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On the Varieties of Heulandite

By

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with 9 Tables and 5 Text-figures

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ABSTRACT: As the results obtained from x-ray diffraction at the elevated temperatures, fluorescent x-ray analyses and infrared absorption concerning some specimens of zeolite with the ordinary patterns of heulandite in case of no treatments and with the similar values for *Al* : *Si* ratio in the framework structure constructed mainly of *Al* and *Si* atoms, though more or less different in the content of alkali and alkaline earth metals, have become considerably clear the transformation of heulandite merely through dehydration as well as the thermal stability of its structure, the effects of mingling of heulandite with clinoptilolite, the presence of four- and six-coordinated *Al* and difference in the wave number and intensity of infrared absorption.

CONTENTS

I. INTRODUCTION

Plenty of the works have hitherto been carried into effect since SCHALLER's proposition of clinoptilolite as a variety of heulandite but there still remains some obscurity concerning the structures of these minerals. As regards this, the following data are worthy mentioning:

$a_0=7.559Å$, $b_0=18.005Å$, $c_0=15.94Å$, $\beta=88°34'$ (WYCKOFF, 1951)

$a_0=7.46Å$, $b_0=17.84Å$, $c_0=15.88Å$, $\beta=91°26'$ C_{2h}^3, $I2/m$
(STRUNZ and TENNYSON, 1956; REGNIER, 1960)

$a_0=15.85Å$, $b_0=17.9Å$, $c_0=15.88Å$, $\beta=91°26'$ (SMITH, 1963)
(*cf.* SCHONER, 1960; SUDO, 1963)

On the other hand, their chemical compositions represented commonly by $(Ca, Na_2)Al_2Si_7O_{18} \cdot 6H_2O$ are somewhat variable specifically in the $Al:Si$ ratio together with the content of Ca and Na while SiO_2 is generally in the range 56. 8~58. 5% with exception of the case with higher content, *e.g.* 61. 74% given by Ross and SHANON (1924). High-silica heulandite has been designated clinoptilolite by SCHALLER (1932) but merely taken as a variety by HEY and BANNISTER (1934). Difference between heulandite and clinoptilolite has been found not in the content of Si and Al but in those of Na and K and moreover the species with heulandite structure including far more predominance of the alkali metals than Ca in content has been defined as a sort of clinoptilolite by MASON and SAND (1960).

Based on the fact mentioned above, ion substitution such as $Ca^{2+}Al^{3+} \geq Na^{+}Si^{4+}$ and $Na^{+}Al^{3+} \geq Si^{4+}$ has also been proved to be possible in heulandite.

Shrinkage of b_0 through dehydration of heulandite has been reported by WYART (1933) and HEY (1935), endotherms at 200°C and 360°C on DTA curve have been combined with dehydration completed at 300°C at the first step and at 400°C at the second step and then breakdown of the structure by KOIZUMI (1953) and GREENBERG (1954) while transformation of heulandite to the high modification (heulandite B) at 210°C and amorphous structure at 350°C as well as the stability of clinoptilolite up to 700°C have been shown by MUMPTON (1960) on the basis of the data obtained from heat treatment and x-ray diffraction.

Since it was deemed in view of the previous data that there remain some problems to be solved more accurately in determination of heulandite from clinoptilolite, their stability, and identification of the species with peculiar composition, several procedures for reaching certain conclusion, though to a slight extent, have been applied to.

II. SCRUTINY OF SPECIMEN

(1) Specimens provided for experiments

Three kinds of the specimens have been provided for the present work, of which the sample 1 is identified with heulandite of E type filling the cavity of the pyroclastic rock from Chichi-jima in Ogasawara Islands, the sample 2 with clinoptilolite of A, B and C types produced by alteration of the pyroclastics in the Kuri formation from Shizuma-chô, Ôta City, Shimane Pref. and the sample 3 with a sort of heulandite of D type filling the interstices of the pyroclastics in Ômori formation from Tamayu-chô, Matsue City, Shimane Pref. (UMEGAKI *et al.*, 1965).

(2) Chemical analyses

The analyses of these specimens are listed in Table 1. Inspection of the data indicates that (a) SiO_2 is more abundant in content in the samples 2 and 3 than in the sample 1 whereas the values of $Al:Si$ are not so much different from one another in all of the specimens, (b) as for the exchangeable cations, Ca is most predominent but the alkalies are least in amount in the sample 1, (c) the remarkable quantity of Ba is characteristically contained in the sample 3, and (d) the chemical composition of the sample 1 corresponds to that of heulandite while those of the samples 2 and 3 are approximately similar to that of clinoptilolite. Based on these data, the samples 1, 2 and 3 will hereunder be defined, heulandite proper, clinoptilolite and *Ba*-bearing heulandite, respectively in order.

TABLE 1a. CHEMICAL ANALYSES OF THE SAMPLES

Sample No. / Comp.	1	2	3
SiO_2	56.36	62.10	57.66
Al_2O_3	16.10	16.80	16.12
Fe_2O_3	1.23	1.63	1.44
MnO	—	—	0.27
MgO	0.06	0.33	0.02
BaO	—	—	4.80
CaO	8.56	4.15	1.59
Na_2O	0.69	1.27	1.98
K_2O	0.13	0.33	0.30
$H_2O(+)$	12.90	11.43	11.48
$H_2O(-)$	3.30	1.51	3.48
total	99.33	99.54	99.14

TABLE 1b. VALUES CALCULATED WITH REFERENCE TO 72 OXYGENS

Sample No. / Comp.	1	2	3
Si	26.59	27.77	27.42
Al	8.96	8.52	9.03
Fe^{+3}	0.45	0.54	0.51
Mn^{+2}	—	—	0.08
Mg	0.03	0.22	0.01
Ba	—	—	0.86
Ca	4.34	2.00	0.81
Na	0.62	1.07	1.82
K	0.06	0.22	0.18
$H_2O(+)$	20.30	17.13	18.24
$H_2O(-)$	5.19	2.24	5.53
Z	36.02	36.83	36.96
R	5.08	3.51	3.68

$Z = Si + Al + Fe^{+3} + Mn^{+2}$
$R = Mg + Ba + Ca + Na + K$

(3) X-ray diffraction data

Concerning the data related to the present work, those given by WYCKOFF (1951), STRUNZ and TENNYSON (1956), REGNIER (1960), SCHONER (1960) and SMITH (1963) etc. are of due significance. The indices for all of the spacings of the specimens in question have been deduced through repeated calculation of Q-values represented by:

$$\begin{aligned} Q_{(hkl)} &= 1/d^2(hkl) \\ &= h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2lhc^*a^*\cos\beta^* \end{aligned}$$

while the results have also been checked with ARTHUR's method (1964).

