

A SODIAN STILBITE FROM ONIGAJŌ, MIÉ PREFECTURE,
JAPAN, WITH SOME EXPERIMENTAL STUDIES
CONCERNING THE CONVERSION OF STILBITE
TO WAIRAKITE AT LOW WATER
VAPOR PRESSURES

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ABSTRACT

A sodium-rich stilbite occurs in the drusy parts of a granite porphyry, Kii Peninsula, Japan. Chemical analysis gave SiO₂ 58.16, Al₂O₃ 17.17, MgO 0.74, CaO 4.08, Na₂O 3.60, K₂O 0.85, H₂O⁻ 4.65 and H₂O⁺ 13.34. Sr, Ba, Rb and Cs were undetected. This corresponds to K_{0.52}Na_{3.30}Ca_{2.07}Mg_{0.57}Al_{9.57}Si_{26.55}O₇₂·28.87 H₂O.

Unit-cell constants calculated from X-ray powder data are very close to those of normal stilbite; $a = 13.67$, $b = 18.16$, $c = 11.31$ and $\beta = 129^{\circ}10'$. The sodian stilbite is nearly colorless with brownish yellow tints, luster is vitreous to slightly pearly, and cleavage is {010} perfect. Hardness = 3.5 and Sp. Gr. = 2.18, $2V(-) = 43.2$, $c \wedge X = 9^{\circ}$, $\alpha = 1.482$, $\beta = 1.489$, $\gamma = 1.496$, $\gamma - \alpha = 0.014$, all ± 0.002 .

Hydrothermal treatment of normal calcium stilbite at temperatures between 400°C and 200°C and at water vapor pressures between 15 and 100 atm produced wairakite at higher pressures.

INTRODUCTION

Stilbite is a calcium zeolite usually containing a small amount of sodium in place of calcium, but none of them show Na > Ca in mole ratio. The writers found a sodium-rich stilbite in the drusy parts of a Miocene granite-porphyry. The present paper describes the mode of its occurrence and some mineralogical properties, together with the experimental data concerning the conversion of stilbite to wairakite at low water vapor pressures.

OCCURRENCE

The granite-porphyry is a member of the Miocene Kumano Acidic Rocks (Kawano and Ueda, 1965) and widely distributed along southeastern Kii Peninsula, Japan (Sawatari, 1932; Harada, 1964; Aramaki and Hada, 1965; Aramaki, 1965).

The stilbite locality is about 0.5 mile north of Kumano city. The mineral is nearly colorless with a yellowish-brown tint, vitreous with a slightly pearly luster. It occurs as sheaf-like aggregates which contain small blades of about 5 mm in width, where phlogopitic biotite [$(-)$ $2V = 3^{\circ} \pm 1^{\circ}$, $d_{001} = 9.98 \text{ \AA}$, and $\gamma = 1.601 \pm 0.002$] is associated with

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minor laumontite and heulandite. The maximum size of aggregates is 3 cm across. Feldspars are lacking in the drusy parts of the granite-porphyrity.

A zonal arrangement is apparent in the druses. Laumontite is abundant in the inner part (2–3 mm), heulandite in the middle part (2–3 mm) and stilbite in the outer part free from other zeolites (2–3 cm). According to Coombs (1961), laumontite is crystallized under the conditions of rather

TABLE 1. CHEMICAL ANALYSES

	1	2	3	4
SiO ₂	56.16	68.90	55.39	55.53
TiO ₂	none	0.73	none	none
Al ₂ O ₃	17.17	14.12	16.57	16.70
Fe ₂ O ₃	0.02	0.14	0.03	none
FeO	0.11	3.31	none	none
MnO	none	0.37	none	none
MgO	0.74	1.39	0.29	0.15
CaO	4.08	1.98	8.13	1.20
Na ₂ O	3.60	3.32	1.10	7.00
K ₂ O	0.85	3.31	0.05	0.03
H ₂ O(–)	4.65 (105°C)	0.54 (105°C)	3.60 (105°C)	6.04 (110°)
H ₂ O(+)	13.34 (105°C)	1.38	15.48 (105°C)	13.02 (110°)
P ₂ O ₅	0.01	0.09	none	0.01
Total	100.74	99.58	100.64	99.68

