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LAUMONTITE IN AN ANDESITE FROM KINZAN, SATSUMA-CHO, KAGOSHIMA PREFECTURE

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A laumontite occurs in the cracks of an andesite at Kinzan, Satsuma-cho, Kagoshima Prefecture. Alkali content of the laumontite is higher than that of laumontites reported in Japan so far. Unit-cell constants calculated from x-ray powder data are very close to those of reported laumontites; $a=14.765\pm0.007$Å, $b=13.135\pm0.005$Å, $c=7.561\pm0.004$Å and $\beta=111.766\pm0.04°$.

INTRODUCTION

Laumontite is a calcium-rich zeolite, and usually contains a small amount of alkalies in place of calcium, but the laumontite from Kinzan, Kagoshima Prefecture, contains higher alkalies than those in laumontites reported in Japan so far. Laumontite is formed to be a replacement product of vitric tuffs or as prismatic crystals in veins and cavities in crystalline rocks. Although laumontite is a common mineral, reports of mineralogical data for laumontite are not so many in Japan. The present paper describes the mode of its occurrence and some mineralogical properties compared with those of laumontites from other localities.

OCCURRENCE

In Satsuma-cho area, Kagoshima Prefecture, andesites of Miocene to Pliocene age are widely distributed, and propylitic alteration is observed in the andesites. The laumontite is found as fibrous crystals in fractures of the andesites at Kinzan. Sampling locality is shown in Fig. 1. The laumontite is white, and its length is about 1 cm. Features of this zeolite assemblages are shown in Fig. 2. Calcite is associated with the laumontite. The exposures from which the laumontite was taken are near the surface of a newly exposed cut, and, as a result, natural dehydration of the laumontite to leonhardite is partially completed. As the dehydration-hydration reaction is reversible (Coombs, 1952), the collected specimens were stored in the water.

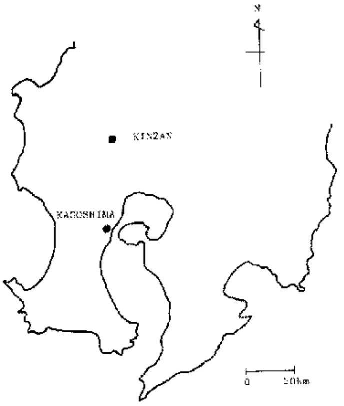

Fig. 1 Map showing the sample locality.

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Fig. 2. Photograph of the laumontite from Kinzan.

MINERALOGICAL DATA

The sample pulverized in an agate mortar was examined by means of X-ray, thermal, infrared absorption and chemical analysis.

X-ray analysis: X-ray powder diffraction data for the laumontite are presented in Table 1 together with data for a natural laumontite from Isle of Mull, Great Britain examined by Bartl and Fischer (1967). Using the proper hkl values and corresponding 2θ values, the cell parameters were calculated. The calculated parameters are presented in Table 2 together with corresponding values for some laumontites. As shown in the table, cell parameters of the Kinzan sample are in agreement with those of natural laumontite reported by previous investigators (Coombs, 1952; Liou, 1971; Bartl and Fischer, 1967).

Chemical composition: The results of chemical analysis and atomic formula calculated on the basis of 48 oxygen atoms per unit cell are presented in Table 3 together with some laumontites exmained by previous workers.

The formula is

$(Ca_{3.35}Na_{0.77}K_{0.27})Al_{8.24}Si_{15.87}O_{48}\cdot 17.10H_2O$

The ideal alkali-free end-member is

$Ca_4Al_8Si_{16}O_{48}\cdot 16H_2O$ (Coombs, 1952)

In calculating the formula, small amounts of Fe_2O_3 and MgO were neglected.

Hey (1932) showed that for a first class zeolite analysis $(Al+Si)=24\pm0.12$ as calculated for 48 oxygen atoms per unit cell. The Kinzan laumontite satisfies the requirement. The Kinzan laumontite is high in alkalies and low in Ca compared with those in the other samples. Atomic proportions of Ca, Na and K for some laumontites are plotted in Fig. 3. The Kinzan material is plotted in high Na content region. It is due to the substitution of the type Ca=2(Na, K).