The data obtained at the ordinary and heated states and in vacuum ($10^{-4\sim-5}$mmHg, in order to avoid oxydation) are presented in the following tables.

(4) Continuous variation of the structures on heating

The behaviors and structures at the elevated temperature have not been clarified by ordinary means of the quenching method put into operation previously since it is impossible to keep the final structures shown only at higher temperature after cooling to the ordinary state owing to the breakdown or at least more or less variation through dehydration, and so forth. Considering these factors, variation of the x-ray diffraction patterns of the specimens with increasing temperature have been continuously pursued at the heated state. The considerable difference has been recognized in the results according to whether the experiments have been carried out at the ordinary pressure or in vacuum and to the easiness or difficulty of dehydration and of oxydation. Since a little contraction of the spacings caused by aspiration of air for some hours is to be neglegible, the heating procedures have been started from the state held in vacuum for 22 hours and the data have been taken respectively at such temperature as have been kept constant least for 4 hours.

(5) Fluorescent x-ray analyses

For finding out difference of the samples in relation to the coordination number of *Al* the ordinary procedures have been put in operation in such conditions as:

Primary x-ray (with W-target): 45kv, 40mA.

Analysing crystal: EDDT, with use of which Alk_{α} (λ=8. 340Å) appears at 142. 509° (2θ).

Scanning speed: 0. 5° (2θ)/min.

Chart speed: 2° (2θ)/min.

Considering variation of the lattice constant of EDDT with increasing temperature during operation, 2θs for the specimens have been checked with metallic *Al* in each experment and the average values with the standard errors have been taken.

(6) Infrared absorption

The tablets prepared through mixing of the pulverized specimens with KBr have been exposed against infrared ray with 2∼25μ in wave-length, correction of which has been based on those for polystilene. At the same time, the samples prepared through mixing with nujol have been subjected to the similar experiments in order to find the absorbed humidity on the dehydrated specimens.

III. RESULTS OBTAINED

It has become evident that three kinds of the specimens are respectively characterized with respect to some properties.

The sample 1, heulandite proper, bears the cell dimension with a_0=7. 46Å, b_0= 17. 90Å, c_0=15. 91Å and β=91°26′ at the room temperature and 1 atm. pressure but with a_0=7. 43Å, b_0=17. 59Å, c_0=15. 71Å and β=91°20′ in vacuum probably due to the loss of 10. 18% water(see tables 2a and 2b).

The data for the röntgenographic variation of its structure with increasing temperature are given in the figures 1 and 2. Inspection of the results indicates that (a) up to 85°~120°C (transition temperature) increase of intensity is recognized on the spacings (020), (002) and (022) but decrease on the spacings (031), (11$\bar{2}$), (004), (042)

Table 2a. X-ray Diffraction Data for the Sample 1 (Heulandite) at the Room Temperature and 1 Atm. Pressure

d obs	d calc	Q obs$\times 10^{-5}$	Q calc$\times 10^{-5}$	ΔQ$\times 10^{-5}$	I/I_0	(hkl)
9.03	8.951	1226	1248	22	100	(020)
7.920	7.955	1594	1580	−14	3	(002)
6.820	6.889	2150	2107	−43	2	(110)
	6.823		2148	− 2		(10$\bar{1}$)
6.662	6.662	2253	2232	21	2	(101)
5.948	5.946	2826	2828	2	2	(022)
5.601	5.587	3187	3203	16	2	(031)
5.252	5.268	3625	3603	−22	3	(11$\bar{2}$)
5.114	5.149	3823	3771	−52	4	(112)
4.656	4.661	4613	4603	−10	11	(130)
4.488	4.475	4965	4992	−27	2	(040)
4.362	4.375	5255	5224	−31	2	(10$\bar{3}$)
3.969	3.977	6348	6320	−28	18	(004)
3.905	3.901	6557	6572	15	19	(042)
3.743	3.742	7138	7140	2	2	(14$\bar{1}$)
3.727	3.720	7199	7224	25	2	(141)
3.563	3.579	7875	7803	−72	2	(21$\bar{1}$)
3.541	3.542	7975	7971	− 4	2	(211)
3.498	3.493	8168	8195	27	2	(051)
3.423	3.411	8535	8592	57	2	(20$\bar{2}$)
	3.411		8595	60		(114)
3.189	3.187	9832	9840	8	4	(22$\bar{2}$)
3.125	3.134	10240	10176	−64	6	(222)
	3.133		10187	−53		(015)
	3.116		10299	59		(23$\bar{1}$)
3.091	3.091	10469	10467	− 2	1	(231)
2.975	2.984	11298	11232	−66	21	(060)
	2.973		11312	14		(044)
2.898	2.898	11902	11880	−22	4	(105)
2.728	2.734	13431	13380	−51	4	(16$\bar{1}$)
	2.725		13464	33		(161)
2.526	2.525	15662	15683	21	2	(071)
2.461	2.465	16505	16456	−49	2	(16$\bar{3}$)
2.444	2.446	16742	16708	−34	2	(163)

$a_0 = 7.46$Å $\quad a^* = 0.13397$
$b_0 = 17.90$Å $\quad b^* = 0.05585$
$c_0 = 15.91$Å $\quad c^* = 0.06285$
$\beta = 91°26'$ $\quad \beta^* = 88°34'$

TABLE 2b. X-RAY DIFFRACTION DATA FOR THE SAMPLE 1 (HEULANCITE) AT THE ROOM TEMPERATURE AND IN VACUUM

d obs	d calc	Q obs$\times 10^{-5}$	Q calc$\times 10^{-5}$	$\triangle$Q$\times 10^{-5}$	I/I_0	(hkl)
8.750	8.797	1306	1292	−14	100	(020)
7.865	7.856	1616	1620	4	4	(002)
7.080	7.168	1995	1946	−49	1	(012)
6.868	6.848	2120	2132	12	2	(110)
6.763	6.783	2186	2174	−12	2	(10$\bar{1}$)
5.886	5.860	2886	2912	−26	2	
5.820		2952		−40	2	(022)
5.480	5.495	3330	3312	−18	6	(031)
	5.464		3349	19		(10$\bar{2}$)
4.611	4.603	4703	4716	13	8	(130)
4.338	4.329	5314	5334	20	2	(10$\bar{3}$)
3.922	3.928	6501	6480	−21	16	(004)
3.840	3.838	6781	6788	7	16	(042)
3.700	3.691	7304	7340	36	3	(14$\bar{1}$)
3.558		7899			2	
3.171	3.167	9945	9972	27	3	(22$\bar{2}$)
2.097	3.093	10426	10454	28	3	(015)
	3.091		10466	40		(23$\bar{1}$)
2.932	2.932	11634	11628	− 6	16	(060)
	2.929		11650	16		(044)
2.777	2.771	12967	13026	59	3	(12$\bar{5}$)
2.688	2.686	13835	13860	25	8	(24$\bar{2}$)
	2.684		13882	47		(161)
2.483	2.484	16213	16204	− 9	6	(15$\bar{4}$)
	2.482		16232	19		(071)