1. Stilbite (sodium-rich) Onigajō, Mié Prefecture (Analyst, K. Harada, 1966).

2. Granite-porphyrity, host rock of the sodium-rich stilbite (Analyst, K. Harada, 1966).

3. Stilbite (normal), Komuroyama, Shizuoka Prefecture (Analyst, K. Harada, 1966).

4. Komuroyama stilbite digested in 1N NaCl solution on water bath for 110 days (Analysts, K. Tomita and K. Harada, 1967).

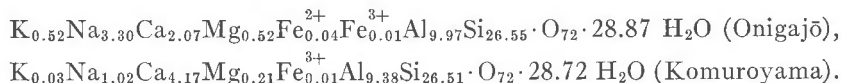
Note: On specimens 1 and 3, Sr, Ba, Rb and Cs were determined by x-ray fluorescent analyses as being less than 0.1% in weight, if present (Analyst, A. Kato, 1966).

higher $p_{\text{H}_2\text{O}}$ and higher temperature than heulandite. In the light of the above results and mode of occurrence observed by the present writers, stalbite might have crystallized under lower $p_{\text{H}_2\text{O}}$, lower temperature, or both, than heulandite did. In general, stilbitites contain a larger proportion of H₂O than heulandite.

CHEMICAL COMPOSITION

Chemical analysis of material purified by hand picking was made by the ordinary wet method. The result is compared in Table 1 with normal stilbite in the drusy parts of andesitic tuff breccia from Komuroyama,

Tagata-gun, Shizuoka Prefecture, Japan, and with the granite-porphry host rock. The calculation of cation proportions assumes $O=72$ and $H_2O=28$ as originally proposed by Sekanina and Wyart (1936) and as advocated by Černý (1965) to give the formulae:



Stilbite from Onigajō contains a remarkable amount of sodium showing $Na > Ca$ in mole ratio and it also contains considerable amounts of

TABLE 2. PHYSICAL PROPERTIES OF SODIUM-RICH STILBITE WITH CORRESPONDING VALUES FOR NORMAL STILBITE

Specimens	Normal stilbite, Komuroyama.	Sodium-rich stilbite, Onigajō.
Optical properties (Na light)	$\alpha = 1.492 \pm 0.002$ $\beta = 1.500 \pm 0.002$ $\gamma = 1.505 \pm 0.002$ $\gamma - \alpha = 0.013$ $2V (-) = 35.6^\circ$ (mean) $X\Delta c = 2^\circ - 3^\circ$ (wavy)	$\alpha = 1.482 \pm 0.002$ $\beta = 1.489 \pm 0.002$ $\gamma = 1.496 \pm 0.002$ $\gamma - \alpha = 0.014$ $2V (-) = 43.2^\circ$ (mean) $X\Delta c = 9^\circ$
Cleavage	(010) (perfect)	(010) (perfect)
Spec. gr. (mean)	2.19	2.18
Hardness	4	3.5

potassium and magnesium. Such stilbite has not previously been reported.

PHYSICAL PROPERTIES

The physical properties of the sodian stilbite are shown in Table 2 with corresponding values for normal stilbite from Komuroyama. These properties generally agree with those of normal stilbite, but closer observation of this mineral reveals that its refractive indices are lower, pearly luster is stronger, and it is more brittle and softer than normal stilbite.

INFRARED ABSORPTION SPECTRA

Infrared absorption spectra were obtained using a DS-401-S grating-type spectrophotometer with the Nujol past method. Figure 1 shows spectra of the sodian stilbite and stilbite from Komuroyama. Both spectra are quite similar and the bands of absorption around 3435 cm^{-1}

are probably due to adsorbed water as indicated by comparison with montmorillonite data of Wolff (1965). The absorption bands around 3600 cm^{-1} may be attributed to structurally bound water. A clear asymmetrical absorption at 1640 cm^{-1} due to adsorbed water is visible. The Si-O stretching region gives the band of adsorption at 1020 cm^{-1} , which is in fair agreement with previous work (Milkey, 1960).