Optical properties: Refractive indices of the laumontite from Kinzan are listed in Table 4 together with those of some laumontites. The range of refractive indices for some laumontites and their corresponding leonhardites are given by Coombs (1952) as:

laumontite leonhardite
$\alpha = 1.509 \pm 0.002 - 1.514 \pm 0.002$
$1.502 \pm 0.002 - 1.507 \pm 0.002$
$\beta = 1.518 \pm 0.002 - 1.522 \pm 0.002$
$1.512 \pm 0.002 - 1.516 \pm 0.002$
$\gamma = 1.521 \pm 0.002 - 1.525 \pm 0.002$
$1.514 \pm 0.002 - 1.518 \pm 0.002$

The Kinzan sample satisfies the condition, but the refractive indices of the Kinzan sample are lower than those of other samples. It has been known that laumontite loses its water to form leonhardite, and simultaneously the refractive indices drop. According to Coombs (1952), refractive indices drop with increasing silica and alkali content. As the silica content of the Kinzan sample is not so high, and its water content is high, the low indices for the Kinzan sample are considered to be due to high alkali content.

Differential thermal analysis: Differential thermal analysis curve taken with an automatic thermal analyser at a heating rate of 10°C per minute for the laumontite is shown in Fig. 4. According to Otsuka *et al* (1970) laumontite dehydrates in three

Table 1. Powder data for laumontite

HKL	1		2	
	d(Å)	I	d(Å)	I
110	9.46	100	9.51	100
200	6.838	38	6.86	45
$\bar{2}01$	6.193	6	6.193	5
111	5.046	2	5.060	9
220	4.730	8	4.745	8
$\bar{2}21$	4.500	13	4.500	11
201	4.178	20	4.171	60
130				
$\bar{1}31$	3.772	2	3.775	3
$\bar{4}01$	3.661	16	3.664	20
002	3.509	40	3.520	23
131	3.412	5	3.420	8
$\bar{3}12$	3.365	9	3.360	5
040	3.275	10	3.278	26
$\bar{3}31$	3.203	7	3.204	16
330	3.153	4	3.163	9
$\bar{4}02$	3.096	1		
420	3.031	7	3.047	22
$\bar{5}11$	2.878	5	2.879	11
$\bar{4}22$	2.799	5	2.795	6
331	2.633	1	2.636	2
241	2.577	6	2.585	11
132	2.543	3	2.543	5
222	2.523	4	2.528	5
$\bar{2}03$				
$\bar{2}42$	2.465	3	2.468	3
$\bar{5}31$	2.444	6	2.444	13
$\bar{4}41$	2.441			
440	2.365	3		
151	2.363			
350	2.272	1	2.278	4
$\bar{6}22$	2.218	3	2.212	3
060	2.183	2	2.190	9
$\bar{5}33$	2.167	3	2.170	11
620	2.153	4	2.159	4
$\bar{1}52$	2.149	4		
$\bar{3}52$	2.094	1	2.095	4
203	1.9964	1	2.002	4
422	1.9901	2	1.994	2
$\bar{5}51$	1.9588	3	1.963	5
133	1.9466	1		
223	1.9096	1		
$\bar{2}62$	1.8860	1	1.892	2
$\bar{3}14$	1.8729	2		
$\bar{7}13$	1.8679	3	1.863	4
062	1.8538	3	1.855	4
$\bar{8}01$	1.8256	1	1.831	1

1. Natural laumontite from Isle of Mull, Great Britain (Bartl & Fisher, 1967)
2. Natural laumontite from Kinzan, Kagoshima Prefecture, Japan.

Table 2. Cell parameters of natural laumontites

	1	2	3	4
a(Å)	14.765 ± 0.007	14.75 ± 0.03	14.737 ± 0.004	14.90 ± 0.05
b(Å)	13.135 ± 0.005	13.10 ± 0.03	13.066 ± 0.002	13.07 ± 0.02
c(Å)	7.561 ± 0.004	7.57 ± 0.02	7.550 ± 0.003	7.55 ± 0.05
β	111.76 ± 0.04	112.0 ± 0.2	111.97 ± 0.02	111.5 ± 0.5
V(Å^3)	1362 ± 2	1346 ± 4	1349 ± 2	1367 ± 5

1. Natural laumontite from Kinzan, Kagoshima Prefecture.
2. Natural laumontite from Isle of Mull, Great Britain (Bartl & Fischer, 1967).
3. Natural laumontite from Tanzawa Mountains, Japan (Liou, 1971).
4. Natural laumontite from Otama, New Zealand (Coombs, 1952).

