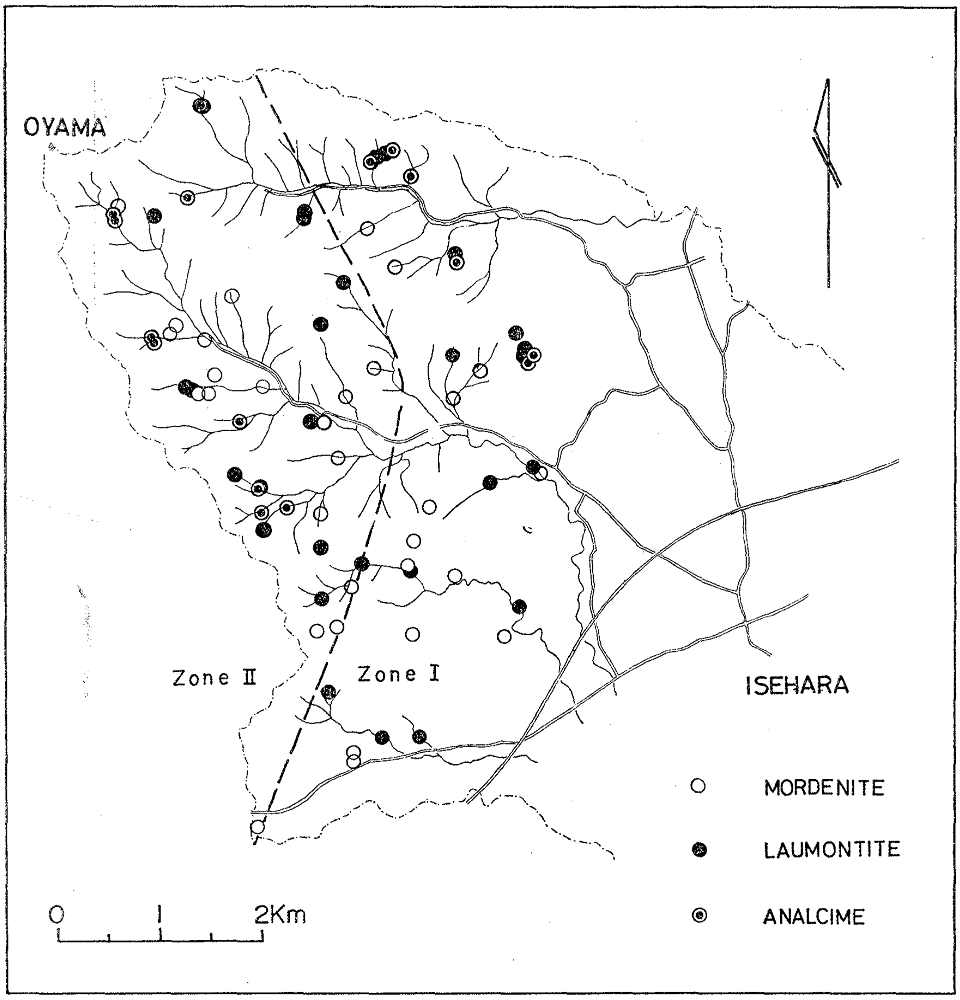

Fig 5. Distribution of laumontite, mordenite and analcime-bearing altered rocks in Oyama-Isehara district, central Japan.

quartz. Druses filled by laumontite with or without mordenite occur in some mordenite-bearing pumice tuffs. In the druses filled with both mordenite and laumontite, mordenite always occurs along the wall whereas the central part is occupied by laumontite.

Fine-grained pumice tuffs having both mordenite and prehnite stably associated with chloritic minerals and quartz have been also found. In these rocks pumice fragments have been almost completely replaced by mordenite and chlorite, and calcic plagioclases have been partly altered to prehnite-celadonite-quartz assemblage.

There can commonly be observed milky white or pale greenish milky white spots with rounded or irregular forms in altered tuff-breccias. The diameter of these spots ranges from several milimeters to three centimeters. These spots are believed to have been formed as seggregation nodules during low-grade metamorphism. Although most of these nodules are composed of prehnite, laumontite, quartz and clay-celadonite, mordenite is also found in some nodules. As far as observed under the microscope the mordenites in nodules are in stable association with laumontite and prehnite. Age relation among these three kinds of minerals cannot be determined, except the development of some laumontite veins in these nodules.