$a_0 = 7.43\text{Å}$ $a^* = 0.13449$
$b_0 = 17.59\text{Å}$ $b^* = 0.05683$
$c_0 = 15.71\text{Å}$ $c^* = 0.06363$
$\beta = 91°20'$ $\beta^* = 88°40'$

and (141, 14$\bar{1}$) etc., (b) above this temperature, abrupt increase of intensity is observed on the spacings (020), (031) and (042), indicative of the high-temperature modification with $a_0 = 7.35\text{Å}$, $b_0 = 16.71\text{Å}$, $c_0 = 15.26\text{Å}$ and $\beta = 90°59'$ (see table 2c) and reach its maximum at 250°C, (c) the structure of high-temperature modification is kept up to 600°C while in case of being treated in the air it is broken down at all at far lower temperature, (d) after transition the loss of water amounts to 4.95%, signifying completion of dehydration, (e) gradual contraction of the interplaner distance is conspicuous and its variation becomes more marked above the transition temperature whereas the indices of the fundamental spacings are found invariable, and (f) when the high-temperature modification attained through heating at the temperature up to 600°C

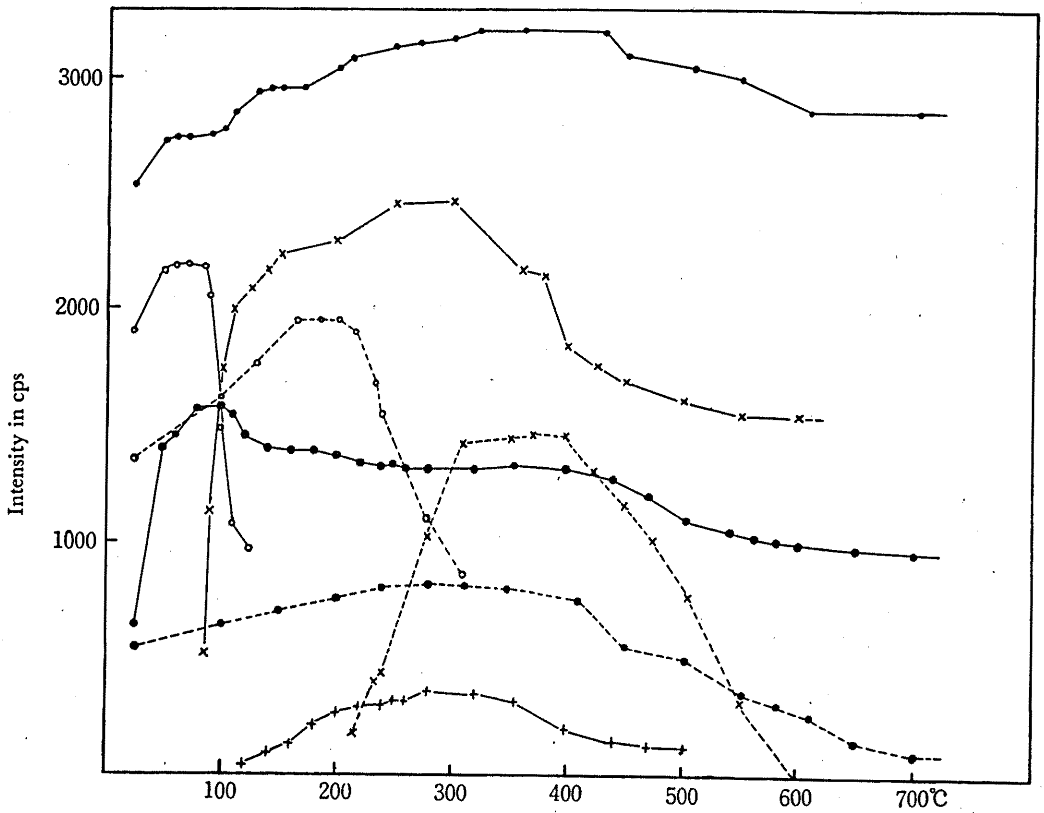

Fig. 1 Variation of intensity on (020)
o heulandite (sample 1)
× high-temperature heulandite
⊙ clinoptilolite (sample 2)
+ high-temperature heulandite
● Ba-bearing heulandite (sample 3)
.... 1 atm. presure
—— in vacuum

is allowed to stand in the air for 1 hour, the diffraction patterns are reversibly recovered to those recognized initially at the room temperature and in vacuum but without addition of heated or compressed water vapor the primary structures are not completely recovered.

The sample 2, clinoptilolite, reveals the lattice constants such as $a_0=7.46Å$, $b_0=17.96Å$, $c_0=15.91Å$ and $\beta=91°26'$ at the ordinary state (see table 2d), showing a little contraction in vacuum. X-ray diffraction data are presented in the figures 1 and 3. It is known that (a) increase and decrease of intensity are similarly ascertained respectively on the spacings almost same as in case of the sample 1 but above 110°C decrease of intensity on the spacings (020) and (002) as well as its increase on the spacings $(11\bar{2})$ and $(141, 14\bar{1})$ become more apparent owing to overlapping of the spacings