DIFFERENTIAL THERMAL ANALYSES

DTA curves were taken by an automatic thermal analyser at a heating rate of $10^\circ\text{C}/\text{min}$. for the sodian stilbite and the normal stilbite from Komuroyama.

The endothermic peak at 230°C for the Komuroyama specimen was identical to those of previous workers (Koizumi, 1953; Černý, 1965), whereas the sodium-rich stilbite shows a characteristic endothermic

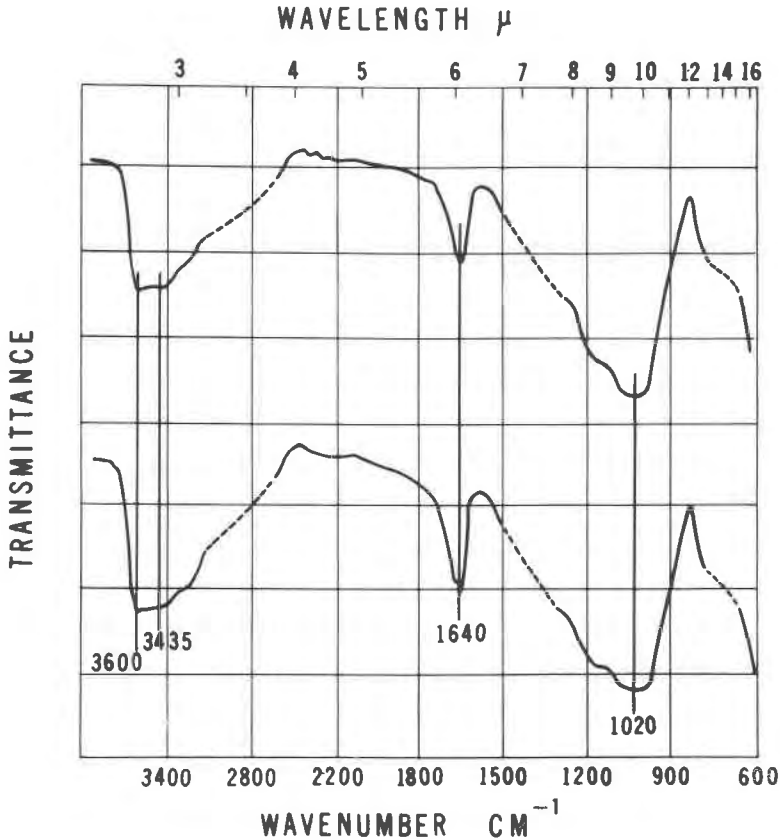


FIG. 1. Infrared absorption spectra of sodium-rich (upper) and normal (lower) stilbite. Note: Dotted line indicates the elimination of the peak due to Nujol.

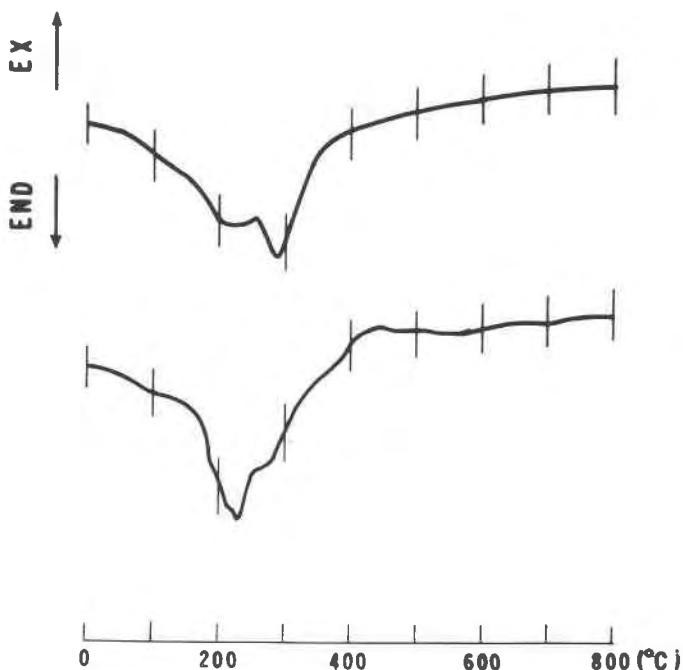


FIG. 2. Differential thermal analysis curves of sodium-rich (upper) and normal (lower) stilbites.

doublet with maxima centered at 225°C and 285°C. Of the two, the lower temperature peak is correlated with that of the normal stilbite (Fig. 2).