From the facts described above, it can be safely concluded that mordenite, laumontite and prehnite were stably formed at almost the same time in Zone I and Zone II during the low-grade zeolite facies metamorphism. If Zone I and Zone II represent higher and lower-grade parts of the laumontite-subfacies of the zeolite facies, mordenite must be said to have been stably formed in whole range of these metamorphic grade.

(b) Previous works on the stability of mordenite in the zeolite facies

Table 5. Assemblages of metamorphic minerals observed in altered Miocene pyroclastic rocks of the Oyama-Isehara district, east Tanzawa Mountains, central Japan.

	Quartz	Sodic Plagio-clase	Chlorite-clay	Prehnite	Epidote	Laumon-tite	Mordenite	Analcime	Calcite	Hematite	Sphene
Zone II	+	+	+	+							+
	+	+	+	+	+						+
	+	+	+		+						+
	+	+	+	+		+					+
	+		+	+		+					+
	+		+	+	+	+				+	+
	+		+	+	+				+	+	+
	+	+	+	+			+				+
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	+		+			+				+	+
	+		+				+			+	+
	+	+	+								+
	+		+								+
	+	+	+			+	+				+
Zone I	+	+	+			+					+
	+		+			+					+
	+		+			+	+			+	+
	+		+			+		+	+		+
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	+		+					+			+
	+	+	+								+
	+		+								+

Mark+ means the stable occurrence. A top rank, for example, indicates the presence of quartz-sodic plagioclase-chlorite. clay-prehnite-sphene association.

Many papers on the stability of mordenite in low-grade metamorphism have been published over the last ten years. Most of them are concerned with the natural occurrence of mordenite. Several experimental works have also been carried out.

YOSHIMURA (1961, 1964) studied the alteration of Miocene pyroclastic rocks of southern Hokkaido, Japan, with the following results: (1) Laumontite associated with chlorite or clay and prehnite was formed in the lower horizon of the thick Miocene volcanic pile but the upper part of the same pile was generally altered into clinoptilolite and/or mordenite-bearing assemblages. (2) SiO_2/Al_2O_3 and Na_2O/CaO ratios of mordenite-bearing rocks are much higher than those of laumontite-bearing rocks.

UMEGAKI and OGAWA (1965) reported that in the area of Miocene pyroclastic rocks of Shimane, Japan, laumontite occurs in altered basaltic and andesitic tuffs but rhyolitic tuffs associated with these laumontite-bearing rocks were altered into mordenite-bearing mineral assemblages without laumontite. Mordenite must have formed in SiO_2- and/or Na_2O-rich rhyolitic tuffs distributed within the laumontite subfacies of the zeolite facies. Similar modes of occurrence of mordenite-bearing rocks have been also described by SUDO and others (1963).

UTADA (1965, 1970) and IIJIMA and UTADA (1966) reported the regional alteration of Miocene pyroclastic rocks (the total thickness of 4000—5000 meters) of northeastern Japan with the clinoptilolite-mordenite zone, heulandite-analcime zone, laumontite-albite-chlorite zone and epidote(-prehnite)-albite-chlorite zone. In this case it was concluded that mordenite must have been formed at temperatures lower than for heulandite and laumontite.

NAKAJIMA and TANAKA (1967) described the occurrence of mordenite and laumontite in acidic tuffs of Cretaceous Izumi formation of western Japan. In this region, mordenite must have been stably formed in or near the area where laumontite was formed. Although both of these two kinds of zeolite were found to replace rhyolitic fine-grained tuffs, it has been suggested that Na_2O/CaO and (Na_2O+K_2O)/CaO ratios of two mordenite bearing rocks are much higher than those of a laumontite-bearing rock as follows:

	mordenite-bearing rocks 1	2	laumontite-bearing rock
Na_2O/CaO	0.41	0.69	0.24
$(Na_2O+K_2O)/CaO$	0.78	3.11	0.60

The zeolite facies area of the Minakami district, central Japan, can be divided stratigraphically into two parts: the lower part characterized by the occurrence of albite, epidote and laumontite, and the higher part characterized by the development of mordenite and heulandite (NEGISHI, 1967). The grade of zeolite facies metamorphism is higher in the stratigraphically lower part than in the higher part. The occurrence of mordenite in this district must have been controlled by both the grade of metamorphism (∼temperature) and chemical composition of rocks. Mordenite occurs in rhyolitic tuffs and intrusive rocks of rhyolitic compositions. Na_2O/CaO and SiO_2/Al_2O_3 ratios of an analysed mordenite-bearing rock are signifantly different from those of an analysed laumontite-bearing rock of almost the same metamorphic grade as follows:

	mordenite-bearing rock	laumontite-bearing rock
Na_2O/CaO	0.75	0.38
SiO_2/Al_2O_3	5.91	2.32