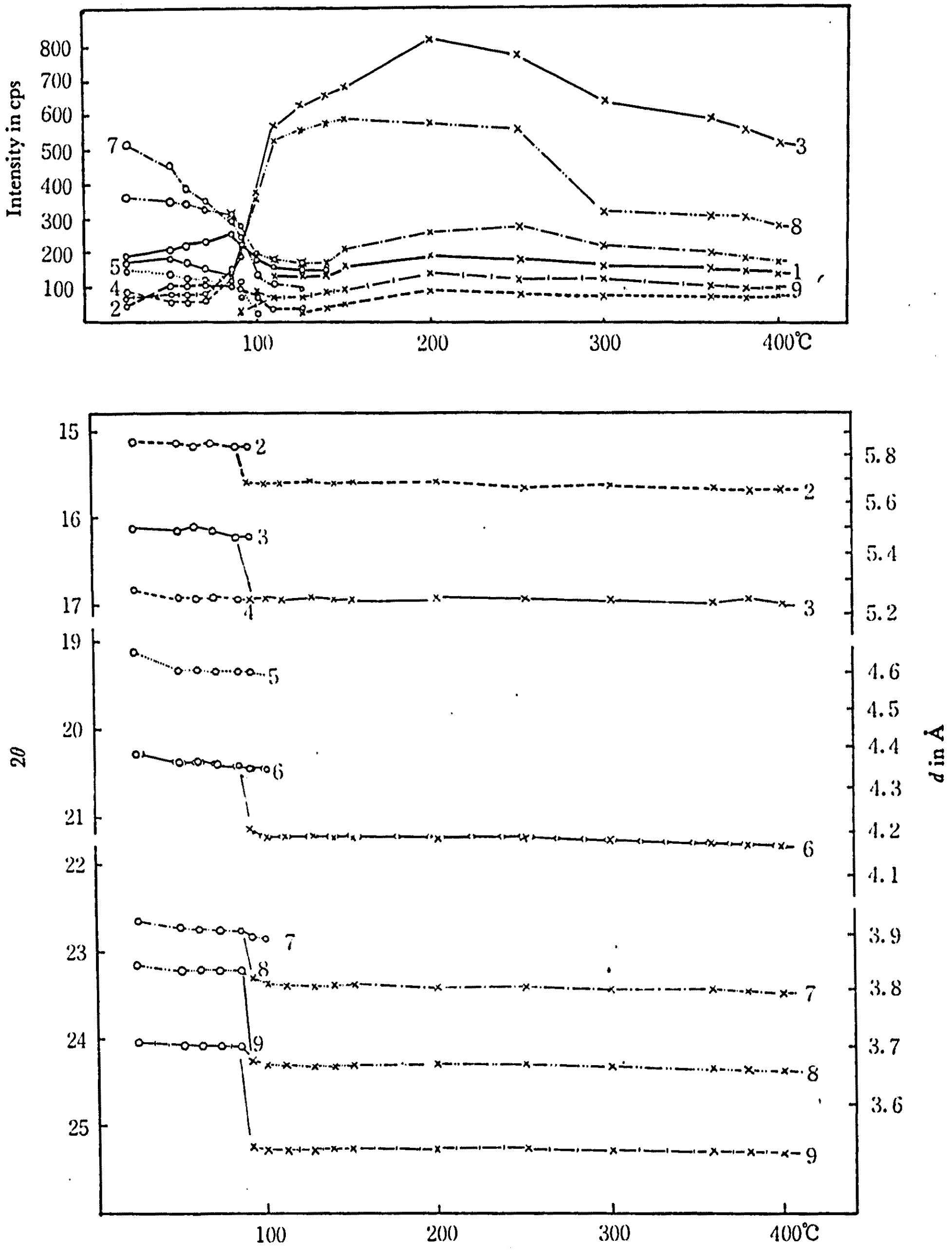

FIG. 2 Variation in the sample 1 (heulandite)

○ heulandite

× high-temperature heulandite

1 : (002) 2 : (022) 3 : (031) 4 : (11$\bar{2}$) 5 : (130) 6 : (040) 7 : (004) 8 : (042)
9 : (141, 14$\bar{1}$)

TABLE 2c. X-RAY DIFFRACTION DATA FOR THE SAMPLE 1 (HEULANDITE) AT 250°C AND IN VACUUM

d obs	d calc	Q obs × 10^{-5}	Q calc × 10^{-5}	ΔQ × 10^{-5}	I/I_0	(hkl)
8.275	8.356	1460	1432	−28	100	(020)
7.635	7.633	1715	1716	1	4	(002)
6.682	6.731	2239	2207	−32	4	(110)
	6.671		2247	8		$(10\bar{1})$
5.230	5.233	3656	3651	− 5	24	(031)
5.005	5.009	3992	3985	− 7	5	(112)
4.442	4.441	5068	5071	3	1	(130)
4.179	4.178	5726	5728	2	1	(040)
3.811	3.817	6885	6864	−21	7	(004)
3.664	3.665	7448	7444	− 4	26	(042)
3.526	3.541	8043	7975	−68	4	$(14\bar{1})$
	3.527		8037	− 6		(141)
3.288	3.291	9249	9231	−18	4	$(14\bar{2})$
3.249		9473			3	
2.836	2.837	12427	12419	− 8	6	$(10\bar{5})$
	2.833		12455	28		$(15\bar{2})$
2.677	2.678	13954	13947	− 7	2	(035)
2.565	2.570	15193	15135	−58	7	$(16\bar{1})$
	2.565		15197	4		(161)
2.387	2.387	17541	17542	− 1	1	(070)
	2.387		17539	− 2		$(15\bar{4})$
2.351	2.352	18081	18073	− 8	1	(320)

$a_0 = 7.35$Å $a^* = 0.13597$
$b_0 = 16.71$Å $b^* = 0.05983$
$c_0 = 15.26$Å $c^* = 0.06549$
$\beta = 90°59'$ $\beta^* = 89°01'$

(031) and (042) of the high-temperature heulandite, implying that clinoptilolite and heulandite coexist in the sample 2, (b) as are clear from the figures, variation at the room temperature is not so much noticeable because of ambiguity caused by paragenesis of two species, (c) above 350°C all of the spacings reveal decrease of intensity but the structures are kept invariable even at 700°C, (d) the manners of variation of the interplaner distance are dividable into two types: one is that accompanying transformation while the other without any other modifications indicates a gradual shrinkage and approaches to that with the patterns appering just before transformation at 250°C, where the cell dimension is of $a_0 = 7.42$Å, $b_0 = 17.54$Å, $c_0 = 15.67$Å and $\beta = 91°20'$ (see table 2e), and (e) the loss of water is estimated 13.01% up to this state.

