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Laumontite in Altered Andesite at Kushikino, Kagoshima Prefecture, Japan

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Abstract

A laumontite occurs as in-fillings of amygdals in hornblende andesite of the Neogene formation in Kushikino area, Kagoshima Prefecture. The mineralogical properties of the laumontite were investigated by X-ray powder diffraction, chemical analysis, thermal analysis, and infrared absorption analysis. The structural formula calculated from its wet chemical analysis is: $(\text{Ca}_{3.86}\text{Na}_{0.04}\text{K}_{0.13})\text{Al}_{8.07}\text{Si}_{15.97}\text{O}_{4816.36}\text{H}_2\text{O}$. The unit cell parameters are: $a = 14.747(4)$, $b = 13.075(3)$, $c = 7.552(4)$ Å, and $\beta = 111.95(3)^\circ$.

Key words: Laumontite, Hydrothermal alteration, Altered andesite, Mineralogical properties

Introduction

Neogene andesitic rocks distributed in southern Kyushu are characterized by greenish color, and contain various clay minerals and zeolites (Minato and Utade, 1968) as hydrothermal alteration products. Only one report is known to described the detailed mineralogical properties of the laumontite in this Neogene formation (Kinzan, Kagoshima Prefecture; Tomita *et al.*, 1979). New occurrence of laumontite as in-fillings of amygdals is found in altered andesite in the Kushikino area, Kagoshima Prefecture. Such occurrence, however, has been well known in volcanic rocks in Izu Peninsula (Utada and Shimizu, 1990). In northeastern Japan, on the other hand, laumontite is widely distributed in Neogene pyroclastic sediments as authigenic crystals of diagenetic origin (Utada, 1965). The mineral rarely occurs as marine diagenetic products in deep sea sediments (Sands and Drever, 1978), and as precipitates from hot spring (McCulloh and Frizzell, 1981).

The present study reports the mineralogical properties of laumontite collected from an al-

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tered andesite in the Kushikino area, Kagoshima Prefecture.

Mode of occurrence

In Southern Kyushu, Neogene formations composed of andesitic rocks and tuffaceous sediments are widely distributed. These formations are hydrothermally altered in various degrees and commonly shows greenish color. The low grade altered andesites are black in color and often contains small amounts of ferromagnesian clay minerals such as Fe-saponite and corrensite, whereas the highly altered ones are characterized by chlorite and aluminous clay minerals such as dioctahedral smectite or mica (Kawano and Tomita, unpublished data). The laumontite in Kushikino area occurs as prismatic crystal in amygdales of a highly altered hornbrende andesite (Fig. 1). The laumontite crystals are white in color and are <1 mm in width and <10 mm in length (Fig. 2). The andesite is greenish in color and contains laumontite, quartz, chlorite, dioctahedral smectite, and small amounts of mica/smectite mixed layer. Under the microscope, laumontites replace plagioclase phenocrysts and sometimes the groundmass. These replaced laumontites are 0.1 to 1.0 mm in length. In fractures of the andesite, small size fibrous laumontite (<1.0 mm in length) associated with calcite often occurs.

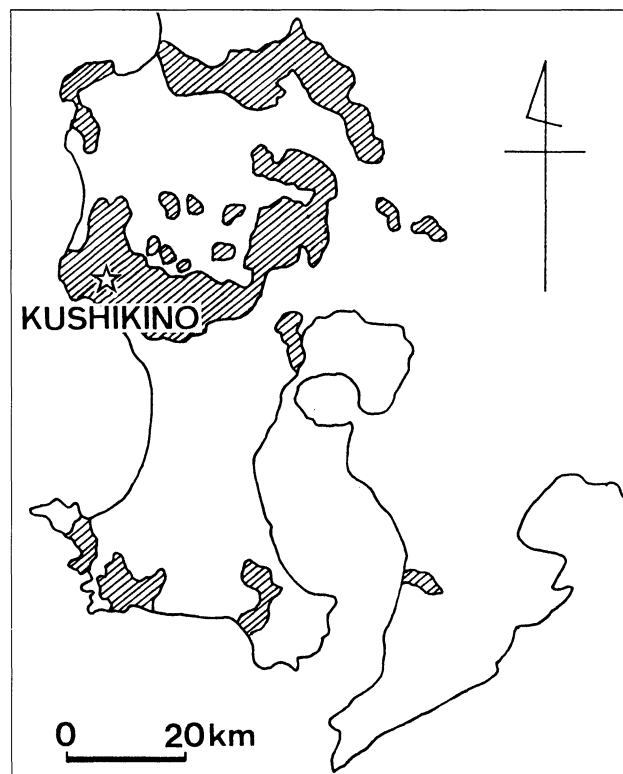


Fig. 1 Map showing the sample locality and distribution of Neogene greenish rocks in Kagoshima Prefecture.

