Title	Zeolitic Alteration of Perlite Complex in Tsuchihata Mining District, Northeast Japan
Author(s)	Hunahashi, Mitsuo; Watanabe, Jun; Kim, Cheoul Woo
Citation	Journal of the Faculty of Science, Hokkaido University. Series 4, Geology and mineralogy, 15(1-2), 41-79
Issue Date	1972-03
Doc URL	http://hdl.handle.net/2115/36011
Туре	bulletin (article)
File Information	15(1-2)_41-80.pdf



ZEOLITIC ALTERATION OF PERLITE COMPLEX IN TSUCHIHATA MINING DISTRICT, NORTHEAST JAPAN

by

Mitsuo Hunahashi, Jun Watanabe, and Cheoul Woo Kim

(With 8 Tables and 17 Text-figures)

(Contribution from the Department of Geology and Mineralogy, Faculty of Science, Hokkaido University, No. 1222)

Introduction

Concerning to the formation of zeolite facies, stress has been laid on the burial process as the main controlling factor to produce suitable mineral assemblages. It is said, that the increase of pressure and temperature caused by the accumulation of sediments at the deeply buried horizons brings the sediment of every depth into the corresponding new mineralogical equilibrium (Turner et al. 1958, Coombs et al. 1959).

The first proposal that the formation of zeolitic mineral is to be dealt with facies conception was made by P. ESKOLA (1939). He himself, however, did not appreciate the zeolitic assemblages to be produced under sufficient equilibrium condition. He was rather in belief that their natures depend largely upon the composition, reaction and concentration of introduced solution, since they are considered to be originated from the imbibition of hydrothermal solution. At their formation, there is no chance to attain true equilibrium here owing to successive overlapping in mineralization. Accordingly, ESKOLA noted that the formation of zeolitic minerals has no claim to set justifiable position in the facies table equivalent to those of the other well defined facies.

Although Turner noted that the conception of his newly defined "zeolite facies" is the revived form of Eskola's original proposal, much attention must be paid for the differences between new and old ones. Furthermore, the materials dealt with respective conceptions seem to have quite different natures to each other. One considers regionally developed zeolitic mineral assemblages derived from thickly buried geosynclinal sediments that are involved in the development of orogenic process. The other deals with rather local phenomenon having metasomatic nature that prevailed in the latest stage of igneous activity.

In Japan, a great deal of occurrence of zeolitic mineral assemblages is mentioned in several parts of the country, which has drawn much attentions about their natures (Hunahashi & Yoshimura 1966, Iijima & Utada 1966, Iwao 1961, Kizaki 1965, Nakajima & Koizumi 1962, Shimazu & Kawakami 1967, Sudo, Nishiyama, Chine and Hayashi 1953, Utada 1970, Yamagishi 1965, Yoshimura 1960). A reason why such alteration phenomena are especially interesting is that they are initimately involved in the development of "green tuff activity". The activity is characterized by the tremendous amount of volcanic effusions and their derivative pyroclastic sediments. Almost all of volcanics and pyroclastics, especially those of Miocene age, are more or less altered hydrothermally in some kinds of autometasomatic style to have greenish tint. They are regarded as a manifesting sign of the fundamental characters of igneous activity carried over the whole green tuff region. The zeolitic alteration may also be defined as one of the constituents of such alteration process.

Recently, the authors have been aquainted with some commonly accepted zeolitic minerals which were replacing with metasomatic appearance the perlite complex of the Tsuchihata mining district. The nature of these zeolite formations seems to be rather suitably interpretated under the conception proposed by Eskola as a representative case of his "zeolite formation (Zeolithbildung)".

1. Geological environment of the perlite complex

The green tuff region, a peculiar geotectonic unit of the Japanese islands, occupies the whole inner side (continental side) of the island arc. Its typical and most prominent development is shown in the region inner half of the northeast Japan. There are three parallel running belts formed of dotted arrangement of effusive centres, viz. the eastern marginal belt, the main belt at the central part and the Dewa-Oga belt in the western side. As to the scale of volcanic activity, that of the main belt is most distinctive than those of the other belts. The main belt is nearly coincident with the site of present topographic back-bone range (Minato et al. 1965).

In the southern part of Iwate prefecture, mid-part of northeast Japan, well studied geological cross section of the back-bone range is exposed along the river course of Waga. The mentioned perlite complex is contained in this cross section, of which tectonic situation is referred to the western wing of the main belt.

According to the recent studies, central part of the main belt is occupied by propylite lavas and their breccias belonging to the earliest effusion of green tuff

activity (Oarasawa formation) and upheaved basement of granite massif. They are conformably covered by the thick formation of dacitic tuff and breccia with intercalation of mudstones in its upper horizon, which is designated as the Oishi formation. Both the Oarasawa and Oishi formations are referred to be of early Miocene in age.

The central part of the main belt began to upheave in the later stage of Oishi epoch forming sinking basin in further external parts at the same time. Since, the site of succeeding effusive activity and the sedimentary accumulations were pushed aside toward more external sides from the activated centres prevailed at the Oarasawa and Oishi epochs. A broad belt of 4 km width flourished in such volcanic effusions and flexural movement at the latest stage of Oishi epoch runs continuously in north-south trend along the western and eastern sides of the central part. The first appearance of liparitic rock including mentioned perlite in the back-bone range is developed in such environment. It is accompanied by dyke swarms of propylite, dacite, basalt and minor instrusive mass of holocrystalline varieties. Several epithermal type of ore mineralizations are associated with them (AKIBA et al. 1966, KITAMURA 1959, 1960, OIDE et al. 1966, OZAWA et al. 1971).

A member formed exclusively of liparitic rocks allied to the upper most horizon of the Oishi formation is localized around Tsuchihata mining district. It is a complex of various kinds of perlitic rock. The details of the complex are to be described in the next chapter.

The perlite complex is covered by marine formation which is developed over a wide extent in western side of the back-bone range. It is designated as the Kotsunagi formation, which is correlated to the Onnagawa formation of the middle Miocene age. This is the most prominently developed marine formation through the green tuff region. In the district, it is composed by the alternation of sandstone and mudstone. The relation of the Kotsunagi formation to the perlite complex is that of unconformity in this district. However, it is conformably transited from the other top member of the Oishi formation to the base of the Kotsunagi formation in the district far apart from the perlite complex. Among the basal part of the Kotsunagi formation, small fragments or pebbles of several kinds of volcanics including perlite wholly converted into zeolitic alteration are found. Except the perlite pebble, none of zeolitic formation can be detected in the matrix of conglomerate or pebbles of the other rock species. It tells us that the zeolitic alteration had already been accomplished before the perlite complex was submerged under the sea of Kotsunagi epoch.

2. Tsuchihata perlite complex

The perlite complex here studied is laid along the course of river Ko-onigase that runs from south to north and joins to the river Waga at the town of Kawashiri. It continues, forming a narrow belt of 2 km width in N-S trend, further to the north beyond the town of Kawashiri. The complex is constituted by perlite lavas and its pyroclastics, and can be divided into upper and lower members.

It is typically represented in the area southwest of the Motoyama deposits of the Tsuchihata mine. Detailed geological arrangements of the complex mapped in this area are given in Fig. 1-a and b.

The lower member of the complex is cropped out along the bottom of the valley spreading more extensively than that of upper member which is restricted in northeastern side. Both members are covered by the Kotsunagi formation that laid nearly horizontal and disposed to the high level on both slopes of the valley. The lower member spreads widely as a formation of 250–300 m in thickness, that is confirmed by boring carried by the mine at the eastern wing of the complex. Concerning to the upper member, it occurs as a local heap having no wide spreading. The perlite complex as a whole laid comformably over widely developed third member (O₃) of the Oishi formation. The complex is considered as a local member formed around the Tsuchihata mining district at the latest stage of the Oishi epoch (Kurosawa & Tokitsu 1961, Matsukuma 1970).

A) Lower member: ---- There can be distinguished several rock types among the constituents of the lower member. In their field occurrence, each rock type is arranged into several zones that stretch parallel in north-south trend. The central part of the distribution domain of the lower member is represented by massive perlite. It forms a narrow belt of $250-350\,\mathrm{m}$ width and runs north to south forming a structural centre of the complex as shown in Fig. 1-b. It is appeared in a massive form without any flowage or preferred orientation. However, in its external part, it transits gradually to that having fluidal texture. At the same time, there exist breccia or agglomeratic varieties of perlite of the same nature.

The external part of the central facies is succeeded by the alternation zone which is formed with lavas and breccias or agglomerate of 2-5 m thickness. Often, thin seams of tuffaceous member which has marine character are intercalated with them. The stratoform due to such alternation becomes clearer to both sides of the complex. The peripheral part observable in this district is exclusively represented by tuffaceous member and fine breccia of perlite having some features of sorting effect.

