Alteration of Sandstone Intercalation in the Upper Nanakura Tuff Member Occurring at Futatsui District, Yamamoto-Gun, Akita Prefecture, Japan

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Abstract The Upper Nanakura tuff member is widely distributed at Futatsui area. This members mainly composed of vitric tuff and altered to clinoptilolite except of the sandstone intercalation. The sandstone is 1-2 m thick and contains mainly montmorillonite. Chemically this sandstone is abundant in MgO and CaO, and tuff which contains clinoptilolite is abundant in Na₂O and K₂O. From the laboratory experimental data montmorillonite is easily formed under Mg environment. So the formation of montmorillonite in sandstone intercalation of vitric tuff is supposed to be depended on some affection of Mg rich solution after origination of clinoptilolite by the low grade metamorphism. The solution passed easily through the sandstone intercalation because of better porosity and permeability than tuff, so Mg addition was occurred only in sandstone.

1. Introduction

The vitric tuff widely distributed in Futatsui district, Akita prefecture, generally contains volcanic glass and clinoptilolite and called Upper Nanakura tuff member. These minerals co-exist with montmorillonite in some parts. Clinoptilolite found in this area is thought to be the alteration materials of volcanic glass by the low grade metamorphism, so it is reasonable to think that there are close relations between the mineral assemblage and geological formation as reported by many authors (Yoshimura, 1961, 1964; Nakajima and Koizumi, 1962; Negishi, 1967; Utada, 1970; Aoyagi, et al., 1975).

But the regularity of the mineral assemblage is sometimes disturbed by the local volcanic activities or ore solutions (Sumi, 1968; Honda and Muffer, 1970; Negishi, 1970), so the geological formation does not show the close relation with the mineral assemblage in such active areas. Futatsui area is far from such active area as Odate Kuroko area or Hachimantai

active volcanic area, and it is thought that the mineral assemblage of this area is correspond to "stage 1" which is established by Coombs, et al., as zeolite facies (Coombs, et al., 1954; Seki, 1968; Honda and Negishi, 1968).

The Upper Nanakura tuff member is mainly composed of vitric tuff associated with thin intercalations of tuffaceous sandstone and mudstone. In Futatsui area, mineral assemblage shows some irregularity according to its mother rock. Tuff contains mainly clinoptilolite, sandstone which is intercalation of tuff contains much more montmorillonite than clinoptilolite and mudstone which is also intercalation of tuff contains clinoptilolite. The chemical composition of those rocks shows somewhat difference depending on the rocks and minerals contained. Although tuff which contains clinoptilolite is abundant in Na and K, sandstone which contains montmorillonite is abundant in Mg and Ca, and mudstone show the same chemical properties as tuff.

In this paper, as to the above mentioned irregularity of the mineral assemblage seen in the

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intercalation of sandstone, the cause was discussed in the view point of the chemical properties and physical properties such as porosity and permeability of the mother rocks.

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2. General Geology

Pliocene pyroclastic rocks, (Maiya, Saito, and Sato, 1976), composed mainly of vitric tuffs, are widely distributed at Futatsui, and called Upper Nanakura tuff member. The volcanic glass in the rocks is wholly altered to clinoptilolite, except of the sandstone intercalations.

The tuffs contain various sizes of pumice and glass which are altered to zeolite by devitrification.

The occurrence of the specimens which are discussed in this paper showed above mentioned feature and were collected in limited area near Futatsui-machi (Honda and Negishi, 1967).

The geological structure of the area where the specimens were collected is NE-SW in strike and 30° - 35° E in dipping. The thickness of the tuff is about 80m. The tuff shows white yellow and light green color, and various type of rocks such as pumice tuff, silty tuff and sandy tuff were seen, and inclined various size of pumice (cm-mm). The pumice in the rocks wholly altered to zeolite and montmorillonite, and some intercalation of sandstone and mudstone (tuffaceous) are seen and they have generally about 1-2 m thickness.

The microscopic observation of the tuff shows commonly vitroclastic texture, and there are many pseudomorphs of pumices and glasses which altered to clinoptilolite. Many small automorphic crystals (0.05 mm) are seen in the center of the cavity. Small amount of quartz, feldspars, biotites and hornblendes are seen as phenocrysts. Quartz commonly shows corroded

forms. In addition, greenish colored spotted mineral which is thought to be ceradonite is seen. The following sample were collected from various kind of rocks and studied by X-ray analysis and chemical analysis.