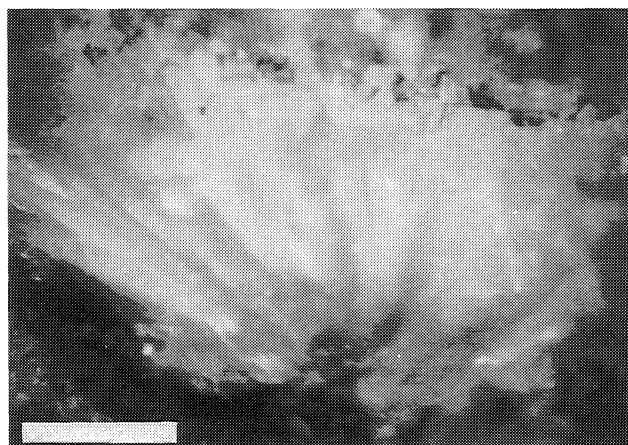


Fig. 2 Photograph of laumontite crystals formed in Kushikino. Scale bar represents 0.5mm.

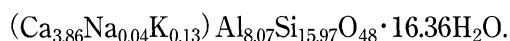
Experimental methods

The laumontite sample collected from an amygdale was pulverized in an agate mortar. The powdered sample was examined by means of X-ray powder diffraction (XRD), thermal analysis, Infrared absorption (IR), and chemical analysis. XRD was performed with a Rigaku diffractometer (30kV, 100mA) equipped with a graphite monochromator, $1/2^\circ$ divergence and scattering slits, using a scanning speed of $0.5^\circ 2\theta / \text{min}$. Thermal analysis was carried out with a Rigaku differential thermal and thermogravimetric analysis (DTA-TG) apparatus. IR spectrum was recorded utilizing the Nihonbunko infrared absorption spectrophotometer using KBr method. Chemical analysis was utilized the gravimetric method for SiO_2 , $\text{H}_2\text{O}(+)$, and $\text{H}_2\text{O}(-)$, colorimetric procedures for TiO_2 , and atomic absorption spectrometry for the other elements.

Results

Chemical analysis and the numbers of cations based on 48 oxygens on the laumontite from Kushikino are presented in Table 1, together with previous data for Kinzan (Tomita *et al.*, 1979), Otama (Coombs, 1952), and Pennsylvania (Lapham, 1963) samples. The theoretical formula of laumontite is: $\text{Ca}_4\text{Al}_8\text{Si}_{16}\text{O}_{48} \cdot 16\text{H}_2\text{O}$.

The structural formula of Kushikino material can be written as:



This is reasonably close to the ideal formula. Ternary diagram of Si-Al-Ca atomic ratios for some laumontites is shown in Fig. 3. The chemical substitutions of laumontite have been considered in two ways. One is $\text{CaAl} \rightleftharpoons \text{NaSi}$, and the other is $\text{Ca} \rightleftharpoons 2(\text{Na}, \text{K})$. These substitutions are represented on Fig. 3 as arrows a and b, respectively. The natural laumontites plotted on this diagram suggest that the $\text{CaAl} \rightleftharpoons \text{NaSi}$ substitution is dominant rather than $\text{Ca} \rightleftharpoons 2(\text{Na}, \text{K})$.

XRD data and unit cell parameters for the laumontite from Kushikino are listed in Table 2, together with previous data for Kinzan and Tanzawa (Liou, 1971) samples. The cell parameters of the Kushikino material are in fair agreement with those of the Kinzan and Tanzawa samples.