X-RAY DATA

On selected specimens of the sodium-rich and the normal stilbite, X-ray powder patterns were taken employing an X-ray diffractometer and $\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$, with a Ni-filter. The cell dimensions of the sodium-rich stilbite were determined by trial and error as $a = 13.62$, $b = 18.16$, $c = 11.31$ and $\beta = 129^\circ 10'$; these values are very close to those of normal stilbite (Sekanina and Wyart, 1936; Mason and Greenberg, 1954). With these cell data, the sodium-rich stilbite can be indexed (Table 3), with a mean $\Delta Q = \pm 3$.

AMOUNTS OF EXCHANGEABLE CATIONS AND CATION-EXCHANGE CAPACITIES

Cation-exchange capacities and amounts of exchangeable cations were measured by Schollenberger and Simon's method (Schollenberger

TABLE 3. X-RAY POWDER DATA FOR SODIUM-RICH STILBITE

$d_{obs.}$	I/I_0 $\times 100$	hkl	$d_{obs.}$	I/I_0 $\times 100$	hkl
9.16	100	$\bar{1}10$ 020	2.489	2	$\bar{1}53$ 062
6.85	1	201			331
6.39	0.5	021	2.350	3	263
5.31	4.5	200			444
5.24	2.5	130, $\bar{1}30$	2.277*	3	
4.67	11	222	2.229	2	371
4.56	2	220, 220 040	2.125*	2.5	
4.46*	2		2.100	2	063 510, 510
4.29	8	312			282
4.07	45		2.090	2	335
4.02	7	041 131	2.048	1.5	370, 370 $\bar{1}54$
3.75	5	203			605
3.71	5		2.029	2.5	464
3.48	6	242			643
3.40	7	402			153
3.20	10	403	1.896*	2	
3.12	4	401 333	1.871*	1.5	
			1.821	7.5	641
3.02	32	152 060	1.807	2	316
		423	1.782	2	173
		151	1.728	1.5	620
3.000	11	421			620
2.974	3		1.636	1	045
2.876*	1.6				2103
2.825*	2		1.594	3	844
2.811	2	352	1.584	2.5	116
2.744	12	023 261			826
		442 204	1.554	3	462, 774
2.724	3				591 175
2.599*	2		1.513	1	4104, 0120
2.566	5	334	1.470	1	865, 264
2.532	1	350 350	1.448	1	801
		420, 420	1.438	1.5	207
					776
2.510*	3		1.411	1	5113

* Unidentified lines.

and Simon, 1945). The results are shown in Table 4 and the method is as follows:

Sodium-rich stilbite and normal stilbite were pulverized in an agate mortar and 0.2 gr of powder was mixed with 2 gr of quartz powder, and a complete mixture thus obtained was packed into a glass tube, which is 12 cm in length and 1.3 cm in inner diameter with a stem of 4 cm. length and 0.3 cm inner diameter. To prevent loss of the samples, absorbent cotton was placed at the bottom of the tube. Ammonium acetate solution (pH=7.0, 1N, 100 ml) was passed through the column for the duration between 8 and 10 hours. The amounts of exchangeable cations in the effluent were chemically determined. Then, the walls of the tube were washed three times with 80 percent ethyl alcohol (pH=7) until leaching of ammonium ions was not detected. In the next step, the column was washed with 10 percent KCl solution to leach adsorbed ammonium ions. The volume of the effluent was made to be 200 ml by adding distilled water, and the content of leached ammonium ions in 10 ml was determined by the distillation method.