Table 3. Chemical analyses and formulae of laumontites.

	1	2	3	4	5	6
SiO_2	49.78%	50.99%	49.85%	50.96%	48.96%	50.90%
TiO_2	tr.	0.02				
Al_2O_3	21.92	21.87	21.30	21.60	22.24	20.30
Fe_2O_3	0.07	0.09	0.21	0.03		1.20
FeO		0.11				
MnO	tr.	0.02				
MgO	0.02	tr.	0.18			0.69
CaO	9.84	12.00	11.74	11.27	12.32	11.20
Na_2O	1.22	0.38	0.36	0.32	0.63	0.93
K_2O	0.67	0.10	0.22	0.16	0.31	0.38
$H_2O(+)$	)16.06	14.02	)16.08	)16.04	)16.41	)15.22
$H_2O(-)$		0.29				
P_2O_5	0.01					
Total	99.59%	99.89%	99.94%	100.40%	100.87%	100.82%

Atomic formulae on basis of 48 oxygen atoms

	1	2	3	4	5	6
Ca	3.35	4.00	4.00	3.79	4.19	3.76
Na	0.77	0.22	0.23	0.19	0.38	0.57
K	0.27	0.04	0.06	0.07	0.13	0.15
Si	15.87	15.88	15.87	16.04	15.54	15.95
Al	8.24	8.01	7.99	8.00	8.32	7.50
H_2O	17.10	14.87	17.07	16.81	17.36	15.91
Ca+(Na+K)/2	3.87	4.13	4.16	3.92	4.45	4.12
Ca+Na+K	4.39	4.26	4.31	4.05	4.70	4.48
Al+Si	24.11	23.89	23.86	24.04	23.86	23.45

1. Laumontite from Kinzan, Kagoshima Prefecture.
2. Vein-forming laumontite in Miocene mafic volcanic rocks, Tanzawa Mountains, Kangawa Prefecture (Seki *et al.*, 1969).
3. Laumontite in diabase from Dillsburg, Pennsylvania (Lapham, 1963).
4. Laumontite, Margaretville, Nova Scotia (Walker & Parsons, 1922).
5. Fresh crystals of laumontite, Baveno (Pagliani, 1948).
6. Laumontite, Sewree, Bombay (Sukheswala *et al.*, 1974).

steps, between room temperature and 190°C, between 190°C and 370°C, and between 370°C and 800°C. The differential thermal analysis curve for the Kinzan sample shows four endothermic peaks at 105°C, 165°C, 300°C and 465°C. The endothermic peaks at 105°C and 165°C are corresponding to the first dehydration step. The endothermic peaks at 300°C and 465°C are corresponding to the dehydration in second and third step respectively. Koizumi (1953) also reported that laumontite dehydrated in three steps.

Infrared absorption analysis: Infrared absorption spectra for the laumontite was obtained using Nujol paste method. The infrared absorption spectra are shown in Fig. 5. The spectra have absorption bands at 1650 cm^{-1} and a broad band between 3300–3600 cm^{-1}. The absorption bands around 3450cm^{-1} are probably due to adsorbed water as indicated by comparison with montmorillonite data of Wolff (1965). The absorption bands around 3450cm^{-1} in the water-stretching region are spread toward higher frequencies. Some amounts