Table 1 X-ray powder diffraction data and unit cell parameters of laumontites.

hkl	1			2		3	
	d _{cal.} (Å)	d _{obs.} (Å)	I	d _{obs.} (Å)	I	d _{obs.} (Å)	I
110	9.451	9.44	100	9.51	100	9.43	78
200	6.839	6.84	19	6.86	45	6.83	56
-201	6.183	6.18	1	6.193	5	6.18	9
111	5.039	5.046	2	5.060	9	5.04	18
220	4.725	4.723	13	4.745	8	4.72	16
-221	4.492	4.491	3	4.500	11	4.49	32
130	4.152	4.152	23	4.171	60	4.15	100
-131	3.764	3.762	1	3.775	3	3.762	8
-401	3.659	3.656	4	3.664	20	3.657	42
002	3.502	3.506	8	3.520	23	3.506	94
131	3.406	3.410	2	3.420	8	3.404	26
-312	3.358	3.357	2	3.360	5	3.358	34
040	3.268	3.267	11	3.278	26	3.265	63
311	3.198	3.197	4	3.204	16	3.196	45
330	3.150	3.149	11	3.163	9		
420	3.030	3.029	13	3.047	22	3.031	45
240	2.949	2.948	2			2.947	8
-511	2.876	2.876	4	2.879	11	2.876	38
-422	2.794	2.794	2	2.795	5	2.876	38
331	2.630	2.630	1	2.636	2	2.628	3
241	2.573	2.575	4	2.585	11	2.571	34
132	2.539	2.541	1	2.543	5	2.537	3
222	2.519	2.519	2	2.528	5	2.517	5
-601	2.454	2.460	1	2.468	3	2.452	7
-441	2.437	2.437	5	2.444	13	2.437	43
151	2.358	2.361	7			2.358	23
350	2.268	2.269	4	2.278	4	2.267	9
-622	2.215	2.215	1	2.212	3	2.215	8
060	2.179	2.179	2	2.190	9	2.178	8
-333				2.170	11		
620	2.152	2.152	4	2.159	4	2.150	28
332	2.089	2.087	1	2.095	4	2.087	4
<hr/>							
a (Å)		14.747 (4)		14.773 (9)		14.737 (2)	
b (Å)		13.075 (3)		13.129 (9)		13.066 (2)	
c (Å)		7.552 (4)		7.561 (7)		7.553 (2)	
(°)		111.95 (3)		111.80 (6)		112.00 (2)	
V (Å ³)		1350.6 (3)		1361 (1)		1348.6 (4)	

1, Laumontite from Kushikino, Kagoshima Prefecture; 2, Laumontite from Kinzan, Kagoshima Prefecture (XRD data from Tomita *et al.* 1979); 3, Laumontite from Tanzawa Mountains (XRD data from Liou, 1971). The cell parameters of samples were calculated by LCLSQ lattice parameter refinement program (Burnham, 1991).

Table 2 Chemical analyses and numbers of cations based on 48 oxygens.

	1	2	3	4
SiO ₂	50.59	49.78	50.63	49.85
TiO ₂	0.01	—	0.05	—
Al ₂ O ₃	21.68	21.92	22.07	21.30
Fe ₂ O ₃	0.02	0.07	0.73	0.21
MgO	0.01	0.02	0.40	0.18
CaO	11.41	9.84	10.72	11.74
Na ₂ O	0.07	1.22	1.08	0.36
K ₂ O	0.33	0.67	0.45	0.22
H ₂ O(+)	11.98	16.06	14.10	16.08
H ₂ O(-)	3.55			
Total (%)	99.65	99.59	100.23	99.94
Si	15.97	15.87	15.73	15.20
Ti	0.00	—	—	—
Al	8.07	8.24	8.08	7.65
Fe ³⁺	0.00	—	0.17	0.07
Mg	0.00	—	0.19	0.11
Ca	3.86	3.35	3.57	3.82
Na	0.04	0.77	0.65	0.27
K	0.13	0.27	0.18	0.07
H ₂ O	16.36	17.10	14.61	16.34

1, Laumontite from Kushikino, Kagoshima Prefecture;

2, Laumontite from Kinzan, Kagoshima Prefecture (Tomita *et al.*, 1979). Total includes 0.01% P₂O₅.

3, Laumontite from Otama, Southland, New Zealand (Coombs, 1952).

4, Laumontite from Pennsylvania (Lapham, 1963).