The sample 3, Ba-bearing heulandite, bears the unit cell with $a_0 = 7.46$Å, $b_0 = 18.08$Å, $c_0 = 15.91$Å and $\beta = 91°26'$ at the ordinary state (see table 2f), displaying the diffraction intensity resembling that of heulandite proper and a little contraction in

TABLE 2d. X-RAY DIFFRACTION DATA FOR THE SAMPLE 2 (CLINOPTILOLITE) AT THE ROOM TEMPERATURE AND 1 ATM. PRESSURE

d obs	d calc	Q obs × 10^{-5}	Q calc × 10^{-5}	ΔQ × 10^{-5}	I/I_0	(hkl)
9.01	8.980	1248	1240	− 8	100	(020)
7.905	7.948	1576	1583	7	14	(002)
6.765	6.892	2185	2105	−80	2	(110)
	6.748		2196	11		$(10\bar{1})$
6.645	6.653	2264	2259	− 5	11	(101)
5.994	5.955	2783	2820	37	3	(022)
5.615	5.603	3171	3185	14	5	(031)
5.245	5.269	3635	3601	−34	14	$(11\bar{2})$
5.118	5.151	3817	3769	−48	12	(112)
4.664	4.670	4597	4585	−12	19	(130)
4.502	4.490	4934	4960	26	5	(040)
4.347	4.375	5292	5224	−68	5	$(10\bar{3})$
3.973	3.977	6335	6320	−15	72	(004)
3.910	3.910	6541	6540	− 1	54	(042)
3.749	3.751	7115	7108	− 7	4	$(14\bar{1})$
3.742	3.728	7141	7192	51	4	(141)
3.544	3.542	7961	7969	8	5	(211)
3.496	3.504	8179	8145	−34	4	(051)
3.424	3.411	8532	8592	60	8	$(20\bar{2})$
	3.411		8593	61		(114)
3.183	3.189	9868	9832	25	3	$(22\bar{2})$
3.123	3.118	10253	10281	28	12	$(23\bar{1})$
2.985	2.993	11221	11160	−61	43	(060)
2.978	2.977	11272	11282	10	35	(044)
2.737	2.741	13347	13308	−39	14	$(16\bar{1})$
	2.732		13392	50		(161)
2.687	2.683	13842	13888	46	5	(242)
2.534	2.533	15565	15585	20	7	(071)
2.452	2.451	16628	16636	8	5	(163)

$a_0 = 7.46$Å $a^* = 0.13397$
$b_0 = 17.96$Å $b^* = 0.05567$
$c_0 = 15.91$Å $c^* = 0.06285$
$\beta = 91°26'$ $\beta^* = 88°34'$

vacuum. Variation of the intensity and interplaner distance is demonstrated in the figures 1 and 4. The results are that the manners of variation are nearly similar to those observable in the former samples, (b) any transformations are not confirmable, (c) above 200°C the intensity for the spacings (004) and (042) gradually increases while that for all of the spacings decreases above 450°C, (d) above 250°C the interplaner distance comes near that appeared just before transformation and the cell con-

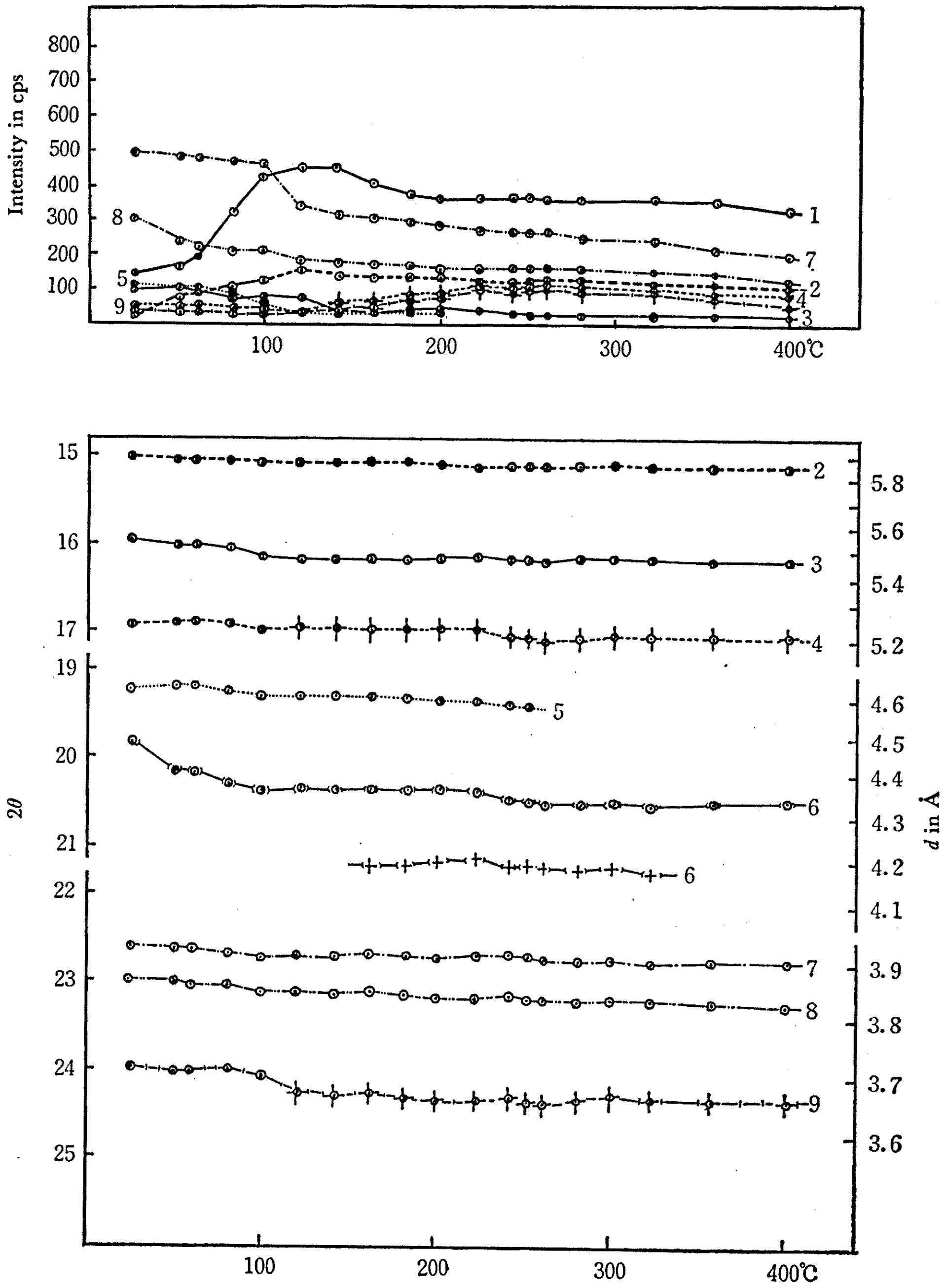

FIG. 3 Variation in the sample 2 (clinoptilolite)