The natural occurrence of mordenite in pumiceous pyroclastic rocks of dacite-rhyolitic compositions has also been reported from many other districts of the world (HARRIS and BRINDLEY, 1954; ERMOLOVA, 1955; HAYASHI and SUDO, 1957; SUDO, 1960; KIZAKI, 1964; MOIOLA, 1964; SHEPPARD and GUDE, 1964, 1969; TOMITA and others, 1970; HAYAKAWA and SUZUKI, 1970; SATO, 1970; MINATO and UTADA, 1968, 1970).

At Wairakei active geothermal area, New Zealand, and Katayama active geothermal area, Japan, laumontite was found in a zone between the mordenite zone and the wairakite zone (STEINER, 1955; COOMBS and others, 1959; SEKI, and others, 1969b). In these areas, the most of the mordenite zone and the wairakite zone occupy the shallowest and deeply buried sections respectively. Temperature at the depths where these zeolite zones were recorded regularly increases in the following order: mordenite zone, laumontite zone and wairakite zone. Laumontite must be stable at higher temperatures than those under which mordenite is stable. In Ohaki-Broadlands geothermal area of New Zealand, mordenite and wairakite are stably found in deep-bore hole cores of the temperature ranges of 60—170°C and 232—270°C respectively, although here laumontite has not been found (BROWNE and ELLIS, 1970).

Mordenite has been reported to occur as an authigenic mineral in marine sandstone of Cretaceous and Paleogene of Ural (RENNGARTEN, 1945; BUSHINSKY, 1950).

BARRER (1948) first synthesized sodium mordenite from a gel mixture of $Na_2O \cdot Al_2O_3 \cdot 8\text{–}12SiO_2 \cdot nH_2O$ composition at 265—295°C. AMES (1963) and SENDEROV (1963) also synthesized sodium mordenite from Na_2O–Al_2O_3–SiO_2–H_2O mixtures at 250—300°C and 150—350°C, respectively. AMES and SAND (1958) concluded from their experimental works that mordenite is a good example of a complete isomorphous series from a pure sodium to pure calcium end-members. The stability range for the synthesis of sodium mordenite was found to be about 190—300°C. Calcium mordenite, however, has been synthesized at higher temperatures of about 340—380°C. Intermediate sodium-calcium mordenite was found to have an intermediate stability limit. BARRER and DENNY (1961) obtained calcium mordenite by crystallizing a gel of $CaO \cdot Al_2O_3 \cdot 7SiO_2 \cdot nH_2O$ composition at 390°C. The range of temperature under which calcium mordenite was synthesized was generally lower than the range of temperature of wairakite stability (AMES and SAND, 1958; COOMBS and others, 1959; NAKAJIMA, 1964).

ELLIS (1960) synthesized mordenite (possibly metastably) from obsidian at 230°C during exposure to natural hydrothermal solutions within a deep drilled hole of New Zealand.

From some experimental studies, the high silica activity has been thought to be a determining condition to form silica-rich zeolites such as mordenite (SENDEROV, 1963, 1967).

(c) Genesis of mordenite-bearing mineral associations in the Oyama-Isehara district.

From many data noted in previous sections (a) and (b), it can be concluded that (1) the range of temperature under which mordenite can stably be formed is so wide as to cover the whole area of the zeolite facies (the laumontite subfacies, heulandite subfacies and even lower), and (2) relatively high ratios of Na_2O (or Na_2O+K_2O)/CaO and SiO_2/Al_2O_3 of host rocks and/or in reacted water must have been important factors promoting the formation of mordenite-bearing mineral associations.