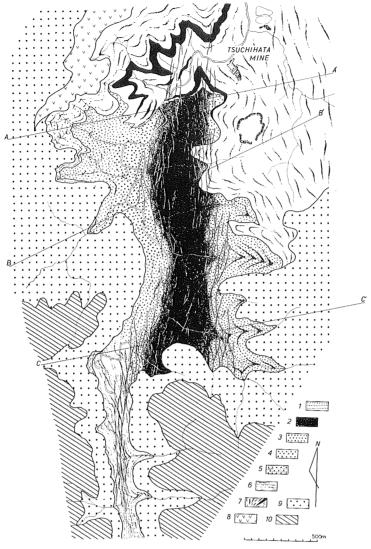


Fig. 1-a
Geological map of southern part of the Tsuchihata mining district.

- 1; Third member (0_3) of the Oishi formation
- 2; massive perlite
- 3; fluidal perlite
- 4; alternation of lava and breccia
- 5; alternation of breccia and tuff
- 6; tuffaceous formation
- 7; upper member
- 8; andesite lava (in Kotsunagi formation)
- 9; Kotsunagi formation
- 10; Kurosawa formation

Network lines drown in the central part of the domain of lower member represent the shearing cracks schematically.

lower member

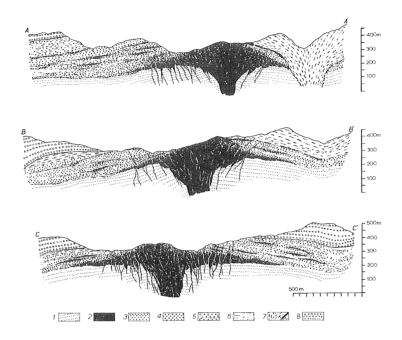


Fig. 1-b
Profiles of Fig. 1-a.
A-A', B-B' and C-C' are to be referred to those cited in Fig. 1-a.
(The legend is similar to that of Fig. 1-a.)

These stratification inclines in low dip of $10^{\circ} - 20^{\circ}$ to the west and east on both sides of central core and forms, as a whole, an anticlinal structure having the axis of N-S trend.

It is considered that the perlite effusion held in this district is carried through a fracture of N-S trend formed along the present Ko-onigase river, and pushes its effusive products aside in agglomeratic or breccia form. It seems to be sure that the central perlite is not the later intrusion into mentioned pyroclastic formation.

B) Upper member: ---- Perlitic rocks developed in northeastern part of the district have somewhat different feature from those of lower member. Stratigraphically, they are disposed as a whole conformably upon the lower member. Greater part of them have pinkish colour and distinct fluidal texture.

Alternation formed of lava, breccia or agglomeratic layers similar to that of lower member is widely developed with them. And also, they often intercalate perlitic lavas having similar feature already mentioned with lower member.

Although both lower and upper members have many common features, some distinct differences between both members in the arrangement of flow layer are present. Greater part of fluidal layer or plane of alternation of the upper member is disposed nearly flat, espcially in northern area. Whilst, several boring results carried around the Motoyama deposits by the Tsuchihata mine confirmed the existence of steeply inclined flow layer within the extent of immediate neighbourhood of the deposit. Flat laying layer transits gradually into steep one as it approaches to that area. Although the original rock facies of that area is obscured by the strong alteration due to ore mineralization, it seems to be constituted by massive perlite wholly devoid of breccia or tuffaceous members.

In this respect, these perlitic rocks were poured out from the site adjacent to the Motoyama deposits and spreaded on all sides horizontally to cover concordantly the lower member. It is considered that this effusive body has a rock of funnel shaped form of large diameter (Fig. 1-b). The style of effusion is rather referrable to that of central eruption to the activity of upper member compared to those of lower member take the style of fissure eruption.

C) Kotsunagi formation: ---- The perlite complex is unconformably covered by widely developed sedimentary formation, Kotsunagi formation. In this district, its succession begins with the basal conglomerate, and it is gradually transited to repeated alternation of conglomerate and sandstone, and further to thick piling of fine sandstone which often intercalates thin seams of mudstones and acidic tuff. The conglomerate contains the pebbles derived from the perlite complex other than that from the Oishi and Oharasawa formations. Greater part of these pebbles is angular or subangular. The amount of pebble of well water worn type is rather scarce. It is worthy of note that the zeolitized green pebbles derived from lower member of the complex are easily detectable by naked eyes. Although the formation is nearly free from volcanic materials near to the basal part, a lava flow of andesite is intercalated.

3. Zeolitic alteration

As already mentioned, the perlite complex of the district is suffered by a prominent zeolitic alteration. The alteration aureole spreads nearly to the top horizon of the upper member. However, strongly altered part is chiefly limited within the level of the lower member. The site of massive perlite proper, the central core of the lower member, is the site of the most prominent alteration.

The zeolitic mineral associations among the mentioned alteration aureole is so much diverse that several associations co-exist even within an area of one thin section. However, there can be discriminated main alteration facies and subordinate ones among them. As a whole, this main alteration facies is well revealed in its rock appearances which are recognizable in field. Zonal arrangement of such alteration facies is remarkably represented in this district. Its field arrangement is nearly the same with that of rock types already mentioned. Their spatial disposition into zones is shown in Fig. 2-a and b as the alteration map.

The grade of alteration is most prominent in the central part of the lower member, zone of massive perlite, and it gradually fades out to both external parts. Thus established alteration zones are as follows.

- 1) celadonitized zone
- 2) light greenish zone
- 3) white coloured zone
- 4) flinty zone
- 5) alteration aureole formed by ore mineralization

They are disposed into long continued zones of N-S trend from central core to the external parts.

1) Celadonitized zone: ----From the neighbourhood of club house of the mine to the south a zone of high grade alteration of $250-350\,\mathrm{m}$ width continues about $1500\,\mathrm{m}$ long to reach spa Nakayukawa where the complex is buried under the Kotsunagi formation. It may be continued further to the south diving beneath the Kotsunagi formation. Its extent nearly coincides the zone of massive perlite.

Within this zone, massive perlite, which would have been originally in the dark gray colour, turns into grass green and is characterized by a network development of deep greenish celadonitized seams which may have been formed following the crushing cracks or opening (Fig. 3).

2) Light greenish zone: ---- Above mentioned celadonitized zone gradually transits to both external parts where the rock appearance, as a whole, turns to that of light green colour. There is no network of deep green celadonitized seams. However, the grade of greenish tint of the rock is variable. Local layer of more greenish coloured network seams containing nearly white blocky masses are often met.

The areal extent of this alteration also nearly coincides the zone of fluidal perlite.

3) White coloured zone: ---- A zone wholly devoid of greenish part is developed in further external parts transited from light greenish zone. In their outlook, several features of their original texture such as breccia, tuff or

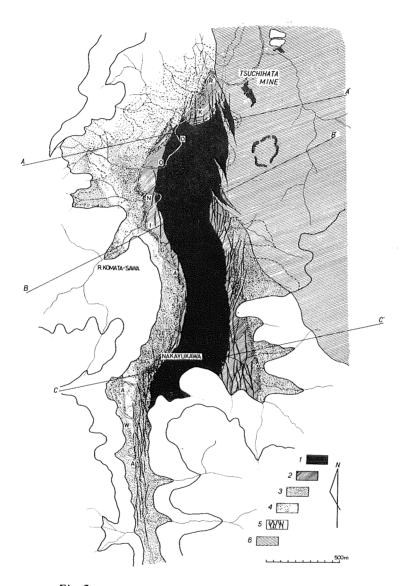


Fig. 2-a

Alternation map of the Tsuchihata perlite complex.

- 1; celadonitized zone
- 2; light greenish zone
- 3; white coloured zone
- 4; flinty zone
- 5; celadonite vein
- 6; alteration aureole due to ore mineralization

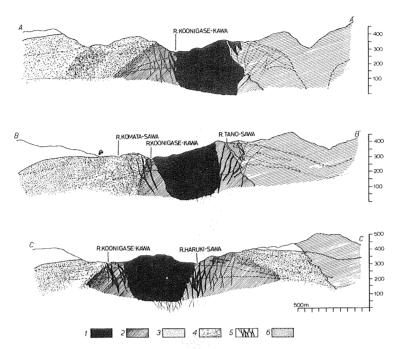


Fig. 2-b Profiles of Fig. 2-a. (The legend is similar to those of Fig. 2-a.)

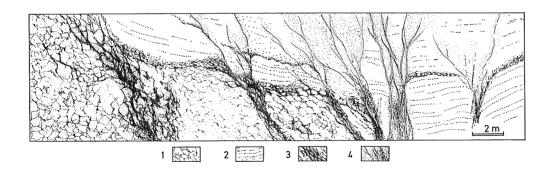


Fig. 3
Sketch of the representative outcrop in celadonitized zone.

- 1; network celadonitized seams
- 2 ; tuffaceous member intercalated between massive lavas
- 3; strongly celadonitized vein formed part
- 4; mordenite-cristobalite vein

stratification are preserved. However, as will be noted in a later chapter, their constituent is full of zeolitic minerals. This zone nearly coincides the zone of alternation of breccia and lava.