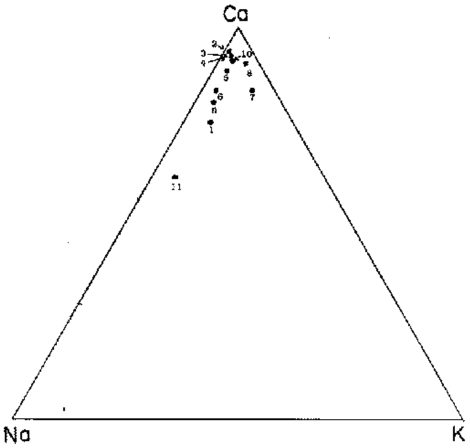

Fig. 3. Ternary diagram showing atomic proportion of Ca, Na and K for some laumontites and leonhardites.
1. laumontite from Kinzan, Kagoshima Prefecture; 2. vein-forming laumontite in Miocene mafic volcanic rocks, Tanzawa Mountains, Kanagawa Prefecture (Seki *et al.*, 1969); 3. laumontite in diabase from Dillsburg, Pennsylvania (Lapham, 1963); 4. laumontite, Margaretville, Nova Scotia (Walker and Parsons, 1922); 5. laumontite, Baveno (Pagliani, 1948); 6. laumontite, Sewree, Bombay (Sukheswala *et al.*, 1974); 7. leonhardite, Cascade Mountains, Southern Oregon (McClellan, 1926); 8. leonhardite, Hungary, no. 192, Mineralogical Museum, Cambridge (Coombs, 1952); 9. laumontite partially dehydrated to leonhardite by exposure, Otama, Southland, New Zealand (Coombs, 1952); 10. laumontite, drusy cavities in quartz porphyry, Halle, Saale, Germany (Koch, 1958); 11. Devon Well, New Plymouth, New Zealand (Hutton, 1944).

of water are considered to be structurally bound. This phenomenon has also been described in stilbite (Harada and Tomita, 1967), erionite (Harada *et al.*, 1967) and mordenite (Tomita *et al.*, 1970). A clear asymmetrical absorption at about 1650^{-1}cm is due to OH-bending vibration.

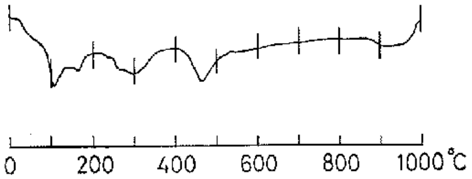

Fig. 4 Differential thermal analysis curve for the laumontite from Kinzan.

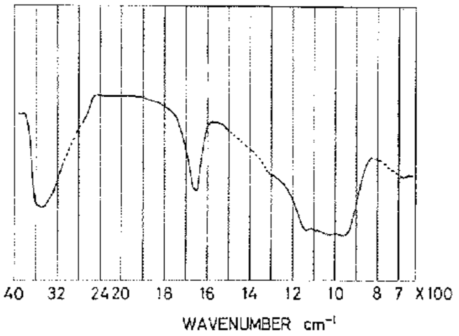

Fig. 5. Infrared absorption spectra for the laumontite from Kinzan.

DISCUSSION

The laumontite from Kinzan contains

Table 4. Refractive indices of laumontites

	1	2	3	4	5	6
α =	1.512±0.002	1.510±0.002	1.514±0.002	1.509±0.002	1.514±0.002	1.510
β =	1.515±0.002	1.518±0.002	1.522±0.002	1.518±0.002	1.522±0.002	1.525
γ =	1.519±0.002	1.522±0.002	1.524±0.002	1.521±0.002	1.525±0.002	1.527

1. From Kinzan, Kagoshima Prefecture.
2. Crush zone in meta-gabbro, Otama, Southland, New Zealand (Coombs, 1952).
3. Laumontite on tuffa, Hungary (Coombs, 1952).
4. Laumontite from laumontitized vitric tuff, North Range, Taringatura Survey District, Southland, New Zealand (Coombs, 1952).
5. From Felso Certes, Translyvania (Coombs, 1952).
6. Fresh crystals of laumontite, Baveno (Pagliani, 1948).

higher alkalies as compared with those in ordinally laumontite. Some amounts of alkalies proxy for Ca without affecting the Si:Al ratio in the Kinzan material. The cell parameters of the laumontite from Kinzan are in agreement with those of some laumontites reported by previous workers. This means that the frame work of laumontite is strong enough and is not affected by the small amounts of substitution of Na and K for Ca. According to Yamamoto (1960), andesite in Kinzan area, host rock of the laumontite, does not contain large amounts of Na_2O and K_2O. The laumontite was formed in the final stage of the magmatic consolidation.

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鹿児島県薩摩町金山の安山岩中の濁沸石について

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鹿児島県薩摩町金山地域に分布する安山岩の空隙中に濁沸石が産出した。従来，日本で報告されたものよりアルカリの量が若干多い。格子定数は，$a=14.765\pm0.007$ Å，$b=13.135\pm0.005$ Å，$c=7.561\pm0.004$ Å．$\beta=111.766\pm0.04^\circ$ で，ほとんど普通の濁沸石と同じ値を示すが，屈折率はやや低く，$\alpha=1.512\pm0.002$，$\beta=1.515\pm0.002$，$\gamma=1.519\pm0.002$ を示す。これはアルカリ含有量が多いためと考えられる。