Evidently the temperature and pressure con-

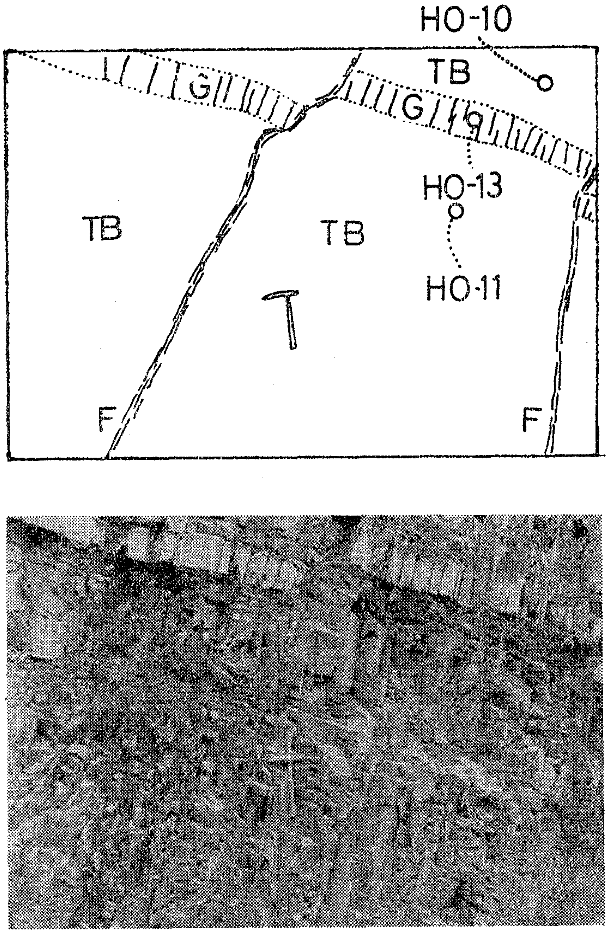

Fig 6. Photograph showing the modes of occurrence of a fine-grained pumice tuff bed in Miocene volcanic formation of Oyama-Isehara district, central Japan
(taken along the Oyama-trail, about 600 m northeast of Sengenyama)
G : Fine-grained pumice tuff
TB : Tuff breccia
F : Fault
HO-10, HO-11 and HO-13 are localities from where samples of these numbers were collected.

ditions to form mordenite-bearing rocks from fine-grained pumice tuffs in the Oyama-Isehara district were not very different from those under which intercalated lapilli tuffs or tuff-breccias were altered into laumontite- and/or prehnite-bearing mineral assemblages. Three specimens H0—10, H0—11 and H0—13 were collected from one exposure represented by Figure 6. Ho-13 is from a homogeneous fine-grained pumice bed the thickness of which is about 30 cm. H0—10 and H0—11, however, are from tuff breccias just above and below the bed of fine-grained pumice tuff. The distances between H0—10 and H0—13 and H0—11 and H0—13 are only 52 cm and 58 cm, respectively. Although petrographic nature of these three specimens are of augite andesitie, a fine-grained pumice tuff (H0—13) was mostly replaced by a mordenite-clay-quartz association and two other rocks were replaced by the laumontite-albite-clay-quartz association. No albite can be found in the modenite-bearing specimen H0—13.

Available geological and petrological evidences indicate that tuff breccia and fine-grained pumice tuff were all marine deposits indicating geosynclinal conditions. The diverse metamorphic mineralogy of these pumiceous rocks does not seem to have been due to the difference in chemical composition of sea water trapped in pyroclastic rocks during their deposition.

As has been said already in this paper, volcanic rocks of this district are of andesitic nature originally composed of augite, calcic plagioclase, magnetite and glass. No hornblende, biotite and alkaline feldspar can be detected in any tuffaceous rocks. The chemical compositions of fine-grained pumice tuffs which were replaced by mordenite-bearing mineral assemblages (Table 3 and 4) are not rhyolitic and are very similar to those of tuff breccias which were replaced by laumontite (with or without prehnite)-bearing mineral assemblages (Tables 1 and 2) (Figures 7, 8 and 9).

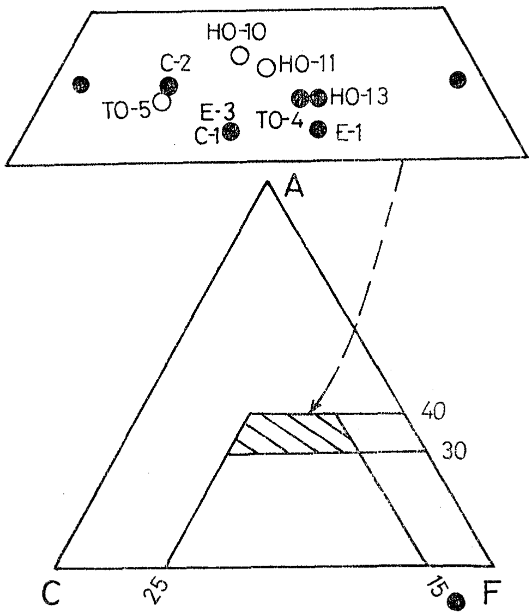

Fig 7. A-C-F diagram of analysed tuff breccias (open circles) and fine-grained pumice tuffs (solid circles) in the Oyama-Isehara district, Tanzawa Mountains, central Japan.