- 4) Flinty zone: ---- The outermost part observable in this district is formed by white compact rock of flinty appearance. Its original rock is chiefly confined to the tuffaceous members, in which the stratification and rock texture of tuff are preserved.
- 5) Alteration aureole formed by ore mineralization: ---- In northeastern part of the district, an aureole of alteration by ore mineralization formed around the Motoyama and other deposits is widely developed. It has finely disseminated pyrite that can never be mentioned for the zeolitic alteration, and is strongly silicified. Its starting material seems to be the rock suffered by zeolitic alteration. Several remnants of zeolitic alteration can be detected in its frontal part of the aureole.

4. Petrographical description of altered rocks

Petrographical description of perlitic rocks of the complex in their unaltered fresh state and in their variously altered state due to the mineralization of zeolites and allied minerals is given in this chapter.

A) Unaltered original rocks

As noted in the foregoing chapter, there are almost no unaltered rocks within the lower member. However, unaltered remnant blocks barely escaped from alteration are seldom obtained especially from external part of the alteration aureole. On the contrary, greater parts of those of upper member stay in unaltered state. From these materials, the following rock types may be discriminated as the starting materials previous to the alteration.

- 1) perlite proper
- 2) fluidal perlite
- 3) perlitic breccia
- 4) perlitic tuff
- 1) perlite proper: ---- Dark grayish colour with perlitic lustre is the characteristic outlook of this rock type. It is massive without any preferred orientation. In its outcrop spheroidal cracks forming blocks of $10-30\,\mathrm{cm}$ diameter are well observed.

Under the microscope, greater part of it is formed of homogeneous glass. The phenocrysts are of plagioclase, quartz and augite less than 5% in total amount. In some cases, part of these phenocrysts are in crushed state. When the quartz is represented in large crystal, it is always strongly corroded. Whilst, when it is not represented as phenocryst, radial aggregation of chalcedonic

quartz are often developed in microporphyroblastic form. The compositional variation range of plagioclase is strikingly limited and each composition is plotted to the extent of An_{28} - An_{40} . Its central value is An_{33} (mean value for 36 individuals measured). The groundmass glass is characterized by the typical spherulitic crack (Fig. 4). Its refractive index is in the range of N = 1.471 - 1.472.

Although greater part of the rock stay in unaltered state, some signs of alteration are feebly developed. They are limited only to the area of chloritization or montmorillonitization of glass developed in filmy seams along the perlitic cracks (Fig. 5). Rarely, around plagioclase phenocryst segregative pools filled by laumontite in radial aggregate grown on the wall of the pools and their core filled by clinoptilolite (Fig. 6).

2) fluidal perlite: ---- This sort of rock type has pinkish colour and strongly orientated fluidal texture in its appearance. However, a transitional type to massive perlite is often present with mixed features in outcrops.

Under the microscope fluidal texture of glass base containing parts of perlitic cracking is rather common. The nature and amount of phenocrystic plagioclase, quartz and augite are nearly the same to those of perlite proper. However, crushing or cracking of phenocrystic minerals are more prominently developed.

The sign of alteration is represented along the cracking surface as the thin films of chlorite aggregation which is also developed along the fluidal line of glass base (Fig. 7).

3) perlitic breccia: ---- This rock type has somewhat different features such as agglomeratic type having the blocks up to 10 cm in size or that of tuffaceous type formed of the aggregation of very fine breccias. Often, a weak stratification due to the alternation of coarse and fine breccias is represented in the outcrop.

Under the microscope, the breccia has the feature of fluidal perlite chiefly composed of glass of similar character above mentioned.

All the phenocrystic minerals are more or less crushed, and are rather rich in fragmental form.

The sign of alteration is represented similarly as those of above mentioned 1) and 2). Besides, it is more thoroughly represented by the part interstitial to the breccias filled with fine crushed fragments.

4) perlitic tuff: ---- This rock type is represented by comparatively more compact, homogeneous lithology of white colour. Often, it shows lamination due to the sorting effect. In its outlook, we can never discriminate the component minerals or glass fragments.

Under the microscope, it is composed of fine fragments of quartz,

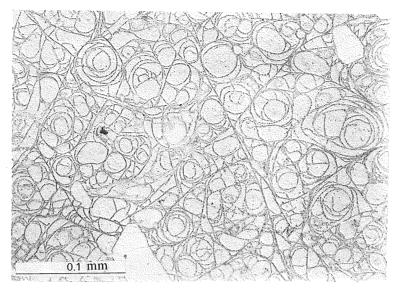


Fig. 4 Unaltered fresh perlite. fresh glass N = 1.472

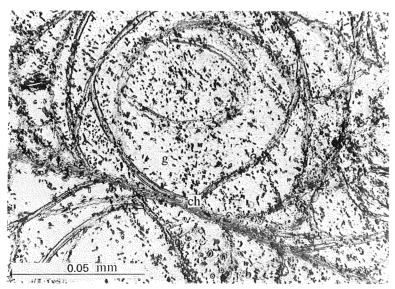
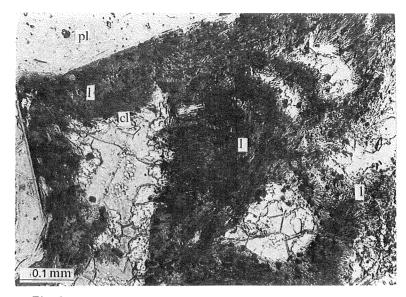


Fig. 5 Chloritization developed along the perlitic crack.

- g) fresh glass N = 1.471
- ch) chlorite film



 $\label{fig.6} \textbf{Fig. 6} \\ \textbf{Laumontite aggregation developed around plagioclase phenocryst.}$

- pl) plagioclase phenocryst
- 1) laumontite $\gamma = 1.519 \ \alpha = 1.508$
- cl) clinoptilolite $\gamma = 1.482$ $\alpha = 1.476$



Fig. 7 Fluidal texture transited from perlitic one.

plagioclase, glass or pumiceous glass, the interstitials of which are filled with a lot of powdery particles not discriminatable as to their natures. With them, remains of radiolarias, foraminifers and spine of sponges are often imbedded, and a few glauconite grains are associated with them.

The alteration is represented by chloritization of powdery base materials, and minor formation of mordenite and cristobalite is ascertained in some cases. *B) Formation of zeolitic minerals*

The following is the detailed description of the altered rocks developed within the Tsuchihata perlite complex. They are dealt with special references to the mode of formation of zeolites and allied minerals that proceeded by stepwise replacements of original rock holding its texture unchanged. In these altered rocks, zeolite minerals such as mordenite and clinoptilolite are abundantly developed. And futher, opal, cristobalite, tridymite, celadonite, chlorite, and montmorillonite are associated with zeolites forming several distinct mineral assemblages. Heterogeneity of texture or the different assemblages dispose side by side even in one thin section is the characteristic feature of these altered rocks. Each alteration zone established in this district is composed of rock type having a definite alteration character. General character of each rock type is given as follows.

The mineral species of zeolite and allied minerals were determined by routine methods such as X-ray diffraction with heating and acid treatments and measurement of referactive indices as well as morphological characters under microscope.

1) rocks of the celadonitized zone: ---- Concerning to the rock type developed within this alteration zone, following minerals are the chief components.

celadonite (chlorite)

mordenite (clinoptilolite)

opal, cristobalite, tridymite

The original rock is completely replaced by these minerals except phenocrystic minerals and there are none of unaltered remnants of glass base. On the contrary, phenocryst plagioclase, quartz and augite are remained in fresh state without any sign of alteration.

The formation of alteration minerals advances, at first, along the perlitic crack or fluidal line of original glass base resulting in a network development of seam having definite mineral assemblage. Secondly, the replacement of the glass proceeds further to inner side of the mesh of first assemblage net to form a ring texture having the rim of first assemblage and its core of second assemblage. Third phase is represented by the mineral formation developed along the open space of crushing fracture.

In such alteration process, following remarks are the distinctive feature.

- a) Celadonite or chlorite are formed in thin filmy space developed along the original perlitic crack. The flow line of original glass also offers the same circumstance (Fig. 8). They are also formed along the crushing crack that crosses the original perlitic or fluidal texture. In some cases, chlorite formation is exclusively confined to those cracks formed along original texture, whereas celadonite formation is only referred to crushing cracks.
- b) In the immediate neighbourhood of thus formed celadonite or chlorite film numerous small drop like grains of opal of 0.001 mm in size are crowded (Fig. 9-a).
- c) Every glass block bounded by such network film filled with celadonite or chlorite is replaced by the growth of radial aggregation of mordenite from external part (Fig. 10). Most of the glass blocks are wholly replaced by mordenite thus formed (Fig. 9-b). But in some cases, the central core of each glass block surrounded by the mordenite turns into an aggregation of prismatic clinoptilolite or of cristobalite (Fig. 11).
- d) Another type of aggregation develops in network vein caused by crushing effect, which cut distinctly the original perlite texture. It is filled by mordenite, which is laid to wall side of the vein in a form of radial aggregate and is overgrown by cristobalite. In another part, celadonite-opal association also takes similar development.

