

# THERMAL ANALYSIS STUDY OF THE NATROLITE GROUP

C. J. PENG\*

## ABSTRACT

The three members of the natrolite group, natrolite, scolecite, and mesolite, from ten different localities have been examined by both static and differential thermal analysis methods. The thermal changes taking place in the specimens at reaction peak temperatures given by the *DTA* curves have been investigated by coordinated optical and *x*-ray diffraction methods. Despite their close similarity in composition and crystal structure, the three zeolites show different thermal behavior. Natrolite gives off its water rapidly in a single temperature range, whereas scolecite and mesolite lose their water in two and three stages respectively. It is thus inferred that there is only one type of water molecule in natrolite, while the water molecules in scolecite and mesolite consist, respectively, of two and three types with different bond strengths. This is supported on structural grounds. The range of stability also is different for the three zeolites. Natrolite will not break down completely until about 940° C., but scolecite collapses structurally at 560° C. and mesolite at a still lower temperature of 490° C. This is explained as a consequence of their different degrees of hydration.

## INTRODUCTION

Much study has been made of the dehydration phenomenon of zeolites and their changes in physical properties that accompany the effect of decomposition. The method generally employed is to determine the loss of water at various elevated temperatures under equilibrium conditions with or without control of the water vapor pressure. Owing to certain technical differences and possible variations in the composition of the specimens studied, the results are not consistent and hence the interpretations of their thermal history vary.

The purpose of this report is to give the results of an investigation of the thermal behavior of the natrolite group by both static dehydration and differential thermal analysis methods. The natrolite group was selected because its members, natrolite, scolecite, and mesolite, have a relatively simple and definite composition and have been nearly completely studied structurally. An attempt has also been made to correlate the thermal effects with the structures of the zeolites.

Although the three zeolites are isostructural and show markedly similar physical properties, they do not undergo the same thermal changes. Further, the intensity of those thermal reactions due to dehydration and the temperatures at which they take place are different for the three because each contains different amounts of water and the water molecules may occupy different lattice positions. Thus, the thermal reaction data

\* Department of Geology, Columbia University, New York, N. Y. Present address: University of Wisconsin, Madison, Wisconsin.

should be useful not only for the purpose of identification but also in the interpretation of the structure.

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#### MATERIALS

The specimens used for the study were obtained from the Egleston Mineralogical Collection of Columbia University and included the following:

- (1) Natrolite, Giant's Causeway, Ireland. White, radiating needle-like crystals.
- (2) Natrolite, West Paterson, N. J. White, radiating hairy needles.
- (3) Natrolite, Brevig, Norway. White accicular crystals, partly admixed with chlorite.
- (4) Natrolite, Auvergne, France. Groups of white, stout, translucent crystals with good prisms and pyramids.
- (5) Scolecite, Poonah, India. White, slender, glassy needles in radiating groups.
- (6) Scolecite, Bombay, India. Thick clusters of long white glassy crystals.
- (7) Scolecite, Moore, Mercer County, N. J. White accicular crystals.
- (8) Mesolite, Peter's Point, Nova Scotia. Divergent groups of white slender needles.
- (9) Mesolite, Cape d'Or, Nova Scotia. A mass of radiating white, fibrous crystals densely matted together.
- (10) Mesolite, Scotland. Groups of white fibrous crystals.

The three zeolites, natrolite ( $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ), scolecite ( $\text{CaAl}_2\text{-Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ ), and mesolite ( $\text{Ca}_2\text{Na}_2\text{Al}_6\text{Si}_9\text{O}_{30} \cdot 8\text{H}_2\text{O}$ ), have practically a constant composition as first pointed out by Winchell (1925) and show only limited ionic substitutions of the types  $\text{Na}_2 \rightarrow \text{Ca}$  and  $\text{Na} \rightarrow \text{K}$  (Hey & Bannister, 1932, 1933, 1936). Chemical analyses of previously described specimens probably from the same localities as a number of the specimens here studied are given in the following table (Table 1). It is believed that they are representative of the chemical composition of the three zeolites since all the tested specimens have been thoroughly examined optically and by means of  $x$ -ray diffraction to ensure purity and identity.