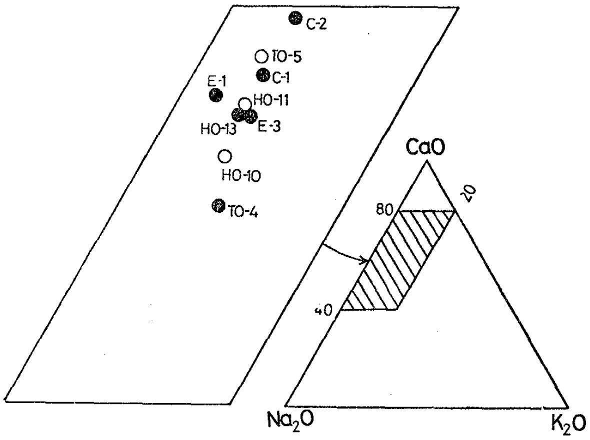

Fig 8. CaO-Na_2O-K_2O (mol ratio) diagram of analysed tuff breccias (open circles) and fine-grained pumice tuffs (solid circles) in the Oyama-Isehara district, Tanzawa Mountains, central Japan.

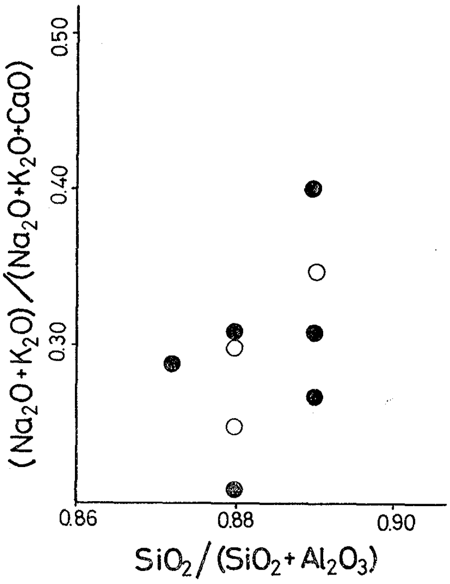

Fig 9. $(Na_2O+K_2O)/(Na_2O+K_2O+CaO)-SiO_2/(SiO_2+Al_2O_3)$ (mol ratios) diagram of analyzed tuff breccias and fine-grained pumice tuffs in Oyama-Isehara district, central Japan.

Solid circle : Fine-grained pumice tuff
Open circle : Tuff breccia

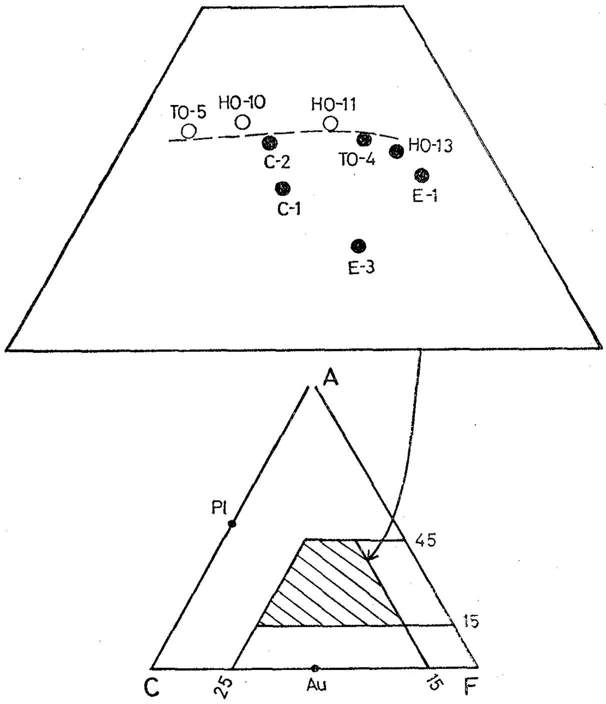

Fig 10. A-C-F diagram of chemical compositions of tuff breccia and fine-grained pumice tuff from which chemical compositions of relic augite, calcic plagioclase and magnetite were subtracted.