⊙ clinoptilolite

\+ high-temperature heulandite

1 : (002) 2 : (022) 3 : (031) 4 : (11$\bar{2}$) 5 : (130) 6 : (040) 7 : (004) 8 : (042) 9 : (141, 14$\bar{1}$)

TABLE 2c. X-RAY DIFFRACTION DATA FOR THE SAMPLE 2 (CLINOPTILOLITE) AT 250°C AND IN VACUUM

d obs	d calc	Q obs × 10^{-5}	Q calc × 10^{-5}	ΔQ × 10^{-5}	I/I_0	(hkl)
8.775	8.770	1298	1300	2	100	(020)
8.305	8.356	1449	1432	−17	25	(020) H※
7.864	7.837	1617	1628	11	28	(002)
6.702	6.775	2226	2178	−48	8	(10$\bar{1}$)
	6.655		2258	32		(101)
5.862	5.844	2910	2928	18	10	(022)
5.460	5.478	3354	3332	−22	2	(031)
5.210	5.233	3677	3651	−26	8	(031) H※
	5.210		3684	7		(11$\bar{2}$)
5.094	5.100	3854	3844	−10	13	(112)
4.585	4.595	4756	4736	−20	2	(130)
4.393	4.385	5180	5200	20	1	(040)
4.330	4.321	5333	5354	21	3	(10$\bar{3}$)
4.923	3.918	6497	6512	18	20	(004)
3.827	3.827	6829	6828	− 1	12	(042)
3.658	3.665	7473	7444	−29	7	(042) H※
	3.661		7458	−15		(141)
3.519	3.514	8075	8096	21	2	(211)
3.423	3.423	8533	8532	− 1	2	(051)
3.370	3.369	8805	8808	3	7	(114)
3.162	3.160	10004	10012	8	2	(22$\bar{2}$)
3.083	3.086	10520	10496	−24	2	(23$\bar{1}$)
	3.086		10500	−20		(015)
2.920	2.923	11728	11700	−28	5	(060)
	2.922		11712	−16		(044)
2.867	2.864	12163	12186	23	1	(105)
2.678	2.681	13943	13912	−31	3	(24$\bar{2}$)
	2.676		13958	15		(161)
2.472	2.474	16361	16332	−29	2	(071)
2.405	2.404	17288	17294	6	1	(163)

a_0 = 7.43Å a^* = 0.13457
b_0 = 17.54Å b^* = 0.05701
c_0 = 15.67Å c^* = 0.06379
β = 91°20′ β^* = 88°40′

※ calculated from a^* = 0.13597 b^* = 0.05983 c^* = 0.06549 β^* = 88°01′

stants at this step are a_0 = 7.43Å, b_0 = 17.56Å, c_0 = 15.67Å and β = 91°20′ (see table 2g), and (e) the loss of water is estimated 14.85%.

At the same time, as is disposed in the table 3, wherein *Al* comprised in microcline is taken as a representative for the four-coordinated and that in muscovite as that for the six-coordinated, the data for the fluorescent x-ray analyses make it clear that *Al*

TABLE 2f. DIFFRACTION DATA FOR THE SAMPLE 3 (BA-BERING HEULANDITE) AT THE ROOM TEMPERATURE AND 1 ATM. PRESSURE

d obs	d calc	Q obs $\times 10^{-5}$	Q calc $\times 10^{-5}$	$\Delta Q \times 10^{-5}$	I/I_0	(hkl)
8.97	8.994	1242	1236	− 6	100	(020)
7.948	7.955	1583	1580	− 3	3	(002)
6.810	6.894	2156	2104	−52	2	(110)
	6.823		2148	− 8		$(10\bar{1})$
6.653	6.693	2259	2232	−27	1	(101)
5.972	5.959	2804	2816	12	2	(022)
5.626	5.611	3159	3176	17	1	(031)
5.270	5.270	3600	3600	0	1	$(11\bar{2})$
5.128	5.151	3802	3768	−34	1	(112)
4.661	4.674	4603	4576	−27	5	(130)
4.507	4.497	4921	4944	23	3	(040)
4.366	4.375	5245	5224	−21	1	$(10\bar{3})$
3.974	3.977	6332	6320	−12	8	(004)
3.907	3.915	6551	6524	−27	8	(042)
3.758	3.755	7080	7092	12	2	$(14\bar{1})$
3.732	3.733	7179	7176	− 3	2	(141)
3.555	3.542	7912	7968	56	2	(211)
3.511	3.509	8111	8120	9	2	(051)
3.449	3.447	8406	8416	10	1	(220)
3.413	3.411	8584	8592	8	1	$(20\bar{2})$
3.187	3.189	9845	9828	−17	1	$(22\bar{2})$
3.135	3.136	10170	10164	− 6	1	(222)
	3.133		10184	14		(015)
3.115	3.120	10303	10272	−31	2	$(23\bar{1})$
2.991	2.998	11172	11124	−48	17	(060)
2.979	2.979	11268	11264	− 4	15	(044)
2.900	2.901	11886	11880	− 6	2	(105)
2.737	2.745	13343	13272	−71	8	$(16\bar{1})$
	2.736		13356	13		(161)
2.687	2.685	13845	13872	27	1	(242)
2.535	2.537	15551	15536	−15	3	(071)
2.456	2.454	16578	16600	22	2	(163)

$a_0 = 7.46$Å	$a^* = 0.13397$
$b_0 = 18.08$Å	$b^* = 0.05558$
$c_0 = 15.91$Å	$c^* = 0.06285$
$\beta = 91°26'$	$\beta^* = 88°34'$

included in the sample 1 is within the area of four-fold coordination, that in the sample 3 within the area of six-fold coordination and that in the sample 2 is found intervening between the former two.