Fig. 1 The idealized sketch map of the sample localities (This map is highly idealized and does not show precise geological feature, sampling points and scale).

tuff contains clinoptilolite; 1a, 2, A-4, 45-46 5t, 51t.

tuff contains volcanic glass; 3, 45d.

mudstone contains clinoptilolite; 51m.

sandstone contains montmorillonite; 45c, 46, 5s.

As shown in Fig. 1, mudstone and sandstone are very tuffaceous, and they are the intercalations of the tuff. The specimens 51m and 51t, 5t and 5s, occurred with each other within about 50cm distance.

3. Mineral Assemblages

The X-ray powder pattern is shown in Fig. 2 as to the specimens taken from different localities and rocks of the upper Nanakura tuff member (specimens 1a, 2, A-4, 45-46 show same X-ray pattern as specimen 5t, so their patterns were omitted). It is clearly seen that tuff and mudstone contain mainly clinoptilolite, and sandstone contains much more montmorillonite than clinoptilolite. The specimen 3 and 45d are mainly composed of unaltered volcanic glass. The specimen occurred at the upper part of this member.

As shown in Fig. 1, specimen 5s and 5t is very closely occurred with each other, and specimen 51m and 51t is also same relation. The distance between 5s and 5t, and 51m and 51t

Fig. 2 X-ray powder patterns of the specimens collected at Futatsui.

s within 50cm. But the mineral composition is apparently different. If the minerals is originated only by the low grade metamorphism,

these specimens have to show same or very close mineral assemblage because the geological condition was almost same and was affected by the same condition of temperature and pressure. So the difference of mineral assemblage in these rocks due to another reason than simple low grade metamorphism.

4. Chemical Compositions

The specimens taken from different rocks and localities of the upper Nanakura tuff member were analysed chemically, and the relation between the alteration minerals contained and the mother rocks was discussed. The chemical analysis is shown in Table 1. The relations of MgO, CaO, Na₂O, and K₂O are shown in Fig. 3 and 4. These figures clearly show the difference of the chemical compositions between montmorillonite-bearing rocks (sandstone) and clinoptilolite-bearing rocks (tuff and mudstone). The chemical composition of montmorillonite-bearing rocks is rich in MgO and CaO, and the chemical composition of clinoptilolite-bearing rocks is rich in Na₂O and K₂O. The tuff composed of unaltered volcanic glass has same chemical composition as clinoptilolite-bearing tuff and mudstone.

Specimens 5s and 5t are in contact with each other, and the former is a thin layer within

Table 1 Chemical composition of the specimens.

sst: sandstone mud: mudstone tuff: vitric tuff

m: montmorillonite cp: clinoptilolite gl: volcanic glass

Specimen	45c	46	5s	5t	51t	51m	1a	2	A4	45-46	3	45d
Rock	sst	sst	sst	tuff	tuff	mud	tuff	tuff	tuff	tuff	tuff	tuff
Composed of	m	m	m	cp	cp	cp	cp	cp	cp	cp	gl	gl
SiO ₂	62.73	60.36	61.76	71.44	65.98	70.37	68.15	66.66	64.60	66.80	68.52	70.06
TiO ₂	0.35	0.35	0.44	0.25	0.32	0.35	non.	tr.	non.	0.90	0.15	0.10
Al ₂ O ₃	12.27	13.99	13.06	13.43	12.35	10.44	10.78	10.40	11.34	9.76	11.47	12.52
Fe ₂ O ₃	3.19	3.60	4.95	1.47	1.06	3.03	1.19	1.23	0.56	0.55	2.08	0.94
MnO	tr.	tr.	0.07	non.	tr.	tr.	tr.	tr.	non.	non.	tr.	0.15
MgO	1.20	1.61	1.32	0.51	0.99	1.49	0.76	0.64	0.53	0.47	0.78	0.08
CaO	1.32	1.35	2.56	2.32	1.49	1.18	1.59	1.49	1.02	0.68	1.38	0.89
Na ₂ O	1.35	1.25	1.55	3.45	1.75	1.20	2.05	5.10	2.70	3.00	2.40	2.75
K ₂ O	1.65	2.35	3.00	2.50	1.85	2.20	3.10	3.05	3.00	3.00	2.65	3.60
H ₂ O ⁺	6.40	7.50	6.57	1.28	6.72	5.72	8.01	7.63	8.24	7.16	5.82	7.12
H ₂ O ⁻	9.53	7.70	4.85	2.87	5.70	3.65	4.04	3.96	8.45	7.86	4.96	1.37
P ₂ O ₅	0.01	tr.	0.09	0.02	--	--	0.02	0.02	0.05	0.05	0.15	0.02
Total	100.00	100.06	100.22	99.54	99.21	99.63	99.69	100.18	100.49	100.23	100.36	99.60

(Analyst ; T. Negishi)

the latter. 5s is sandstone and composed mainly of montmorillonite and 5t is tuff composed mainly of clinoptilolite. Specimen 51t and 51m are also in contact with each other, and the latter is a thin layer within the former. Both specimens are composed mainly of clinoptilolite. The reason why montmorillonite occurs only in sandstone and clinoptilolite in tuff and mudstone is not clear, but it seems attributable to some local condition, not only to the low grade metamorphism or diagenesis.