Solid circle : Fine-grained pumice tuff
Open circle : Tuff breccia
Pl : Calcic plagioclase
Au : Augite

In most of altered volcanic rocks of the Oyama-Isehara district, remains of augite and calcic plagioclase can be observed which escaped replacement by zeolites, chlorite-clay and other kinds of minerals. All specimens represented in Tables 1 and 3 contain relic crystals of augite, calcic plagioclase and magnetite as shown in Tables 2 and 4. Table 6 shows the chemical compositions of altered tuff breccias and pumice tuffs from which chemical compositions of relic augite, calcic plagioclase and magnetite are subtracted. Chemical composition of subtracted augite is hypothetically supposed as shown in the same Table. Chemical composition of calcic plagioclase can be estimated from their optical data as shown in Tables 2 and 4. Modes of these relic minerals were measured by thin sections of these analysed specimens (Tables 2 and 4).

Figures 10, 11 and 12 are $(Al_2O_3+Fe_2O_3-Na_2O-K_2O)-CaO-(FeO+MgO)$, $CaO-Na_2O-K_2O$ and $(Na_2O+K_2O)/(Na_2O+K_2O+CaO)-SiO_2/(SiO_2+Al_2O_3)$ diagrams in which thus calculated chemical compositions of altered volcanic rocks are plotted. In these Figures broken lines indicate the boundaries between two fields in which calculated chemical compositions of rocks with mordenite and of rocks without mordenite are plotted.

Mordenite-bearing mineral associations are less aluminous and more siliceous than mineral

Table 6. Chemical compositions of altered tuff breccias and fine-grained pumice tuffs from which chemical compositions of relic augite, calcic plagioclase and magnetite were subtracted. Chemical composition of augite in these rocks was hypothetically supposed to be as follows: SiO_2, 50.0; TiO_2, 0.5; Al_2O_3, 2.5; Fe_2O_3, 2.5; FeO, 10.0; MgO, 15.0; CaO, 19.0; Na_2O, 0.5; Total 100.0. Chemical composition of calcic plagioclase was estimated from optical data as shown in Tables 2 and 4.

	E-1	E-3	C-1	C-2	HO-13	TO-4	HO-11	TO-5	HO-10
SiO_2	59.3	63.3	61.3	62.8	64.8	64.7	61.2	64.5	64.6
TiO_2	0.9	1.0	0.8	1.0	0.7	0.7	0.8	0.8	0.8
Al_2O_3	12.3	10.4	11.4	12.0	11.3	13.0	13.2	14.0	13.3
Fe_2O_3	1.5	1.1	1.0	0.6	0.6	1.6	4.3	1.3	2.9
FeO	2.9	3.1	3.8	3.4	3.0	3.9	3.0	3.0	2.9
MgO	3.9	3.6	2.3	1.7	3.1	2.3	3.7	1.8	2.1
CaO	3.2	4.5	5.0	5.4	3.2	3.6	4.7	6.3	4.0
Na_2O	2.5	1.7	1.7	1.0	1.5	2.3	1.8	2.0	2.3
K_2O	0.6	1.3	1.0	1.0	0.8	1.3	0.9	0.9	1.0
H_2O	12.9	10.0	11.7	11.1	11.0	6.6	6.4	5.4	6.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

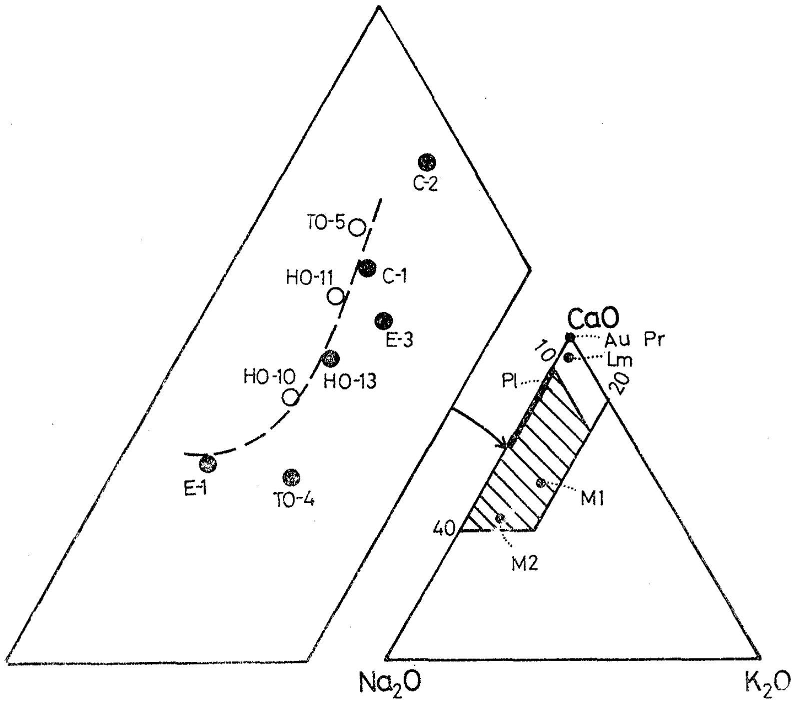

Fig 11. CaO-Na_2O-K_2O (mol ratio) diagram of tuff breccia and fine-grained pumice tuff from which chemical compositions of relic augite, calcic plagioclase and magnetite were subtracted.