TABLE 4. CATION EXCHANGE CAPACITIES OF SODIUM-RICH AND NORMAL STILBITE, IN meq/100 g

	1	2
Ca ²⁺ +Mg ²⁺	98.07 (149.18)*	187.62 (304.32)*
Na ⁺ +K ⁺	124.07 (133.09)*	58.51 (36.53)*
Total	232.14 (282.27)*	246.13 (340.86)*
CEC	259.45	269.03

1. Sodium-rich stilbite from Onigajō, Mié Prefecture.

2. Normal stilbite from Komuroyama, Shizuoka Prefecture. (Analysis by K. Tomita and T. Negishi, 1966).

* Calculated on the basis of chemical analyses in Table 1.

The ideal values of exchangeable cations calculated on the basis of chemical analyses presented in Table 1 and the total amounts of exchangeable cations from the present examinations show considerable departures. These departures might be explained in that some cations might not have been leached from stilbite by the ammonium acetate solution. The CEC values agree well with experimental values of the total amounts of exchangeable cations.

ARTIFICIAL REPLACEMENT OF Na⁺ FOR Ca²⁺ IN STILBITE STRUCTURE AT ROOM PRESSURES AND AT 100°C

The starting material was stilbite from Komuroyama. The stilbite was pulverized to fine powder, placed in a beaker (500 ml in capacity), and warmed on a water-bath with 1N NaCl solution for 110 days. Evaporation was avoided by placing a glass plate on the top of the beaker.

The 1N NaCl solution was changed every two days. The obtained powder was washed with pure water 6 times in a centrifuge (2500 rpm), and examined with an X-ray diffractometer. No changes were apparent between starting material and the treated stilbite; the latter was analysed chemically (Table 1, Column 4). The chemical formula of the treated material is: $\text{Ca}_{0.62}\text{Na}_{6.52}\text{K}_{0.02}\text{Mg}_{0.11}\text{Al}_{9.52}\text{Si}_{26.86}\text{O}_{72} \cdot 30.74\text{H}_2\text{O}$

The Na:Ca ratio of this formula is the reverse of the starting stilbite from Komuroyama, but the total amount of Ca, Na, K and Mg in the treated stilbite has diminished. This may be explained by substitution of some H^+ for other cations during the experiments.

CONVERSION REACTIONS OF STILBITE INTO WAIRAKITE AT LOW WATER VAPOR PRESSURES

Experimental.

The starting material was stilbite from Komuroyama. It was ground into fine powder in an agate mortar. Using closed autoclave (Morey type, 500 ml), water was put into the vessel and pressures were measured on heating. The powder was put into an open silver crucible placed on a stainless steel stand on the bottom of the vessel to avoid mixing of sample and water. The runs were made at heating rate $2^\circ\text{C}/\text{min}$. and were maintained under confining pressure at temperature for 2 to 94 hours. This type of autoclave is unquenchable, and it takes 3 hours at 100°C to reach room pressure and temperature. Temperature was controlled automatically, and the accuracy of measurements is believed to be within $\pm 5^\circ\text{C}$. Pure-phase and converted-phase assemblages were obtained at water vapor pressures between 100 and 15 atms, between 200 and 400°C , from 2 to 94 hours, and were examined with an X-ray diffractometer immediately after cooling.

Results. Stilbite was easily converted into wairakite (Fig. 4) at water vapor pressures less than 100 atms. The 6.82 \AA line which was discussed by Coombs (1955) and Ames (1966) for distinguishing wairakite and analcime was clearly exhibited and all diffractometer peaks agreed well with previous wairakite data, shown in Table 5 and Figure 3, together with synthesized wairakite from heulandite (at 300°C , $p_{\text{H}_2\text{O}} = 100$ atms, and 100 hours) and natural wairakite from Japan.