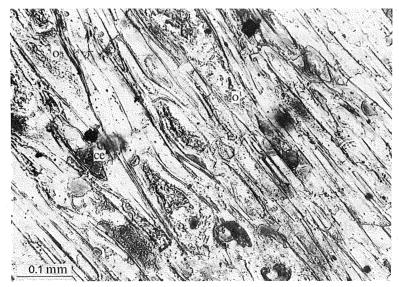


Fig. 8 Celadonite formation developed along fluidal line. ce) celadonite $\gamma = 1.619$ $\alpha = 1.600$

o) opal N = 1.444

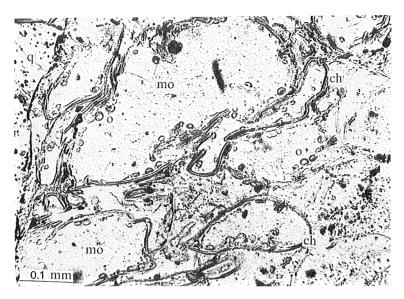


Fig. 9-a Drop-like opal formed so as to follow about chlorite film.

- opal grain N = 1.444
- mo) mordenite $\gamma = 1.479$ $\alpha = 1.473$
- ch) chlorite film
- mordenite (brown) $\gamma = 1.477 \alpha = 1.472 q$) quartz phenocryst

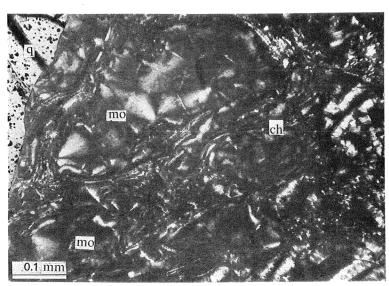


Fig. 9-b Mordenite replacing the glass mesh surrounded by chlorite film developed in network. The figure is the same with Fig. 9-a. It is taken under crossed nicols. mo) mordenite

- ch) chlorite film
- quartz phenocryst

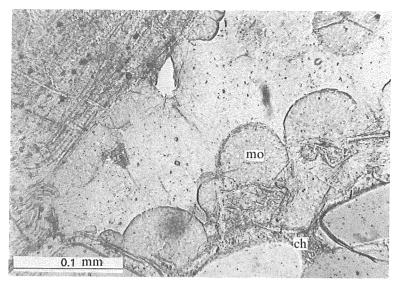


Fig. 10 Mordenite clusters arranged their initial cores close to the chlorite films. mo) mordenite cluster $\gamma=1.475$ $\alpha=1.471$ ch) chlorite film

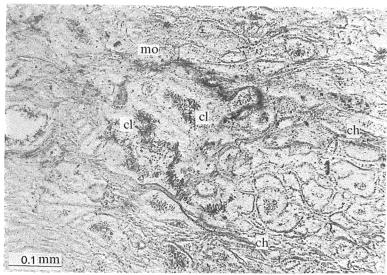


Fig. 11 Mordenite-clinotilolite association. Clinoptilolite is always formed after mordenite successively. ch) chlorite film

mo) mordenite $\gamma = 1.476 \alpha = 1.472$

cl) clinoptilolite aggregate $\gamma = 1.480 \ \alpha = 1.476$

e) Concerning to the formation of celadonite, two types may be mentioned. The one is that cited in (a). The other is represented by vein formed occurrence (Fig. 12), which is developed in microscopic scale as well as in macroscopic network seams including blocks of 10 cm in size (cfr. Fig. 3). All these networks of vein-formed seams are filled with crushed materials, which are cementated by prominent amount of celadonite and opal.

Moreover, another celadonite rich vein of macroscopic scale is detected in

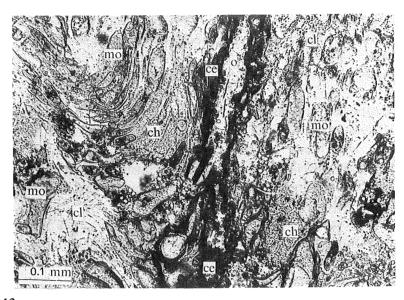


Fig. 12 Celadonite-opal vein crossing the part of chlorite-mordenite-clinoptilolite assemblage.

ce) celadonite $\gamma = 1.628$ $\alpha = 1.605$ o) opal N = 1.448ch) chlorite mo) mordenite $\gamma = 1.476$ $\alpha = 1.472$ cl) clinoptilolite $\gamma = 1.481$ $\alpha = 1.477$

some parts where the above mentioned group of network seams are cut by it as shown in Fig. 3.

f) Macroscopic veins formed of mordenite-cristobalite similar to that cited in (d) are also known accompanied with celadonite vein (Fig. 3).

Three successive steps in the alteration process may be established based on above mentioned features.

The formation of celadonite or chlorite with opal and mordenite cited in (a) - (c) develops to take a greater part of the volume of altered rock. It is the "main phase" of this alteration. Succeeding phase may be called "pool phase" that means seggregative formation of clinoptilolite, mordenite or cristobalite

main phase	pool phase	vein phase
celadonite- chlorite	clinoptilolite (mordenite)	mordenite- cristobalite
mordenite (opal)	cristobalite	celadonite-opal

cited in (d). The last phase is represented by "vein phase" which fills the networkly developed cracking space by celadonite-opal or mordenite-cristobalite as cited in (e) - (f).

2) rocks of the light greenish zone: ---- Rocks found in this zone is not so different from that of the above described. Its constituent alteration minerals are as follows.

mordenite, clinoptilolite

chlorite

opal, cristobalite, tridymite

Distinct feature of this rock type is a prominent increase of the amount of clinoptilolite and nearly complete retreat of celadonite. Volumetrically, mordenite and chlorite take the part of main constituent. The development of crushing effect is not so prominent that there are not any attractive network pattern in their outlook.

Following remarks are the conspicuous features of this rock type.

- a) Chlorite is formed in nearly similar textural feature to that of celadonite.
- b) The formation of mordenite is carried in quite similar manner to that mentioned in celadonitized zone.
- c) Although clinoptilolite is formed more abundant than that of celadonitized zone, its relation to mordenite is the same as already noted.
- d) The formation of cristobalite is also successive after mordenite as mentioned in the foregoing section. Rarely, it is aggregated to the vein formed pool with accompanying cristobalite.

In the case that the original rock is breccia, some interstices of breccias are filled by cristobalite and tridymite. In both cases, newly formed minerals are always so arranged that cristobalite fill the wall side and tridymite is to fill up the inner core.

As a whole, the alteration character of this type can be summarized into following table.

main phase	pool phase	vein phase
mordenite	clinoptilolite	crustobalite
chlorite (opal)	cristobalite	tridymite

3) rocks of the white coloured zone: ---- The alteration minerals prevailed in

this zone are as follows.

clinoptilolite > mordenite

chlorite

opal ≥ cristobalite

In this rock type, there are no trace of crushing effects remarkably developed in the foregoing rock types.

Following remarks are the main features of this rock type.

- a) Similar to those described in foregoing sections, the alteration begins with the chloritization along the crack or fluidal line of original glass base and the replacement by mordenite within the neighbourhood of the chlorite film. Greater parts of the remaining glass turn into clinoptilolite. The amount of clinoptilolite is greater than that of mordenite in this rock type.
- b) The amount of chlorite is minor one compared to those of foregoing rock types.
- c) Opal is formed in very small sized droplets and is uniformly disposed through the rock.
- d) Pool like aggregation of cristobalite surrounded by clinoptilolite is often met with (Fig. 13).

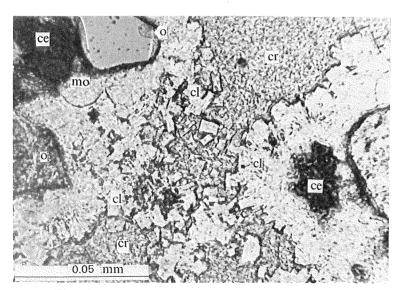


Fig. 13 Clinoptilolite-cristobalite association filling open space.

CILLIC	pullonic chistodan	ice association	ming open
ce)	celadonite	$\gamma = 1.615$	$\alpha = 1.602$
cl)	clinoptilolite	$\gamma = 1.479$	$\alpha = 1.475$
mo)	mordenite	$\gamma = 1.476$	$\alpha = 1.471$
cr)	cristobalite	$\gamma = 1.488$	$\alpha = 1.485$
o)	opal (white)	N = 1.444	
	opal (brown)	N = 1.445	

e) Vein phase is not represented in their rock type.

A table summarizing the characteristics of this rock type may be established from the above mentioned as below.

main phase	pool phase	
mordenite-clinoptilolite	clinoptilolite	
chlorite	cristobalite	
opal		

4) rocks of the flinty zone: ---- The following alteration minerals can be enumerated from this rock zone.

chlorite, opal

mordenite, clinoptilolite

The original rock of this zone is chiefly confined to tuffaceous rocks. The main part of alteration minerals is represented by chlorite and opal. The amount of mordenite and clinoptilolite are far smaller than those of the other minerals already mentioned.