Solid circle : Fine-grained pumice tuff
Open circle : Tuff breccia
Pl : Calcic plagioclase
Au : Augite
Pr : Prehnite (SEKI and others, 1971)
Lm : Laumontite (SEKI and others, 1971)
M 1 : Mordenite (TOMITA and others, 1970)
M 2 : Mordenite (SHEPPARD and GUDE, 1969)

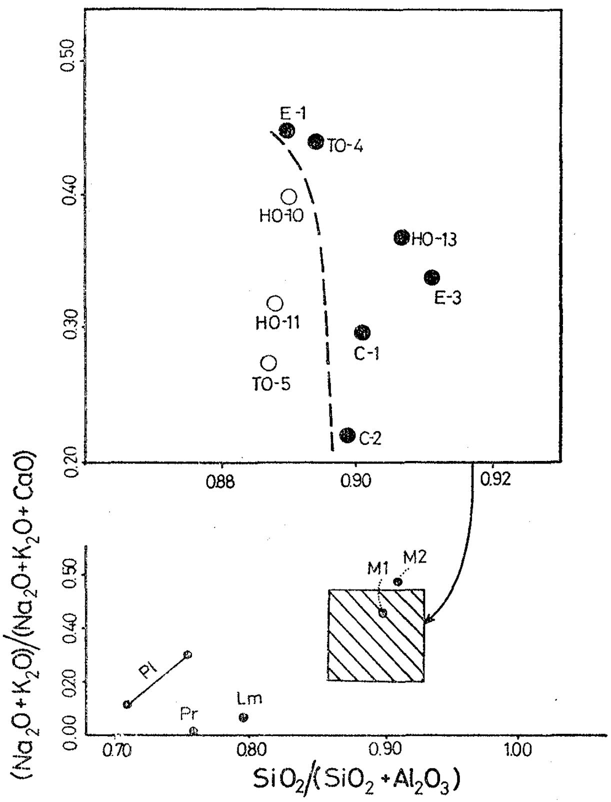

Fig 12. $(Na_2O+K_2O/(Na_2O+K_2O+CaO)$-$SiO_2/(SiO_2+Al_2O_3)$ (mole ratios) diagram of tuff breccia and fine-grained pumice tuff from which chemical compositions of relic augite, calcic plagioclase and magnetite were subtracted.
Solid circle : Fine-grained pumice tuff
Open circle : Tuff breccia
Pl : Calcic plagioclase
Pr : Prehnite (SEKI and others, 1971)
Lm : Laumontite (SEKI and others, 1971)
M1: Mordenite (TOMITA and others, 1970)
M2: Mordenite (SHEPARD and GUDE, 1969)

associations with laumontite but without mordenite (Figures 10 and 12). This is in harmony with the fact that laumontites are more aluminous and less siliceous than mordenites.

Figure 12 indicates that mordenite-bearing assemblages have higher ratios of $SiO_2/(SiO_2+Al_2O_3)$ than those of mordenite-free and laumontite-bearing assemblages. $SiO_2/(SiO_2+Al_2O_3)$ ratios of mordenites are much higher than those of laumontite and prehnite.

It must be noted that water contents (H_2O+ plus H_2O-) of mordenite-bearing rocks derived from fine-grained pumice tuffs are much higher than those of mordenite-free rocks derived from tuff breccias (Figure 13). Mineral associations in pumice tuffs and tuff breccias can be represented by the left hand side and right hand side of the following reaction respectively:

$$\underset{\text{Mordenite}}{Na_2CaAl_4Si_{20}O_{48}\cdot 14H_2O} \rightleftharpoons \underset{\text{Laumontite}}{CaAl_2Si_4O_{12}\cdot 4H_2O} + \underset{\text{Albite}}{2NaAlSi_3O_8} + \underset{\text{Quartz}}{10SiO_2} + \underset{\text{Water}}{10H_2O}$$

The oxidation states of altered volcanic rocks do not show any clear difference of their original natures such as pumice tuff and tuff breccia, or of their alteration products such as mordenite-bearing and mordenite-free varieties (Figure 13).