On the other hand, as is evident from the figure 5, the data of the infrared absorp-

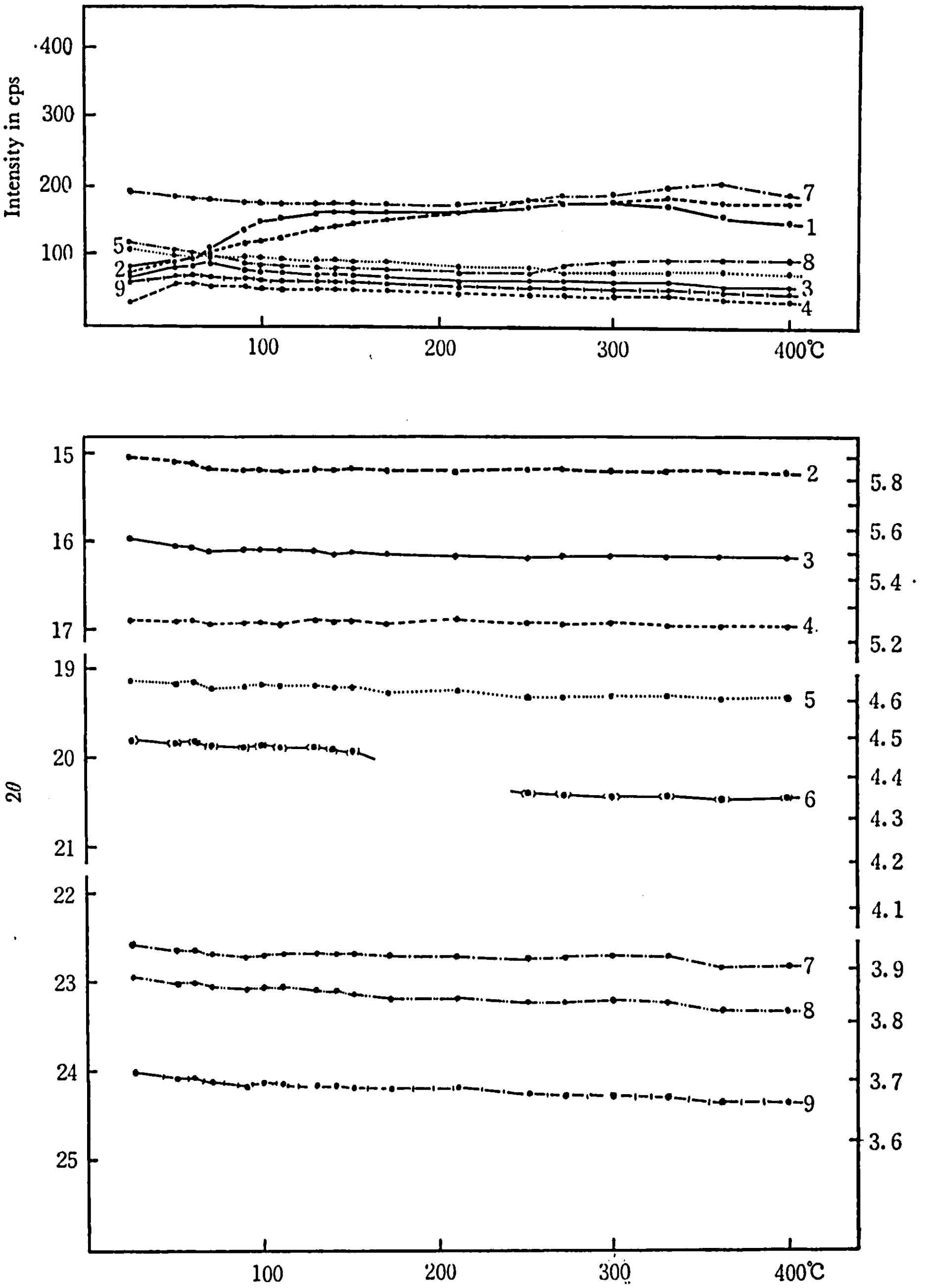

FIG. 4 Variation in the sample 3 (Ba-bearing heulandite)
● Ba-bearing heulandite
1 : (002) 2 : (022) 3 : (031) 4 : (11$\bar{2}$) 5 : (130) 6 : (040) 7 : (004) 8 : (042)
9 : (141, 14$\bar{1}$)

Table 2g. X-ray Diffraction Data for the Sample 3 (Ba-bearing heulamdite) at 250°C and in Vacuum

d obs	d calc	Q obs$\times10^{-5}$	Q calc$\times10^{-5}$	$\Delta Q\times10^{-5}$	I/I_0	(hkl)
8.89	8.784	1265	1296	31	100	(020)
7.766	7.837	1653	1628	−25	5	(002)
6.716	6.777	2216	2177	−39	1	$(10\bar{1})$
	6.656		2257	41		(101)
5.870	5.848	2902	2924	22	5	(022)
5.498	5.485	3308	3323	15	2	(031)
5.190	5.211	3712	3682	−30	1	$(11\bar{2})$
5.122	5.102	3812	3842	30	2	(112)
4.589	4.602	4748	4720	−28	2	(130)
4.387	4.392	5195	5184	−11	1	(040)
3.340	4.322	5349	5353	4	1	$(10\bar{3})$
3.919	3.919	6511	6512	1	6	(004)
3.830	3.831	6817	6812	− 5	2	(042)
3.673	3.675	7410	7401	− 9	1	$(14\bar{1})$
3.662	3.665	7456	7441	−15	1	(141)
3.373	3.370	8789	8806	17	2	(114)
3.163	3.161	9995	10004	9	1	$(22\bar{2})$
3.084	3.088	10514	10483	−31	1	$(23\bar{1})$
	3.086		10499	−15		(015)
2.924	2.928	11700	10664	−36	7	(060)
	2.924		10696	4		(044)
2.677	2.680	13952	13921	−31	4	(161)
2.477	2.479	16292	16262	−30	1	$(15\bar{4})$
	2.478		16283	− 9		(071)
2.408	2.407	17246	17257	11	2	(163)

$a_0=7.43$Å	$a^*=0.13453$
$b_0=17.56$Å	$b^*=0.05692$
$c_0=15.67$Å	$c^*=0.06379$
$\beta=91°20'$	$\beta^*=88°40'$

Table 3. Fluorescent X-ray Data for *Al*

State of *Al*		2θ for *Al Kα* (in degree)	$\Delta\ 2\theta$ (in degree)
metallic		142.509*	—
contained in	microcline	142.453±0.003	0.056±0.003
	muscovite	142.393±0.003	0.118±0.003
	sample 1	142.453±0.003	0.056±0.003
	sample 2	142.425±0.005	0.084±0.005
	sample 3	142.381±0.006	0.128±0.006