Wairakite is known to be easily synthesized from various starting materials under rather high pressure hydrothermal conditions, as reported by many workers (Ames and Sand, 1958; Barrer and Denny, 1961; Koizumi and Roy, 1960). From dehydrated heulandite Coombs *et al.*, (1959) obtained anorthite and wairakite at water vapor pressure and 370°C , at 2000–2600 bars $280\text{--}410^\circ\text{C}$ assemblages containing wairakite, mordenite and analcime. From chabazite they obtained wairakite and phillipsite at temperatures $220\text{--}310^\circ\text{C}$ and water vapor pressure; and from stilbite they obtained epistilbite at 370°C , 5000 bars, and wairakite at 403°C , 5000 bars. The present writers obtained wairakite from stilbite at rather low water vapor pressures.

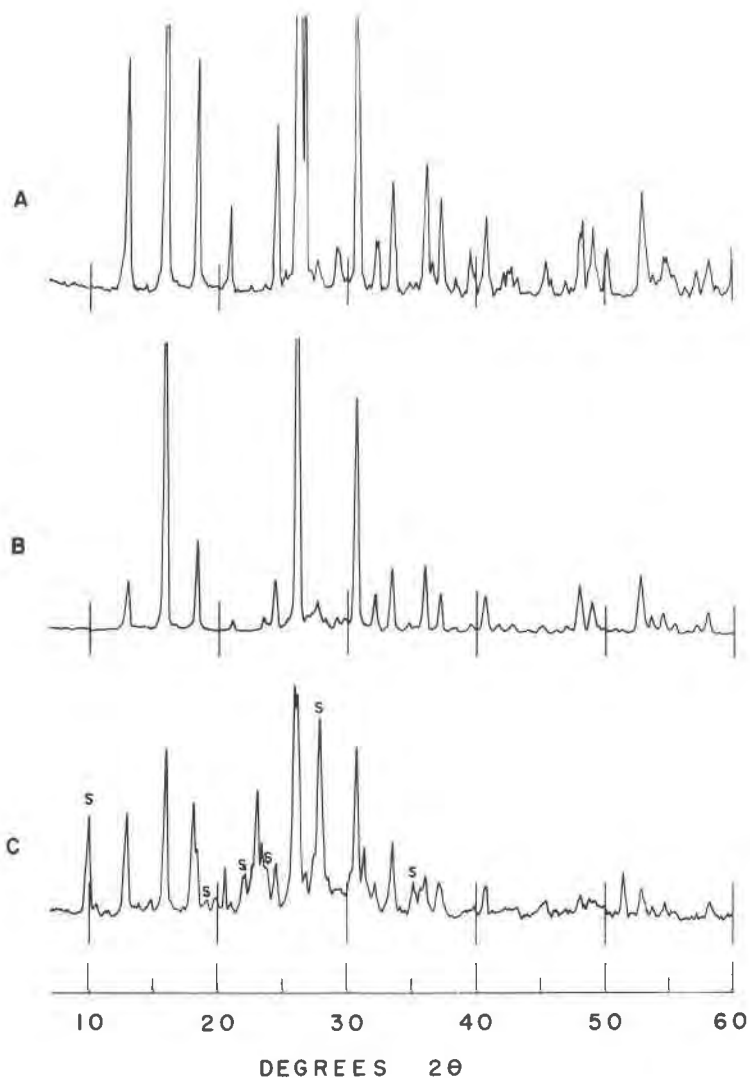


FIG. 3. Selected X-ray diffraction patterns of natural and synthesized wairakites.
 A: Natural wairakite from Hanawa Mine, Akita Prefecture (wall rock of the Kurokō ore deposit of epithermal type). Specimen from Professor Y. Seki.
 B: wairakite after heulandite (300°C, 100 atms and 70 hours).
 C: wairakite after stilbite (300°C, 100 atms and 70 hours).
 Note: S indicates peaks of stilbite surviving conversion.