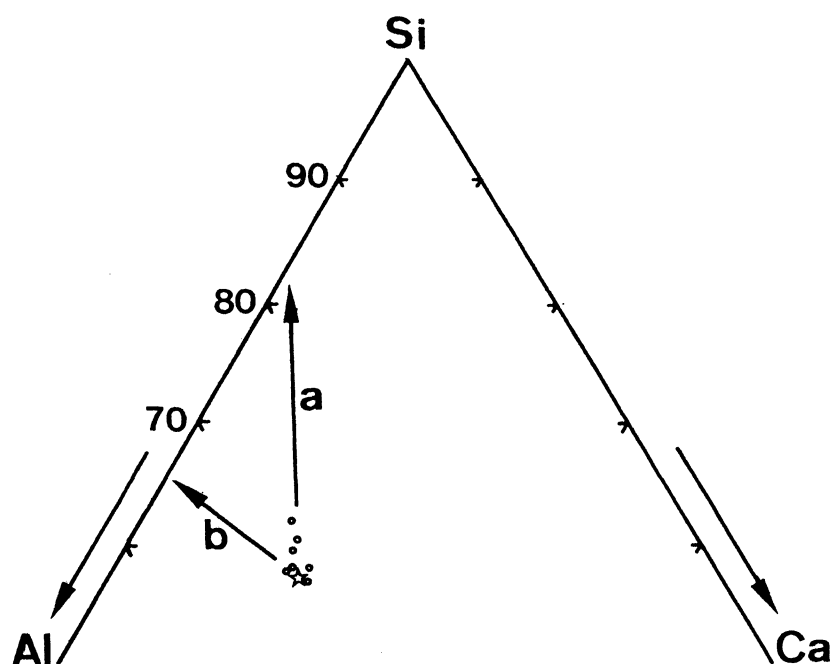


Fig. 3 Si-Al-Ca ternary diagram for laumontites. Open star, laumontite from Kushikino; Open circles, chemical analyses data from Gottardi and Galli (1985).

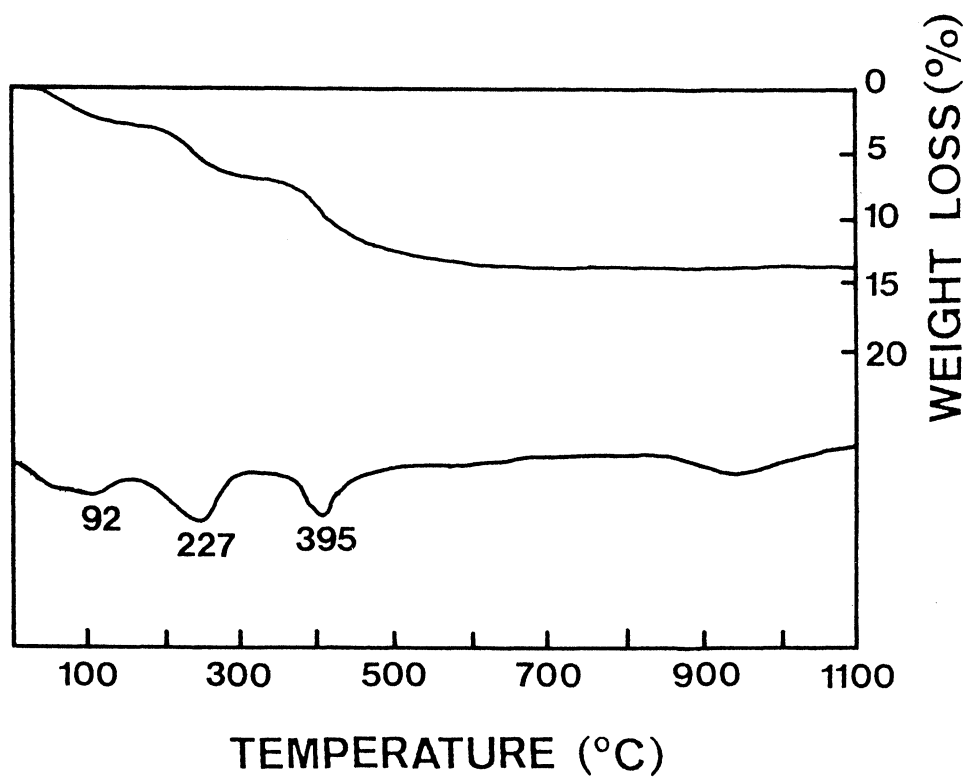


Fig. 4 DTA-TGA curves of laumontite from Kushikino.