#### EXPERIMENTAL EQUIPMENT AND PROCEDURE

Specimens were first examined with a binocular microscope and material was selected for further study. The standard immersion method was used to determine the optical constants.  $X$ -ray powder photographs of

all specimens were taken by means of a Philips  $\alpha$ -ray unit to confirm the identity of the minerals. X-ray spectrometer measurements were made on some of the specimens. Copper—K radiation with nickel filter was used throughout.

Both static dehydration and differential thermal analysis methods were applied to the study of the thermal behavior of the zeolites. The procedure to obtain dehydration data is similar to that generally followed. Material was heated in a Freas electric oven for successive periods of

TABLE 1. CHEMICAL ANALYSES OF NATROLITE, SCOLECITE AND MESOLITE

	Natrolite			Scolecite		Mesolite	
	1	2	3	4	5	6	7
SiO <sub>2</sub>	47.22	47.88	47.60	45.16	46.10	46.01	46.26
Al <sub>2</sub> O <sub>3</sub>	27.21	26.12	27.40	25.90	26.32	26.66	26.48
Na <sub>2</sub> O	15.86	15.63	15.36	0.16	0.12	4.66	4.98
K <sub>2</sub> O	0.06	—	0.23	0.06	—	0.20	—
CaO	—	0.45	0.13	14.86	14.22	9.88	9.24
H <sub>2</sub> O	9.70	9.80	9.47	13.66	13.60	12.69	13.04
Total	100.05	99.88	100.19	99.80	100.36	100.10	100.00

1. Kinbane (White Head), County Antrim (Giant's Causeway), Ireland. Analyst F. N. Ashcroft, *Mineral. Mag.*, **17**, 307 (1916).
2. Tour de Gevillat, Auvergne, France. Analyst F. Gonnard, *Bull. Soc. Franc. Mineral.*, **14**, 170 (1891).
3. Puy de Marmant, Puy-de-Dome, France. Analyst M. H. Hey, *Mineral. Mag.*, **23**, 246 (1932).
4. B. M. 33887, Syhadree Mts., Bombay, India. Analyst M. H. Hey, *Mineral. Mag.*, **24**, 228 (1936).
5. Poonah, Bombay, India. Analyst G. Tschermak, *Sitzungsber. Akad. Wiss. Wien, naturwiss. Kl., Abt. I*, **126**, 541 (1917).
6. Cape d'Or, Nova Scotia. Analyst E. W. Todd, *Univ. Toronto Studies, Geol. Ser. no. 14*, 57 (1922).
7. Isle of Skye, Scotland. Analyst M. F. Heddle, *Mineral. Mag.*, **5**, 118 (1883).

20 hours at about 20° intervals up to 350° C. The temperature was measured with a thermometer inserted into the furnace through a hole on the top of the chamber. For higher temperatures, heating was carried out in a rheostat-controlled electric muffle for 3 hours at about 50° C. intervals; the temperature was measured with a Brown portable electric pyrometer with an accuracy of about 5°. After a desired temperature was reached, the sample was cooled to room temperature in a desiccator and then weighed. This was followed by reheating it at the same tempera-

ture for another 2 hours in order to check the weight previously obtained. Weight losses were practically the same before and after reheating and only in a few cases was further heating called for to reach a constant weight, indicating that heating over a period of 20 hours up to 350° C. and 3 hours at higher temperatures is sufficient to bring about equilibrium at a given temperature. The process was then repeated at higher temperatures. Each sample to be heated was ground to pass a 200-mesh sieve. No attempt was made to control the water vapor pressure in the furnace.