* calculated from $\lambda=8.3401$

$\Delta\ 2\theta=2\theta(\text{metallic } A_1)-2\theta(\text{sample})$

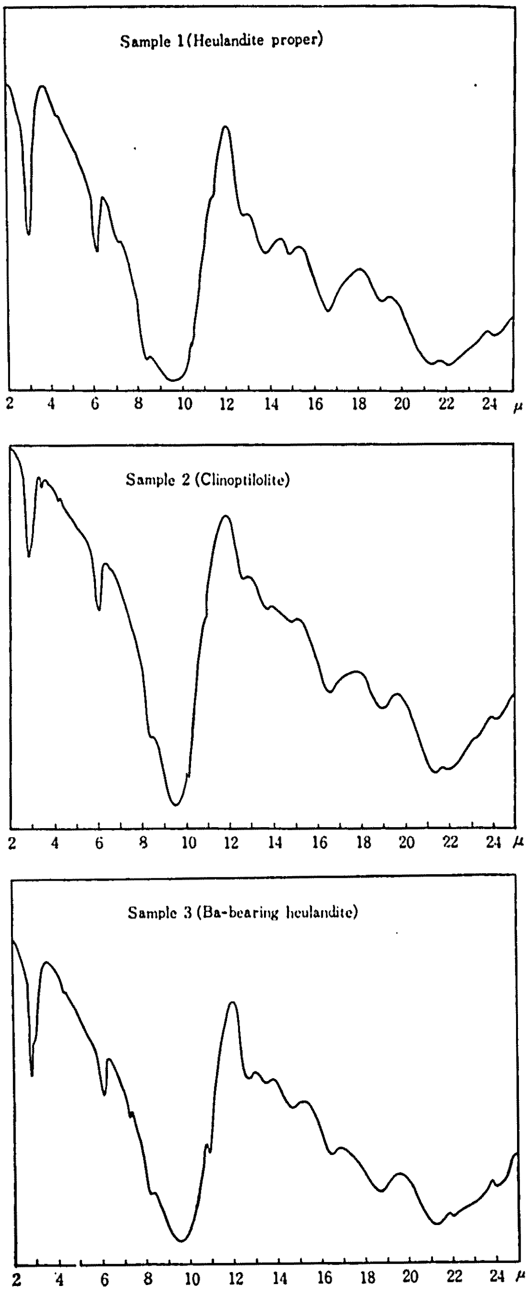

FIG. 5 Infrared absorption

tion indicate that the related patterns and intensity are somewhat distinguished from one another: for example, the absorption bands for *OH* stretching in the samples 1, 2 and 3 are observed respectively at 2. 9, 2. 85 and 2. 8μ in order and those occurring near 19. 0μ are also mutually more or less deviated while the absorbability is alined almost in order of the sample number within the range of 13. 5～13. 7μ and of 16. 5～16. 6μ and partly quite different from one another. As for these data there is a room for further investigation since a considerable obscurity might have been derived through use of the not-oriented, pulverized specimens.

IV. CONSIDERATION

The *Al* : *Si* ratio concerned with the framework structure in all of the samples is not distinguishable from one another whereas there is a remarkable difference in quantity of the cations absorbed. The alkaline earths are involved in more amount in the sample 1 and the alkalies are rather abundant in the other two. Content of *Ba* in the sample 3, nearly equivalent with *Ca* in the others, is to be noted concerning its origin or its relation to coexistence of harmotome, even if in a little amount. So far as the chemical compositions are concerned, it seems that the sample 1 bears a characteristic of heulandite and the other two are clinoptilolite (*cf.* MASON and SAND 1960).

Nevertheless, scrutiny of the x-ray diffraction patterns obtained at the room temperature suggests that the samples 1 and 3 have the structures corresponding to that of heulandite and the sample 2 is clinoptilolite (*cf.* MUMPTON, 1960). In addition, there is not so much difference in the cell dimension exclusive of the b_0 values arranged in order of the samples 3, 2 and 1.

The X-ray data related to the continuous heat treatments of the samples in vacuum point to that (a) transformation to the high-temperature modification is possible only in case of the sample 1, coexistence of the structures representing heulandite as well as clinoptilolite and the clinoptilolitic character without any other modifications are observable respectively in the samples 2 and 3, (b) as for the relation of dehydration to the thermal stability, the sample 1 shows a sort of contraction of its cell dimension owing to the loss of about 2/3 content of water before transformation and to that of the remainder after transformation while the samples 2 and 3 are not transformable and keep the preceding lattice constants although their dehydration is completed up to 250°C, (c) the breakdown of the structure, ascribed to dehydration (*cf.* KOIZUMI, 1953; GREENBERG, 1954; and MUMPTON, 1960), is not ascertainable up to 600°C probably on account of difficulty of oxydation in vacuum whereas in the experiments carried out in the air completion of transformation through dehydration is found duplicated with destruction of the structure, as to which certain factors other than the thermal effect are to be considered, (d) through heat treatments the sample 1 becomes unstable above 250°C, the sample 2 above 350°C and the sample 3 above 450°C. Besides, the effects of exchangeable cations on the thermal stability of the framework structure remain yet to be pursued in more detail though pointed out already by BARRER and LANGLEY (1958) concerning natural chabazite.

Fluorescent x-ray analyses for determining *Al* coordination with use of the reference minerals such as microcline containing the four-coordinated *Al* and muscovite comprising the six-coordinated have been in good harmony with the values of 0. 06∼0. 07 and 0. 040∼0. 061 in $\Delta 2\theta$ (deviation from the metallic state) for the former and 0. 69∼0. 11 and 0. 080∼0. 120 in $\Delta 2\theta$ for the latter given respectively by BRINDLY and MCKINSTRY (1961) and DELBERT (1963). As for $\Delta 2\theta$, $0.056^\circ \pm 0.003^\circ$, $0.084^\circ \pm 0.005^\circ$, and $0.128^\circ \pm 0.006^\circ$ are measured respectively for the samples 1, 2 and 3 although *Al* atoms in the latter two are normally to be four-coordinated.

On the other hand, the coordination number of *Al* is considered to depend on the surrounding effects on its L-shell (*cf.* MCKINSTRY, 1961 and LÉONARD, SUZUKI, FRIPIAT and KIMPE, 1964), the kinds of the cations supplying the negative charges specifically in case of the *Al-O* tetrahedron, *Al-Si* distribution and the distortion of their linkages.

The infrared absorption patterns for the respective samples are different from one another in detail but as a whole reveal the resembrance reflecting the close relation of their frameworks. Absorption appearing at 10.9μ in case of the sample 3 at a glance corresponds to that for *Al-OH* given by STUBICAN and ROY (1961) but is not strictly identifiable because of their induction derived through application of isomorphic substitution especially to the layer silicate.

It is very difficult to add any more allusion to the infrared absorption due to scarcity of the data and to use of the pulverized specimens.

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