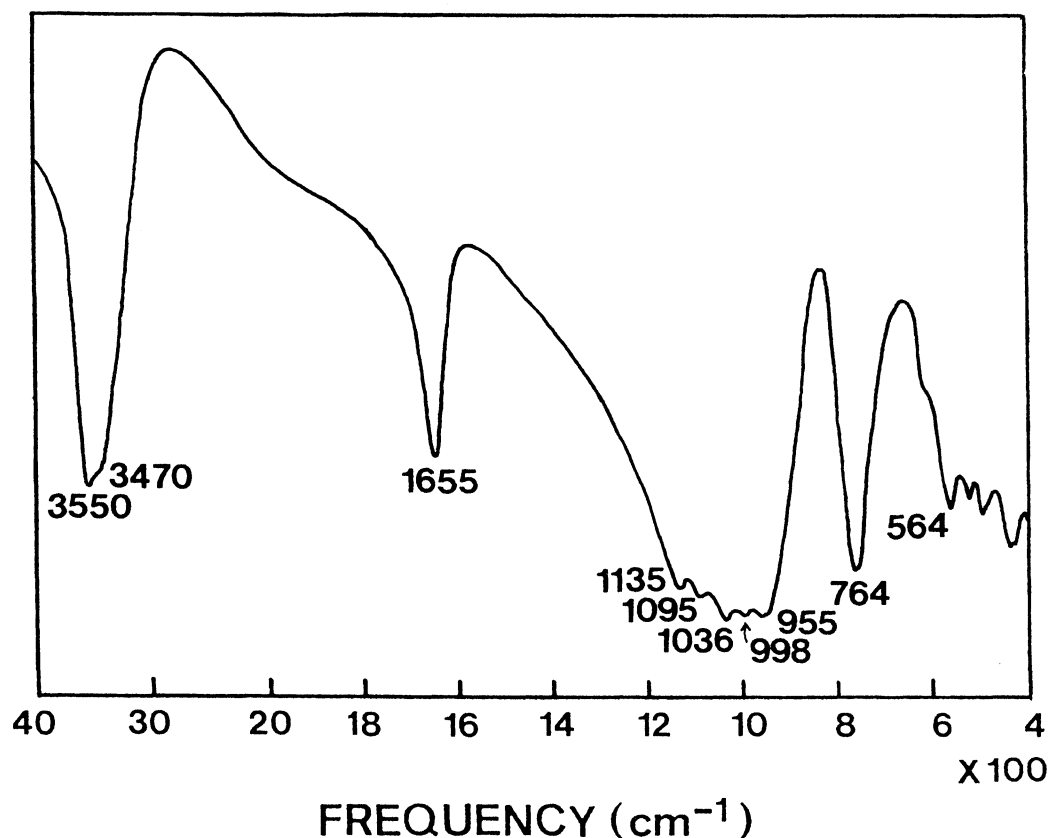


Fig. 5 IR spectrum of laumontite from Kushikino.

However, the values are consistent with those of partially dehydrated form (leonhardite) rather than fully hydrated one (Pipping, 1966). Yamasaki *et al.* (1991) reported that laumontite contains $14\text{H}_2\text{O}$ between 5 to 70% RH and 16 to $18\text{H}_2\text{O}$ between 70 to 100% RH.

Fig. 4 shows DTA-TGA curves obtained with a micro differential thermal and thermogravimetric analysis apparatus. The DTA curve exhibits three endothermic peaks at 92° , 227° , and 395°C . The TGA curve clearly indicates that dehydration reaction occurred in three steps. The weight loss of first step corresponds to $3\text{H}_2\text{O}$, the second to $4\text{H}_2\text{O}$, and the third to $7\text{H}_2\text{O}$.

The IR spectrum of the Kushikino laumontite was given in Fig. 5. The absorptions due to OH vibration of water molecules are clearly observed at 3550, 3470, and 1655cm^{-1} . At 1135-955 cm^{-1} absorptions are due to Si-O stretching vibration while absorptions at $800 - 400\text{cm}^{-1}$ are caused by Si-O linkage of tectosilicate structure (Oinuma and Hayashi, 1967).

Conclusion

The laumontite collected from the highly altered andesite of the Neogene formation of Kushikino, Kagoshima Prefecture showed similar mineralogical characteristics to those of materials previously reported as hydrothermal alteration products. The wall rock contained highly altered aluminous clay minerals as described in the previous section. This study likewise showed

similarity with laumontite that locally occurs as highly altered diagenetic products in Neogene pyroclastic sediments in northeastern Japan. Zonal distribution of diagenetic zeolites in this area is: volcanic glass \rightarrow clinoptilolite + mordenite \rightarrow analcime + heulandite \rightarrow laumontite (Utada, 1965). Similar field observations have been reported on other areas (Iijima and Utada, 1966; Nakajima and Tanaka, 1967; etc.). Therefore, it can be concluded that the laumontite in Kushikino area must have formed by higher degree hydrothermal alteration.

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