5. Discussions

The alteration minerals in Upper Nanakura tuff member were composed of clinoptilolite and montmorillonite, which were altered from volcanic glass. There are close relations between the alteration minerals contained and the mother rocks, and there are close chemical relations between the alterations minerals and the mother rocks. Tuff and mudstone contain clinoptilolite and are abundant in $\text{Na}_2\text{O} + \text{K}_2\text{O}$. On the other hand, sandstone which is intercalation in tuff contains montmorillonite and is abundant in $\text{MgO} + \text{CaO}$. Tuff which contains unaltered volcanic glass shows the same chemical properties as clinoptilolite bearing tuff and mudstone. So only sandstone is different in altered mineral contained and in chemical composition.

These rocks occur very close localities, especially specimen 51m and 51t, and 5t and 5s occur within 50cm distance. So the occurrence of montmorillonite in sandstone is not due to only the low grade metamorphism. The cause seems to depend on some additional local phenomena.

1) Effect of Mg

As seen in Fig. 3 and 4, distribution area of chemical composition of montmorillonite-bearing rocks is abundant in $\text{MgO} + \text{CaO}$. Montmorillonite is thought to have been altered from volcanic glass added by MgO (Iijima, 1972) and clinoptilolite-bearing tuff is easily altered to

Fig. 3 Fields of the chemical composition of clinoptilolite bearing-tuffs, -mudstone and montmorillonite bearing sandstones plotted on the triangular diagram of $\text{MgO} + \text{CaO} - \text{Na}_2\text{O} - \text{K}_2\text{O}$

Specimen mainly composed of;

- clinoptilolite,
- volcanic glass,
- ▲ montmorillonite.

Fig. 4 Triangular diagram of $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO} - \text{MgO}$. (symbols are same as Fig. 3)

montmorillonite in MgO environments as mentioned in the following. So montmorillonite is thought to easily occur where Mg component is added. The writer synthesized the zeolite X from clinoptilolite bearing tuff by the treatment with sodium hydroxide under normal condition (1 atm. 100°C) (Negishi, 1970 b). In the same study, montmorillonite was synthesized under high pressure (300°C, 110 atm.) by treated with Mg-hydroxide (Fig. 5). In the same condition (300°C, 110 atm.), when the sample was treated with Na-hydroxide, zeolite, such kind of an alcline, was formed.

Fig. 5 X-ray powder patterns of the synthesized montmorillonite from clinoptilolite-bearing tuff in the environment of Mg.
Orientated: orientated on the glass slide.
E-G: treated with ethylen glycol.

This shows that montmorillonite easily formed under Mg environment and zeolite was formed under Na environment. This fact is not contradictory to the field data seen in Futatsui district.

2) The Physical property of sandstone

The difference between sandstone and tuff is seen in the value of porosity and permeability.

Table 2 Porosity and permeability of tuff and sandstone (after Sekiyu Kogyo Benran, 1963)

	Yabase tuff	Yabase sandstone
Porosity (%)	25.5 - 25.6	35 - 40
Permeability (md)	4.9 - 4.5	160 - 600

The data of porosity and permeability is shown in Table 2. Yabase tuff and Yabase sandstone are correlated geologically to Upper Nanakura tuff member, so the physical nature is thought to be almost same as tuff and sandstone of the Nanakura member in Futatsui area.

The value of porosity in tuff shows 25%, and sandstone shows 35-40%. As to permeability, tuff has 5^{md}, but sandstone has 160-600^{md}. So the permeability of sandstone is 50-100 times as much as the tuff. Mudstone is more compact

than tuff. These data show that sandstone is thinkable as a channel of some solution. If this solution was abundant in MgO, sandstone was much more affected by MgO than tuff and mudstone.

It was not clear whether there was such activity of solution in truth, but if such kind of solution existed, it is obviously said that sandstone was much more affected by such solution than tuff or mudstone, and Mg-component was selectively added to only sandstone.

Honda (1975) also discussed the similar mode of occurrence of clinoptilolite and montmorillonite in Wyoming Bentonite (U.S.A), and thought some reaction of pore water for the secondary formation of montmorillonite in porous part of the deposit.