- a) Chlorite of similar character to those of the other alteration zones is the most abundant alteration mineral, which replaces the filling materials.
- b) Drop like opal is disposed uniformly through the rock. Another opal that wholly replaces the glass fragments is also seen.
- c) The formation of mordenite and clinoptilolite is the same to those of the other alteration zone. Their mode of occurrence is only observable in the form replacing large glass fragment. Others which may be formed among fine powdery material can not be traced under the microscope.

In this rock type, the subdivision into successive phase relations can not be defined by the obscured tuff texture and by micro-grain size not detectable under the microscope, though they can be checked by X-Ray analysis.

5) rock alteration in the frontal part of the alteration aureole: ---- In the northern extreme part of the alteration aureole where the altered rock transits to unaltered fresh state, particular style of alteration can be detected (Fig. 14).

Prominent montmorillonitization is developed along the original perlite crack as in the case of chloritization or celadonitization in the above described alteration styles. Greater parts of the glass surrounded by montmorillonitized film is remained in unaltered state, though minor amount of mordenite is formed with them. Alteration is also macroscopically developed along the perlitic joint with $10-30\,\mathrm{cm}$ width. In such parts, perlite is completely converted into an aggregation formed of only montmorillonite, clayey part of deep pinkish colour. Several transitional types are found with them (Fig. 16).

6) Alteration due to ore mineralization: ---- The detailed arrangement of

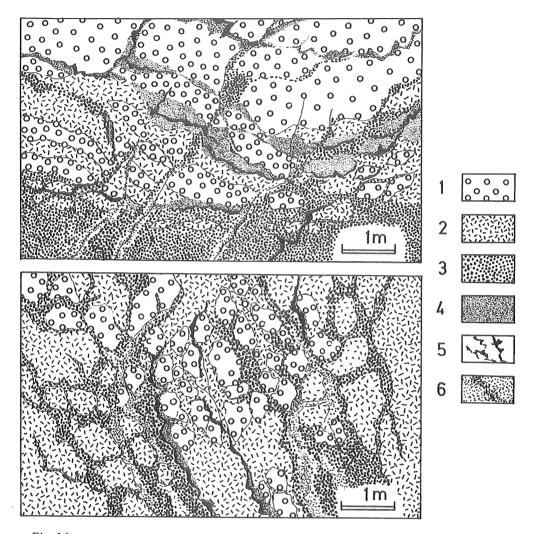


Fig. 14
Sketches showing the mode of montmorillonitization of perlite developed around the frontal part of the zeolitic alteration, the northern extreme part of the aureole.

- 1) unaltered fresh perlite (Analysis No. 16)
- 2) light yellow perlite
- 3) light green perlite (Analysis No. 17)
- 4) dark green coloured perlite
- 5) pool of the dark reen coloured chalcedonic vein
- 6) pinkish montmorillonitized clayey part (analysis No. 18) Analysed samples were obtained from the parts (1), (3) and (6).

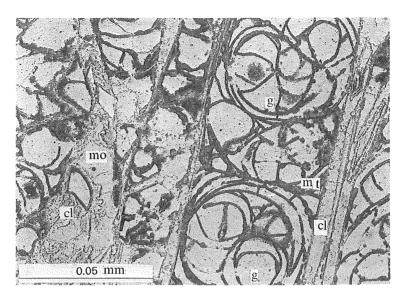


Fig. 15
Perlite suffered by slight alteration.

g) glass N=1.471-1.472 mo) mordenite $\gamma=1.477$, $\alpha=1.472$ mt) montmorillonite $\gamma=1.499$, $\alpha=1.479$ cl) clinoptilolite $\gamma=1.480$, $\alpha=1.476$

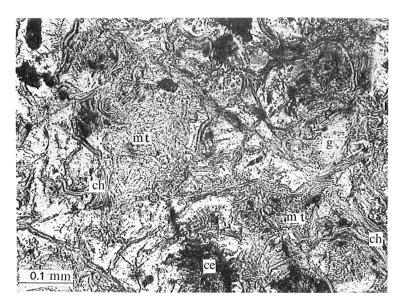


Fig. 16
Montmorillonitized perlite.

Greater part of perlite is transformed into the aggregation of montmorillonite. The sample is obtained from rock facies represented by (4) in Fig. 14.

ce) celadonite = 1.623 = 1.604 mt) montmorillonite = 1.499 = 1.480 ch) chlorite film g) glass N = 1.472

alteration due to ore mineralization have not been clearly known in this district. Several diverse mineral assemblages such as adularia-quartz or sericite-chlorite-quartz are known in close connection to the course of ore mineralization.

One of distinctive difference of this type alteration from zeolitic one is seen in the style of formation of silica mineral. Although it is represented by opal, cristobalite and tridymite in zeolitic alteration, silica mineral is exclusively exhibited in the form of quartz by the alteration of ore mineralization.

In the frontal part of the alteration aureole where the silicification is only represented by dotted formation of chalcedonic quartz, some transformations of zeolite formed by previous alteration are recognized. With them, the mordenite, which is judged after its remaining texture turns into aggregation of laumontite needles, or in other case into laumontite-vermiculite aggregation (Fig. 17).

Further, in the inner part of the alteration aureole such remnant minerals or texture are wholly vanished by the formation of a lot of quartz and allied minerals.

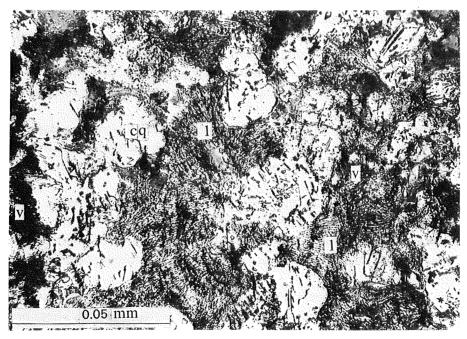


Fig. 17
Laumontite-vermiculite-chalcedonic quartz assemblage due to ore mineralization.

v) vermiculite

1)

laumontite

- $\gamma = 1.524$ $\alpha = 1.512$
- cq) chalcedonic quartz $N_o = 1.540$ $N_e = 1.533$

5. Mineral assemblage

Viewed through the whole alteration processes, some mineral associations comparatively easy to form within these altered rocks can be distinguished. In this regard, the following mineral associations, as a whole, may be referrable to the representative mineral assemblages prevailed in the zeolitic alteration of the Tsuchihata perlite complex.

- a) celadonite-mordenite-(opal)
- b) chlorite-mordenite-(opal)
- c) chlirite-mordenite-clinoptilolite
- d) chalcedonic quartz-laumontite-vermiculite
- e) celadonite-opal
- f) clinoptilolite-cristobalite

The main part of almost all the altered rocks except those formed by ore mineralization is composed by assemblages (a), (b) and (c). The framework of the altered rock is constituted by celadonite or chlorite in intimate association with mordenite (in some case accompanied with clinoptilolite). Other minerals associated with them seem to be of only subordinate meaning for the framework. They are formed as segregative components or fillings of open space. Assemblages (e) and (f) are to be referred for such situation.

Concerning to the zeolite species formed in this alteration, it is confined only to that of mordenite and clinoptilolite. Other species is not detected here. In this regard, the zeolitic alteration of the district may be corresponded only to one limited subfacies that is arranged in a progressive series studied in other districts (Seki 1968).

Although mordenite and clinoptilolite are formed in close association, the latter is always crystallized after mordenite, which seems to be, in a sense segregative product after mordenite. Successive relation between both zeolite species can be found there.

Laumontite is known as the main component of the assemblage (d), it is the product derived from ore mineralization which is of far different circumstances from those of zeolitic alteration. It is associated with vermiculite and chalcedonic quartz which are never seen in afore-mentioned zeolitic alteration proper.

Although the main part of the altered rocks is formed by above mentioned circumstance, it is always succeeded by those of segregative pool phase or vein phase composed of some minerals having deviated composition from those of the main phase. A trend is proceeded to clinoptilolite-cristobalite formation (assemblage (f)), while the other to celadonite-opal formation (assemblage (e)). They appear in microscopic scale as well as in macroscopic network seams or clean cut veins (cfr. Fig. 3 and 12).

Homogeneous mineral equilibrium even within the extent of a thin section is not attained here. It is more or less accompanied by segregative compositional variation as already described.

6. Chemical composition

Chemical analysis* on 22 samples selected from several rock types of altered and unaltered perlitic rocks of the district was carried out. Its results are shown in following tables group into each rock type.

* The measurement of water content is carried by Karl-Fischer's solution method.

Table I is concerned to the original unaltered rocks.

	Tabl	e I	
Sample No.	1	2	0
SiO ₂	71.52	70.83	70.23
TiO_2	0.18	0.15	0.16
Al_2O_3	12.51	12.08	12.24
Fe_2O_3	0.06	0.29	0.76
FeO	1.01	0.84	1.13
MnO	0.10	0.08	0.04
MgO	0.53	0.39	0.90
CaO	3.11	2.62	2.15
Na_2O	3.50	2.95	2.92
K ₂ O	2.14	2.76	1.64
P_2O_5	0.01	none	0.13
$H_2O(+)$	3.48	3.70	4.78
H ₂ O(-)	1.41	2.96	2.41
total	99.56	99.65	99.49
Sp.Gr.	2.38	2.35	n.d.