In nature, wairakite occurs in active geothermal areas characterized by a steep thermal gradient (Steiner, 1953, 1955, 1958; Seki, 1966b), and also in some metamorphic terraines (Wise, 1959; Donnery, 1962; Whetten, 1965), or in some epithermal mineral deposits (Seki, 1966b). These

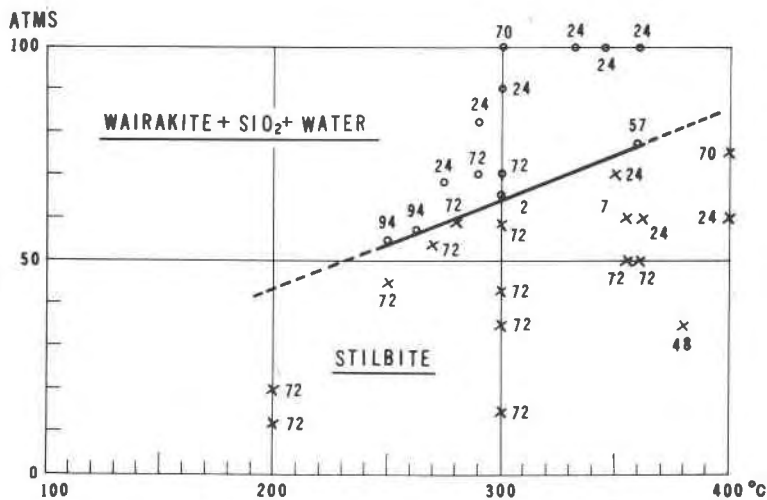
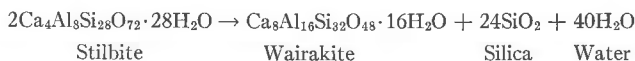


FIG. 4. Diagram showing the conversion reaction of stilbite into wairakite at low water vapor pressures. Hydrothermal conversion may have taken the following form:



Since no silica lines were observed, it was assumed to be in the noncrystalline state. Numbers represent the time in hours at confining water vapor pressures.

facts may agree well with our experimental studies, as well as with the result by Coombs *et al.*, (1959).

ORIGIN OF NATURAL SODIUM-RICH STILBITE

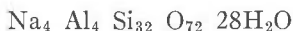
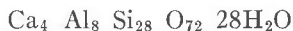
According to Shibata *et al.*, (1959) and Shibata (1962), granite-porphry and granite rocks from the Kii Peninsula show remarkable chemical compositions since $\text{Fe}_2\text{O}_3 + \text{FeO}$ surpasses CaO , and K_2O , Na_2O and MgO occur in considerable amounts, as is well represented by the sodium-rich stilbite as well as the host rocks of the stilbite (granite-porphry) (Table 1, Columns 1 and 2). Considerable amounts of Na_2O , K_2O and MgO in sodium-rich stilbite might have come from the magma of the granite-porphry in the final stage of the magmatic consolidation.

DISCUSSION

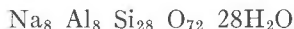
Our experimental studies suggest that almost all Ca^{2+} , Mg^{2+} and Na^+ in stilbite should be exchangeable, which is in contrast to the wairakite-analcime substitutions. Such replacement is possible from the standpoint of the crystal structure of stilbite (Galli and Gottardi, 1966).

Since $\text{Na} > \text{Ca}$, a case can be made for considering the mineral a calcium-bearing representative of the sodium analogue of stilbite. If so, a new mineral name might be justified. However there are two ways in which Na (or Na,K) can replace Ca (or Ca,Mg) in a zeolite, either NaSi for CaAl or Na_2 for Ca.

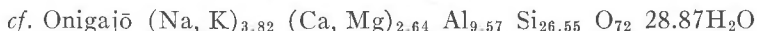
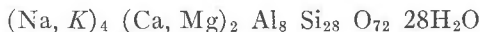
Idealized formulae would be:



or



In the present case the second type of replacement would appear to be dominant. Fifty percent replacement would give:



On this basis, the Onigajō mineral is seen to have less than 50 percent of the Na_2 end member, and we believe is correctly termed sodian stilbite. Actually a further replacement, (Na, Al) (or Na, K, Ca, Al) for Si has clearly occurred to give $\text{Al} > 8$, $\text{Si} < 28$. This is a common phenomenon in zeolites.

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Stability relations of some calcium-zeolites are now being investigated in the laboratory of Professor Dr. W. G. Ernst and Dr. J. G. Liou, Department of Geology, University of California; their preliminary comments are appreciated.

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