Probable mechanisms to explain the formation of mordenite-bearing rocks from fine-grained pumice tuffs are as follows:

(1) Fine-grained pumice tuffs probably were easily compacted to relatively impermeable beds during the diageteic stage. Sea water trapped in such impermeable pumice tuffs was easily reacted with glass shards to devitrify them into zeolite-bearing mineral assemblages. Most of crystals of augite and calcic plagioclase were preserved without alteration into zeolites and clay. Average amounts of relic crystals of calcic plagioclase and augite in altered pumice tuffs are 12.1% and 4.8%, respectively. Chemical compositions of pumice fragments are unknown, but must have been very close to those calculated by the subtraction of the chemical composition of relic calcic plagioclase, augite and magnetite from the bulk chemical composition of pumice tuff. It means that the pumice fragments must have had moderately higher ratios of $(Na_2O+K_2O)/CaO$ and $SiO_2/(SiO_2+Al_2O_3)$ than those of bulk compositions. Thus the devitrification of glass shards in pumice tuffs formed mordenite-bearing assemblages.

(2) Tuff breccias which were chiefly composed of relatively coarse-grained crystalline pyroclastics with small amounts of pumice materials were relatively permeable to water. Sea water trapped in these rocks reacted with calcic plagioclase and augite to form laumontite and/or prehnite-bearing mineral associations. Average amounts of relic crystals of calcic plagioclase and augite in altered tuff breccias are less than those of pumice tuff as follows: calcic plagioclase 5.5%, augite 3.4%.

(d) Substitution of Ca for Na in mordenite and its stability

As has been noted in this paper, synthetic works show that stability temperature of mordenite generally increases with the substitution of Ca for Na.

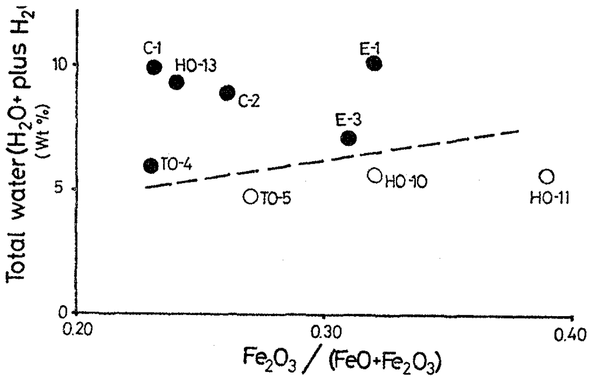

Fig 13. Water (H_2O+plus H_2O-)-Fe_2O_3/ ($FeO+Fe_2O_3$) (mol ratio) diagram of analysed tuff breccias (open circles) and fine-grained pumice tuffs (solid circles) of the Oyama-Isehara district, Tanzawa Mountains, central Japan.

Mordenite in nature is formed in relatively wide range of metamorphic grade from the higher-grade part of the laumontite subfacies to lower-grade part of the heulandite and the mordenite subfacies (SEKI, 1969). MIYASHIRO and SHIDO (1970), who summarized petrographic data recently accumulated from New Zealand, Japan and Iceland on zeolite facies metamorphism, stated that the Na-rich mordenite-quartz association may have been formed at temperatures lower than for laumontite-quartz association.

It is highly probable that the Ca/(Ca+Na) ratio of mordenite which have been formed in the laumontite subfacies area is higher than that of mordenite formed in the conditions of the heulandite and the mordenite subfacies areas. This problem will be discussed in detail in another paper.

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丹沢山地東部，大山・伊勢原地域の低変成相におけるモルデナイトの安定性

関　陽太郎・大木　靖衛・小鷹滋郎・小沢　清

（要　旨）

大山・伊勢原地域の中新世火山堆積岩層は，プレーナイト，ローモンタイト，エピドート，曹長石，緑泥石鉱物の組合せのちがいによって，2つの Zone に分けられる．これらの Zone は，それぞれ，沸石相のローモンタイト亜相の比較的高温部と比較的低温部を示すものであろう．

モルデナイトはこの地域全体にわたり見出されるが，その産出は，細粒の軽石質凝灰岩の薄層に限られている．

これらと互層する，軽石をほとんどふくんでいない凝灰岩・凝灰角礫岩にはモルデナイトはほとんど出来ていないで，ローモンタイトが特徴的に産出する．沸石相でのモルデナイトをふくむ鉱物組合せの形成には，すくなくとも岩石の組織が，かなり重要な役割りをはたすらしい．