(Analyst No. 1, 2 J. Watanabe, No. 0, T. Kushida)

No. 1 is of wholly fresh state and the sample is obtained from northern extreme part of the alteration aureole where alteration effect is only represented by network development of montmorillonitization remaining a lot of fresh perlite in between.

No. 2 is obtained from a block remained in unaltered state amidst strongly altered rock of celadonitized zone.

The sign of alteration is only represented by feeble chloritization developed along perlitic crack in No. 2 in a similar manner of montmorillonitization as in No. 1. Very minor amount of mordenite and clinoptilolite is formed in both

samples.

No. 0 is already published result made by Kushida (KAWANO 1950). Although its rock character is not fully described, it may be a similar rock obtained from the neighbour of locality No. 1.

Table II is concerned to the rocks developed in the celadonitized zone. The samples No. 3–5 are the rocks having the assemblage of celadonite-mordenite-opal. Those of No. 6–8 are of celadonite-opal assemblage that developed as the deep green seam networkly spreads through the blocks having the character shown in Table I. No. 9 is of fine breccia origin intercalated between perlite layas.

Table II

Sample No.	3	4	5	6	7	8	9
SiO ₂	71.45	72.08	72.83	55.47	58.82	63.64	56.65
TiO_2	0.18	0.12	0.10	0.35	0.11	0.28	0.35
Al_2O_3	11.48	9.43	7.91	6.15	8.29	11.05	8.79
Fe_2O_3	0.61	0.73	2.00	10.48	11.26	4.98	10.26
FeO	0.26	0.15	0.59	3.09	3.58	1.74	3.29
MnO	0.14	0.08	0.12	0.07	0.28	0.31	0.20
MgO	0.75	0.73	0.30	2.79	2.66	1.00	4.40
CaO	2.45	2.18	1.92	1.69	0.44	2.47	1.31
Na ₂ O	1.49	0.78	0.47	0.59	0.14	0.87	0.75
K ₂ O	1.86	1.98	2.20	3.69	6.18	3.04	7.46
P_2O_5	n.d.	none	none	0.10	none	none	0.04
H ₂ O(+)	3.89	5.36	5.10	6.69	4.00	5.15	3.41
$H_2O(-)$	5.11	5.96	6.00	8.31	4.08	5.17	2.96
total	99.67	99.58	99.54	99.47	99.84	99.70	99.87
Sp.Gr.	2.30	2.23	2.31	2.64	2.33	2.72	3.07

(Analyst J. Watanabe)

The main constituents of No. 3 are mordenite and celadonite, in which the amount of the former is far abundant and associated opal and clinoptilolite are of very minor ones. No. 4 is almost similar to No. 3. But, it has more large amount of opal and clinoptilolite. Although general feature of No. 5 is similar to those above mentioned, it contains several pools and cracks filled with cristobalite.

The mineral composition of No. 6–9 are exclusively confined to abundantly developed celadonite and interstitially formed opal. However, it is associated with a fair amount of mordenite in No. 8. The amount of celadonite is most abundant in No. 7. In No. 6, celadonite rich veins in microscopic scale are

developed along the cracks formed in network. No. 9 is a fine breccia having its filling base wholly replaced by celadonite.

Table III is concerned to the rocks developed in the light greenish zone.

The analyzed rocks are formed of mordenite, chlorite and opal as their chief constituents. Minor amount of clinoptilolite, cristobalite and tridymite are accompanied with them.

The sample No. 10 is obtained from the northern extreme part of the light greenish zone, which is derived from fluidal perlite. It has representative feature of this alteration zone already described.

No. 11 is the sample of altered rock derived from perlite breccia. The amount of clinoptilolite and cristobalite is much higher than that of No. 10.

Table IV is referred to those occurred in white coloured zone. As already noted, clinoptilolite and mordenite are the chief components of this rock type. In two samples analyzed, their starting material was a rock having very prominent fluidal texture and high porosity.

Table III

Sample No.	10	11
SiO ₂	79.57	74.92
TiO_2	0.10	0.15
Al_2O_3	7.69	6.17
Fe_2O_3	0.97	0.08
FeO	0.36	0.16
MnO	0.20	0.11
MgO	0.63	0.23
CaO	0.66	1.82
Na ₂ O	0.59	1.92
K ₂ O	3.69	1.72
P_2O_5	0.01	none
$H_2O(+)$	2.31	6.04
$H_2O(-)$	2.90	6.15
total	99.68	99.47
Sp.Gr.	2.23	2.49

(Analyst J. Watanabe)

Table IV

Sample No.	12	13
SiO ₂	70.36	80.72
TiO_2	0.16	0.17°
Al_2O_3	11.86	6.88
Fe_2O_3	0.74	0.82
FeO	0.23	0.07
MnO	0.05	0.03
MgO	0.02	0.38
CaO	1.84	1.09
Na_2O	0.66	0.21
K ₂ O	2.72	1.02
P_2O_5	0.07	0.01
$H_2O(+)$	5.36	2.73
$H_2O(-)$	5.41	5.38
total	99.48	99.51
Sp.Gr.	2.46	2.41

(Analyst J. Watanabe)

The sample No. 12 is obtained from northern extreme part of the alteration aureole, No. 13 from southern end of the mapped area. No. 12 is the type enriched in clinoptilolite and the amount of mordenite is small. They associate with chlorite having nearly the same textural feature to those of the foregoing rock types, but it is leached to a nearly isotropic variety. Although cristobalite

is not detected under the microscope as visible from in both samples, X-ray diffraction shows its vivid existence.

Table V is concerned to the rocks occurred in flinty zone. Their original rock is a fine breccia formed of minute glass fragments having fluidal texture. Their main alteration minerals are chlorite, mordenite and opal, with which a minor amount of clinoptilolite is associated.

The samples No. 14 and No. 15 are obtained from the western wing of the alteration aureole (R. Komatsuzawa). No. 14 is formed of chlorite and mordenite with minor amount of opal and localized clinoptilolite. Opal is more abundant in No. 15.

Table VI is concerned to the rocks occurred in frontal part characterized by montmorillonitization.

As shown in Fig. 14, several rock facies variegated from fresh perlite to highly montmorillonitized ones co-exist in an outcrop.

Table VI

Sample No.	16	17	18
SiO ₂	69.91	63.28	58.59
TiO_2	0.15	0.23	0.13
Al_2O_3	10.28	14.42	13.02
Fe_2O_3	2.78	1.66	1.55
FeO	0.17	0.12	0.06
NnO	0.10	0.35	0.25
MgO	0.65	0.73	2.31
CaO	2.27	4.02	1.59
Na ₂ O	1.14	1.62	1.06
K ₂ O	2.49	1.81	0.90
P_2O_5	0.01	none	0.03
$H_2O(+)$	3.66	4.12	4.65
H ₂ O(-)	5.99	7.62	15.73
total	99.60	99.98	99.87

2.26

2.35

(Analyst J. Watanabe)

Sp.Gr.

Table V

Sample No.	14	15
SiO ₂	76.83	77.29
TiO_2	0.16	0.25
Al_2O_3	7.83	7.14
Fe_2O_3	0.10	0.13
FeO	0.14	0.23
MnO	0.14	0.03
MgO	0.01	0.26
CaO	1.76	1.83
Na ₂ O	1.12	0.85
K ₂ O	1.84	1.84
P_2O_5	none	0.01
$H_2O(+)$	3.92	3.60
$H_2O(-)$	5.79	6.31
total	99.64	99.77
Sp.Gr.	2.38	2.42

(Analyst J. Watanabe)

No. 16 is obtained from the fresh part, of which montmorillonite formation is only confined along perlitic cracks.

2.26

No. 17 is referred to the light greenish part, of which two third of the rock is replaced by montmorillonite and the rest by mordenite.

No. 18 is that of wholly montmorillonitized part, which is transformed into soft clayey rock of pinkish colour.

Table VII is concerned to the alteration which is involved to the ore mineralization of the district.

The details of this sort of alteration are not yet clearly defined. They may be in diverse trends concerned to their relation on time and space in the course of ore mineralization.

Tal	.1.	17	T
1 21	nе	v	11

Sample No.	19	20	21	22	
SiO ₂	71.83	81.08	66.82	75.25	
TiO ₂	0.22	0.20	0.22	0.20	
Al_2O_3	9.63	9.47	16.03	8.95	
Fe_2O_3	0.67	0.10	1.32	1.89	
FeO	1.02	0.07	0.89	0.62	
MnO	0.31	tr.	0.25	0.14	
MgO	0.01	0.04	3.56	1.11	
CaO	1.47	0.43	0.04	1.63	
Na ₂ O	2.68	1.88	0.02	0.82	
K ₂ O	3.17	5.13	3.55	2.68	
P_2O_5	0.02	0.04	0.04	0.01	
$H_2O(+)$	4.28	1.49	6.80	2.92	
$H_2O(-)$	4.58	0.01	0.68	3.27	
total	99.89	99.94	100.22	99.49	
Sp.Gr.	2.60	2.73	3.10	2.50	

(Analyst J. Watanabe)

- No. 19 is a nearly fresh perlite with slight alteration due to ore mineralization. It is obtained from immediate neighbour of No. 20 which is altered into adularia-quartz assemblage with pyrite impregnation.
- No. 21 is obtained from the site around the Motoyama deposits. It is composed of sericite and quartz with pyrite, which may be derived from the zeolitized perlite belonging to the lower member.
- No. 22 is a strongly silicified rock obtained from southern part of the Motoyama deposits, which may be derived from the upper member of the complex.