3) The difference between P_{H_2O} and P_{load}

The porous part which is surrounded by compact materials shows the different condition of $P_{H_2O} > P_{load}$, and the local irregularity of the mineral assemblage is often seen in such porous part (Coombs, et al., 1959, Nakajima and Tanaka, 1967). In Katsurane area, which is 40 Km S-E from Futatsui, analcime is seen in the porous part of tuff, and surrounding tuff is generally composed of clinoptilolite (Negishi, unpublished). This reason through to be the difference of P_{H_2O} and P_{load} in sandy part. The origin of montmorillonite in sandstone in Futatsui district can be thought to depend on such reason. But the ideal system of the condition of $P_{H_2O} < P_{load}$ is closed system, and the Futatsui sandstone has some difficulties to be thought as closed system, because of having about 1-2 m thickness and some continuities. Moreover, if sandstone was situated in closed system, it is difficult to think that Mg component was added only to sandstone selectively.

6. Conclusion

The clinoptilolite bearing tuff is widely distributed in Futatsui district, Yamamoto-gun, Akita Prefecture. The tuff is called Upper Nanakura

tuff. In this tuff bed, there are some intercalation of sandstone and mudstone having 1-2 m thickness. The sandstone is tuffaceous and contain much more altered montmorillonite than clinoptilolite.

The chemical composition of sandstone show high content of MgO, and tuff and mudstone does not show the same native as sandstone, and its chemical nature is similar to the unaltered volcanic glass which is thought to be original rocks of these altered rocks. The chemical relation between the alteration minerals contained and the mother rocks are clearly recognized in these tuff, mudstone and sandstone.

If these altered minerals were originated by the low grade metamorphism, it is reasonable to say that they show similar mineral assemblage and chemical properties. But in this area whole data do not show such close relation, and the irregularity of mineral assemblage in different mother rocks was discussed and will be concluded as follows.

Firstly this area was widely affected by low grade metamorphism with increasing the burial depth, and originated authigenetic altered minerals, especially clinoptilolite from volcanic glass.

Secondary, some activities of Mg-solution happened, and this solution mainly passed through sandstone intercalation because of good porosity and permeability. And montmorillonite originated in only sandstone being affected by Mg-solution.

This presumption was supported by the experimentation of the laboratory. Although it is impossible to confirm that such Mg-solution really existed, comparing with the chemical composition of original rocks, only the sandstone is apparently added by Mg-component.

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要 旨

秋田県山本郡二ツ井地方の上部七座
凝灰岩の砂岩夾在層の変質について
根岸 敏雄

秋田県山本郡二ツ井地方には、上部七座凝灰岩と呼ば

れる凝灰岩層が良く発達している。この凝灰岩の変質鉱物は斜ブチロル沸石が主であり、埋没沈下による低度変成作用および続成作用で形成されたと考えられている。しかしこの凝灰岩中に夾在される1~2 Mの凝灰質砂岩には、斜ブチロル沸石が見られず、主としてモンモリロナイトから成っている。また同時に凝灰質泥岩も挟在されるが、鉱物組成は凝灰岩と同じく斜ブチロル沸石である。これらの母岩と含まれる変質鉱物および化学組成の間には興味ある関係が認められた。すなわち斜ブチロル沸石を含むものは Na_2O と K_2O に富み、モンモリロナイトを含むものは MgO と CaO に富んでいた。またこれらの変質岩の原岩と考えられる未変質の火山ガラスより成る凝灰岩が、これらの地層の上部に存在するが、その化学組成は斜ブチロル沸石を含むものに近い値を示した。もしこれらの変質が低度変成作用あるいは続成作用だけからであるなら、これらの作用は比較的広域的であることから、母岩が異なるとはいえ鉱物組成も化学組成も比較的近い性質を示すことになるだろう。しかるにこの地区では、砂岩夾在層だけが異なった性質を示した。また室内実験で斜ブチロル沸石凝灰岩を Mg 状態下で処理するとモンモリロナイトが形成され、同一条件でも Na 状態では沸石（方沸石）が形成された。

以上のことから、この地区に見られる砂岩夾在層のみに見られるモンモリロナイトの変質は、何らかの2次的な Mg の添加があったとすると容易に説明される。すなわち何らかの Mg 溶液の活動があり、それが選択的にポロンティーおよびパーミアビリティのよい砂岩中をより多く通過し、Mg の添加が砂岩に集中的に起こり、火山ガラスあるいはすでに形成されていた斜ブチロル沸石がモンモリロナイトに変化したと考えられた。