Variation in chemical composition: ---- Cation calculation on the analysed results above listed was carried out after Barth's method which is to arrange each cation into assumed standard cell having 160 0 atoms. The calculated results are summarized into Table VIII, and also are represented in variation diagrams (Fig. 18). Through the variation of these cation values, following features may be mentioned as the chemical characteristics of zeolitic alteration

Table VIII

	1.	2.	0.	3.	4.	5.	6.	7.	8.	9.	10.
Si 4+	60.0	58.9	57.4	56.8	58.0	58.8	47.9	52.2	53.3	51.4	65.4
Ti 4+	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.2	0.2
Al 3+	12.4	11.8	11.7	10.8	8.9	7.5	6.3	8.7	11.0	9.4	7.4
Fe 3+	0.1	0.2	0.5	0.4	0.5	1.2	6.8	7.5	3.1	7.0	0.6
Fe 2+	0.7	0.6	0.8	0.2	0.1	0.4	2.2	2.6	1.2	2.5	0.2
Mn^{2+}	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.2	0.2	0.1
Mg 2+	0.7	0.5	1.1	0.9	0.9	0.4	3.6	3.6	1.2	6.0	0.8
Ca 2+	2.8	2.4	1.8	2.1	1.6	1.7	1.5	0.4	2.2	1.2	0.6
Na 1+	5.7	4.8	4.6	2.3	1.2	0.7	1.0	0.3	1.4	1.2	1.0
K 1+	2.3	2.9	1.7	1.9	2.1	2.3	4.1	7.0	3.2	8.6	3.8
P 5+	_	****	0.2		_	_	0.1		None	0.1	
(OH)-	(12.8)	(17.8)	(19.6)	(23.9)	(31.0)	(25.0)	(41.1)	(20.6)	(24.5)	(17.5)	(12.9)
Total	84.9	82.3	80.0	75.6	73.5	73.2	73.8	82.8	77.0	87.8	80.1
1 1	12	12	14	15	17	17	1.0	10	20	21	

11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.
59.6	56.8	64.4	61.5	60.3	55.9	50.0	43.1	58.9	68.1	54.7	62.0
0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.2
5.8	11.3	6.5	7.4	6.5	9.7	13.5	11.3	9.3	7.8	15.5	8.8
0.1	0.4	0.4	0.2	0.1	1.7	1.0	0.9	0.4	0.2	0.8	1.2
0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.7	0.1	0.6	0.5
0.1	0.1	_	0.1	_	0.1	0.2	0.2	0.2		0.2	0.1
0.3	0.1	0.4	_	0.3	0.8	0.9	2.6		0.1	4.3	1.4
1.6	1.6	0.5	1.5	1.5	1.9	3.5	1.2	1.3	0.4	0.1	1.4
3.0	1.0	0.4	0.9	1.3	1.8	2.5	1.5	4.2	2.5	0.1	1.4
1.7	2.7	1.0	1.0	1.8	2.5	1.8	0.9	3.3	4.5	3.7	2.8
_	0.1		_	_	_	_			0.1	0.1	-
(27.3)	(24.7)	(18.6)	(22.2)	(25.8)	(25.8)	(30.9)	(50.1)	(15.2)	(30.0)	(18.5)	(15.2)
72.4	74.3	73.8	72.8	71.9	74.6	73.7	61.9	78.5	84.0	80.3	79.8

of the Tsuchihata perlite complex.

- 1) Si^{4+} varies to the most wide range of 43 68%, in which some are increased, while the others are decreased from that of original fresh perlite.
- 2) Distinct decrease of Na⁺ from that of fresh perlite without exception is a prominent feature.
- 3) Similar distinctive decrease in Al³⁺ is also seen with a few exceptions (montmorillonitization or ore mineralization).
- 4) Increase of OH⁻ is also a prominent feature of this alteration.
- 5) The value for K⁺ is in most cases increased, especially, in connection to the

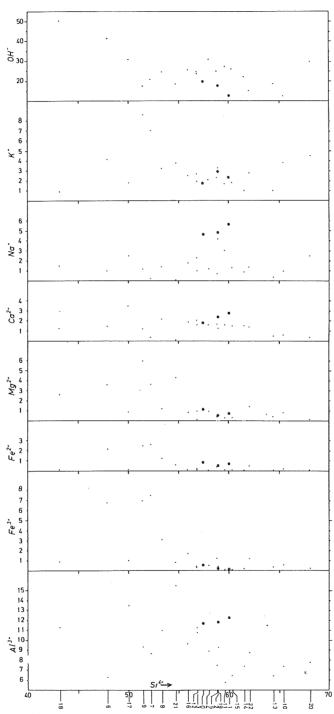


Fig. 18
Variation diagram of every cation and anion against cation Si.
(The circles represent those of original fresh perlite.)

formation of celadonite. However, in those rocks occurred in external part of the alteration aureole, flinty and white coloured zones, its value is somewhat decreased.

- 6) Fe³⁺ is distinctively increased with celadonite formation.
- 7) Concerning to the behaviour of Fe²⁺, there is no particular variation, and Mg²⁺ also shows any special variation in general. However, for those enriched in celadonite or montmorillonite as well as in sericite due to ore mineralization, both values are increased.
- 8) The proportion of Ca^{2+} is slightly decreased in general. There is no particular increase.
- 9) As to the montmorillonitization, its chemical trend is to advance for the distinctive increase of Al^{3+} and OH^- confront to the decrease of Si^{4+} . At the same time, decrease in K^+ , Na^+ and Fe^{2+} is also prominent.

Conclusions

All the evidences described in the foregoing chapters lead us to the following conclusions.

- 1) Perlite complex suffered by zeolitic alteration having the features already described is not an unique occurrence only confined to that of the Tsuchihata mining district, but similar occurrences are known in several districts of the "green tuff region". Their modes of occurrence and petrographical features are quite identical with each other. In some districts, they have been called as "green liparite". Their occurrence seems to be fixed to the uppermost horizon of lower Miocene, and the sites of their effusion are closely connected to the fields of Miocene ore mineralization.
- 2) It is worthy of note that the zeolitic alteration of the district had already been accomplished before the submergence of the perlite complex under the sea of the Kotsunagi stage, early middle Miocene. The duration between the time of deposition of basal member of the Kotsunagi formation and the time of mentioned alteration of perlite complex is not so long that it is shown in stratigraphically conformable relation by both corresponding members in surrounding district. Since, the zeolitic alteration must be carried within a short time range immediately after the effusion of these perlite and is almost accomplished before the Kotsunagi stage begins. There is no burial chance for perlitic complex under the thick piling of overlaying sediments. And also, the alteration was evidently finished before the commencement of ore mineralization of the district, which affected the perlite complex as well as the overlaying Kotsunagi formation.
- 3) The alteration may be developed by the thoroughly permeating hydrous

solution introduced along the several cracks of microscopic and macroscopic scales. In fact, the perlite and its pyroclastics are rich in the passage for solution such as proper perlitic cracks, fluidal lines, original vesicular pores, interstices of breccias, etc. The alteration mineral formation described above strictly followed the patterns of such textural interstices. Further, shearing movements carried in the central part of the alteration aureole produce many crushing cracks, which also offer suitable passage to the solution.

The stepwise mineral formation mentioned in this alteration is commenced, at first, in and around such textural interstices, which spreads its alteration domain to the immediate glass part. It may be designated as "main phase", the first step of the alteration.

Pool-like aggregation formed of different mineral species such as clinoptilolite or cirstobalite surrounded by the products of main phase are very often observed. Their morphological feature suggests that some segregative processes enforce to form the mineral of different composition. The name of "pool phase" may be given for this step of alteration.

Vein formed open spaces produced by crushing effect are filled with mordenite or clinoptilolite-cristobalite or celadonite-opal that show quite different features from those of the main phase. And this is considered to be the products of segregative process. It may be designated as "vein phase", the latest step of the alteration.

Vein formed mineralization as well as celadonite seams developed in network shown in Fig. 3, may also be an extreme segregative product of this alteration process as a whole, though they celarly cut all the previous mineralization texture. It is considered that the segregative process grown gradually from microscopic scale to macroscopic network development and lastly arrived at the large scale vein cut already accomplished parts.

There are several features to suggest zeolitic alteration as the results of active permeation of solution into mentioned perlite complex. It is developed as a hydrous post action of effusive activity of the perlites, that ascend along the feeder of the complex from the deep.

- 4) The zeolite minerals prevailed in this alteration are confined to mordenite and clinoptilolite only. They are associated with celadonite and chlorite, and form the mineral assemblages listed as follows.
 - a) celadonite-mordenite-(opal)
 - b) chlorite-mordenite-(opal)
 - c) chlorite-mordenite-clinoptilolite

The assemblages are comparatively simple in this alteration, compared to the other regional zeolitic development, it may correspond to one limited subfacies situated in the progressive series characterized by the alternation of different zeolite species.

Although, the main part of the altered rock is represented by the above mentioned mineral assemblages, there accompany always several segregative facies among the products of main phase as already mentioned. Chief component of the segregative facies is clinoptilolite, cristobalite, tridymite and opal as well as celadonite and opal. Their amount and mode of formation make the proper feature of every alteration zone that is easy to discriminate in field observation.

5) The circumstance of the formation of zeolitic assemblages of the district may be measured by the behaviour of silica mineral. It is represented in the form of cristobalite, tridymite or opal in close association with celadonite, mordenite, chlorite and clinoptilolite in zeolitic alteration.

When the zeolitic rock is suffered under ore mineralization that characterized by the silica mineral in the form of crystalline quartz, all the zeolitic and allied minerals are wholly vanished. However, in frontal part of ore alteration aureole where its alteration is not so effective, mordenite of the suffered rock transformed into laumontite under the circumstance of the formation of silica mineral in the form of fibrous chalcedonic quartz.

- 6) The spatial arrangement of these mineral assemblages in this alteration aureole can never be interpretated as the one controlled by the difference of depth zone as similar cases are to be found in many regionally developed zeolitic alteration of the other districts. The differences in the textural state of original rocks and in the distance from the central part of the aureole seem to be the main controlling factors to produce such prominent zonal arrangement of different alteration states.
- 7) Although the altered rocks are wholly replaced by zeolites and allied minerals without any remnants of original rock except phenocrysts, their chemical characters are not so deviated from those of original perlite. Even in the most high grade alteration found in central part of the aureole, those of mordenite-celadonite-opal assemblage, leaching in Na⁺, Al³⁺ and Fe²⁺ and increase in OH⁻ are only carried in to some extents.

For those of the other alteration zones, similar circumstances are also prevailed, where minor scale of subtraction or addition of some cations that correspond to the composition of the flourished mineral formation in respective zone are the only conspicuous features.

Vivid concentration or leaching of special cations are only demonstrated for the segregative formation of special minerals such as celadonite, montmorillonite or sericite.

Viewed through all the mode of alteration, it may be said in general that the main part of the rearrangement of perlite to those of zeolitic assemblages is carried within a limit not so deviated from the chemical character of original perlite. It seems to be enforced by a undoubted introduction of a lot of water into the system, with which prominent leaching of Na⁺ and Al³⁺, and local, diverse segregative sweeping of some cations by water may be carried out to make up the detailed features of these altered rocks.

Acknowledgement

During their field investigation, the writers were much benefited by the courtesy of the staff of the Tsuchihata Mine, Tanaka Mining Company Ltd. The writers are greatly indebted to them for their kind offer for permission to use some unpulbished data; they wish to express their gratitude to the staff.

References

- AKIBA, C., YASHIMA, R., WATANABE, J., YOSHITANI, A. and YAJIMA, J. (1966): Early Miocene green tuff activity along the national railway Yokote-Kurosawajiri line over the back-bone range of northeast Japan. Ass. Geol. Coll. Japan, Monograph 12, p. 25 34.
- COOMBS, D.S., ELLIS, A.J., FYFE, W.S. and TAYLOR, A.M. (1959): The Zeolite facies, with comments on the interpretation of hydrothermal synthesis. Geoch. Cosmoch. Acta, vol. 17, p. 53 107.
- ESKOLA, P. (1939): Die metamorphen Gesteine, p. 263 407. in Barth, T.F.W., Correns, C.W. and Eskola, P., Die Entstehung der Gesteine. Springer-Verlag, Berlin, 422 p.
- Fujita, Y., Kakimi, T., Kutsuzawa, A., Mitsunashi, T., Mizuno, A., Sato, J. and Yamashita, N. (1966): Neogene tectonic movement in the back-bone range of northeast Japan. Ass. Geol. Coll. Japan, Monograph 12, p. 42 58
- Hunahashi, M. (1966): Igneous Activity of the "Green Tuff Region" Ass. Geol. Coll. Japan, Monograph 12, p. 138 146.
- Hunahashi, M. and Yoshimura, T. (1966): Characteristic Rock Alterations in the "Green Tuff Region". Ass. Geol. Coll. Japan, Monograph 12, p. 147 164.
- IIIMA, A. and UTADA, M. (1966): Zeolite in sedimentary rocks, with reference to the depositional environment and zonal distribution. Sedimentology, Vol. 7, p. 327 357.
- IJIRI, S. (1941): Stratigraphy and geological structure of Neogene Tertiary between Yokote and Sen-nin Pass. Jour. Japanese Assoc. Petroleum Technologists, vol. 9, p. 106 133.
- IWAO, S. (1961): On the alteration of volcanic rocks in Green Tuff region,

- "Problems of Geology" no. 1, p. 7 15. (Geol. Soc. Japan).
- KATO, I. (1955): Petrogenetic considerations of the green tuffs found in the lower part of the Neogene developed in the Yokote basin in Akita prefecture and the Shinjo basin in Yamagata prefecture. Sci. Rep. Tohoku Univ. 3rd ser., vol. 5, no. 1, p. 1 95.
- KAWANO, Y. (1950): Natural glasses in Japan. Geol. Surv. Japan, Report 134, p. 1-29.
- KITAMURA, N. (1959): Tertiary orogenesis in northeast Honshu, Japan. Contr. Inst. Geol. Palaeont., Tohoku Univ., no. 49, p. 1 98.
- KITAMURA, N. (1960): A cross section through the back-bone range in northeast Honshu, Japan. Sci. Rep. Tohoku Univ. 2nd ser., spec. vol. no. 4, p. 236 251.
- KIZAKI, Y. (1965): Diagenetic Alteration of Tertiary Tuffs of southern Gunma Prefecture. Faculty of Liberal Arts and Education, Gunma University vol. 13, no. 11, p. 153 203.
- Kurosawa, N. and Tokitsu, T. (1961): On the geology and ore deposits at the Tsuchihata mine. Min. Geol., vol. 11, p. 121 126.
- Matsukuma, T. (1970): Some considerations on the volcanic activities and mineralization of the Tsuchihata mining area. Rep. Resa. Inst. Undg. Res., Akita Univ., no. 35, p. 1-23.
- MINATO, M., GORAI, M. and HUNAHASHI, M. (Ed) (1965): The geologic development of the Japanese islands. Tsukiji Shokan, Tokyo.
- NAKAZIMA, W. and KOIZUMI, K. (1962): Zeolites in the Tertiary Beds located along the Okoku line, Northeastern Honshu, Japan Studies on minerals in the Green Tuff Formation, II. Earth Science, vol. 58, p. 26 31.
- OIDE, K., YAJIMA, J., ORIMOTO, S., YAMAGISHI, I., YASHIMA, R., URUNO, K. and KATO, Y. (1966): On a Tertiary granitoid mass in back-bone range of northeast Japan. Ass. Geol. Coll. Japan, Monograph 12, p. 35 41.
- OZAWA, A., FUNAYAMA, Y. and KITAMURA, N. (1971): Geology of the Kawashiri District. Quad. ser. Geol. Surv. Japan.
- Seki, Y. (1968): A consideration to the zeolite facies metamorphism in the Green Tuff region of Japan. Jour. Japan. Assoc. Miner., Petrol., and Econ. Geologists, vol. 59, p. 118 123.
- SHIMAZU, M. and KAWAKAMI, T. (1967): Distribution of zeolite and other minerals in the Maze basalts, Niigata Prefecture. Sci. Rep. Niigata Univ., Ser. E, no. 1, p. 17 32.
- Sudo, T., Nishiyama, T., Chine, K., and Hayashi, H. (1963): Mordenite and clinoptilolite in glassy tuffs of Japan. Jour. Geol. Soc. Japan, vol. 69, p. 1 14.
- Turner, F.J., Fyfe, W.S. and Verhoogen, J. (1958): Metamorphic Reactions and Metamorphic Facies. Geol. Soc. Amer. Memoir, no. 73.
- UTADA, M. (1970): Occurrence and distribution of authigenic zeolites in the Neogene pyroclastic rocks in Japan. Sci. Pap. Coll. Gener. Educt. Univ. Tokyo, vol. 20, p. 191 262.
- YAMAGISHI, I. (1965): Alteration Minerals of Green Tuffs in the Uchimura

District, Nagano Prefecture (part I). Jour. Geol. Soc. Japan, vol. 71, p. 215 - 227.

YOSHIMURA, T. (1960): A Type of the Alteration of the Tertiary Volcanic Rock - Studies on the Alteration of the Green Tuff Formation, I. Earth Science, vol. 52, p. 19 - 29.