The differential thermal analysis method not only provides dehydration data, but also reveals those thermal reactions that are not accompanied by changes in weight, such as structural breakdown, recrystallization, phase transition, etc. The multiple *DTA* unit developed in the Mineralogical Laboratory of Columbia University (Kerr & Kulp, 1948) was used in the present study. The pulverized samples were packed uniformly in the specimen recesses which,  $\frac{1}{8}$  in. in radius and  $\frac{1}{2}$  in. deep for each, are spaced symmetrically with the alundum holes with respect to the vertical axis of the furnace. Heating was carried out without covering from room temperature up to about 1050° C. at the rate of 12 $\frac{1}{2}$ ° per minute. Two or three runs were made on each sample. The high sensitivity scale 2000 for the d.c. amplifier was used throughout, for which the amplification is about two. For identifying each thermal reaction, the specimen was first heated up to the peak reaction temperature and then examined by optical and *x*-ray powder methods.

The endothermic peaks on the *DTA* curves of the zeolites due to loss of water in general correlate well with the shoulders on their dehydration curves. But as a rule, they occur at higher temperatures than corresponding shoulders, although initial decomposition usually takes place at approximately the same temperature in both cases. The difference in temperature maximum between these two kinds of thermal curves observed in the present study is about 100° C. The reason for the reaction-temperature lag in the *DTA* curves lies in the dynamic character of the method by which the sample is heated at a constant rate, thus extending the reaction over a longer temperature range, while each water loss shown on a dehydration curve is determined at a constant temperature under equilibrium conditions.

With the zeolites some experimental difficulties were encountered and the most serious one concerned the *DTA* method. The three zeolites all fuse at about 1000° C. Since they adhere firmly to the sample holder after fusing, the thermocouple head was often found to be either dislocated or broken when a heated sample was taken out of the specimen hole for further study. This caused considerable trouble and discouraged the application of the technique to other zeolites.

## THERMAL ANALYSES

*(A) Dehydration Curves*

Two specimens of each member of the natrolite group were selected for the static thermal analysis in order to verify their dehydration course. Two groups of specimens were tested, one comprising (1) natrolite, Giant's Causeway, Ireland, (2) scolecite, Bombay, India, and (3) mesolite, Peter's Point, Nova Scotia; and the other group including (1) natrolite, Auvergne, France, (2) scolecite, Moore, N. J., and (3) mesolite, Cape d'Or, Nova Scotia. The specimens of each group were heated simultaneously, but the study of the first group was made in January while the second group in June of the same year. The dehydration curve of each of the zeolites is essentially constant, although the specimens of the first group generally showed a water-loss at a lower temperature than the corresponding ones of the second group (Fig. 1 and Table 2). The discrepancies are explained as being chiefly due to the usual lower humidity of the air in winter.

The dehydration curves of the three zeolites are markedly distinctive. Scolecite loses its water in two stages and mesolite in three as shown by the shoulders on their curves, while natrolite completes its dehydration in a single stage, represented by a smooth straight line. Further, each stage represents the loss of a definite number of water molecules in proportion to the total water content of the mineral. The last shoulder on the curves of both scolecite and mesolite does not level off sharply but slopes upward gently over a large temperature range. Such an extended and slow dehydration may result from an increasing firmness of binding of water molecules in the structure at higher temperatures so that their probability of escape from the tightest lattice positions may be decreased exponentially. But the considerably pronounced secondary break of the last shoulder on the scolecite curve at about 450° C., although not sharp enough, indicates a possibility that the two water molecules removed during the shoulder may differ slightly in structural capacity.

The general shape and water-temperature relationship of the curves of natrolite and scolecite are in good agreement with those of previous workers (Rinne, 1890; Walker & Parsons, 1922; Cavinato, 1927; Hey & Bannister, 1932, 1935). Milligan and Weiser (1937) reported that natrolite loses its water in two stages; but an examination of their curve reveals that it is very similar to their scolecite curve and hence suggests that their specimen might be actually scolecite.

Some of the published curves of mesolite show a nearly continuous dehydration (Zambonini, 1908; Pelacani, 1908; Hey & Bannister, 1933), but others bear a striking similarity to the writer's curve (Fig. 2). It is believed that the discrepancies are not a difference of matter but of de-

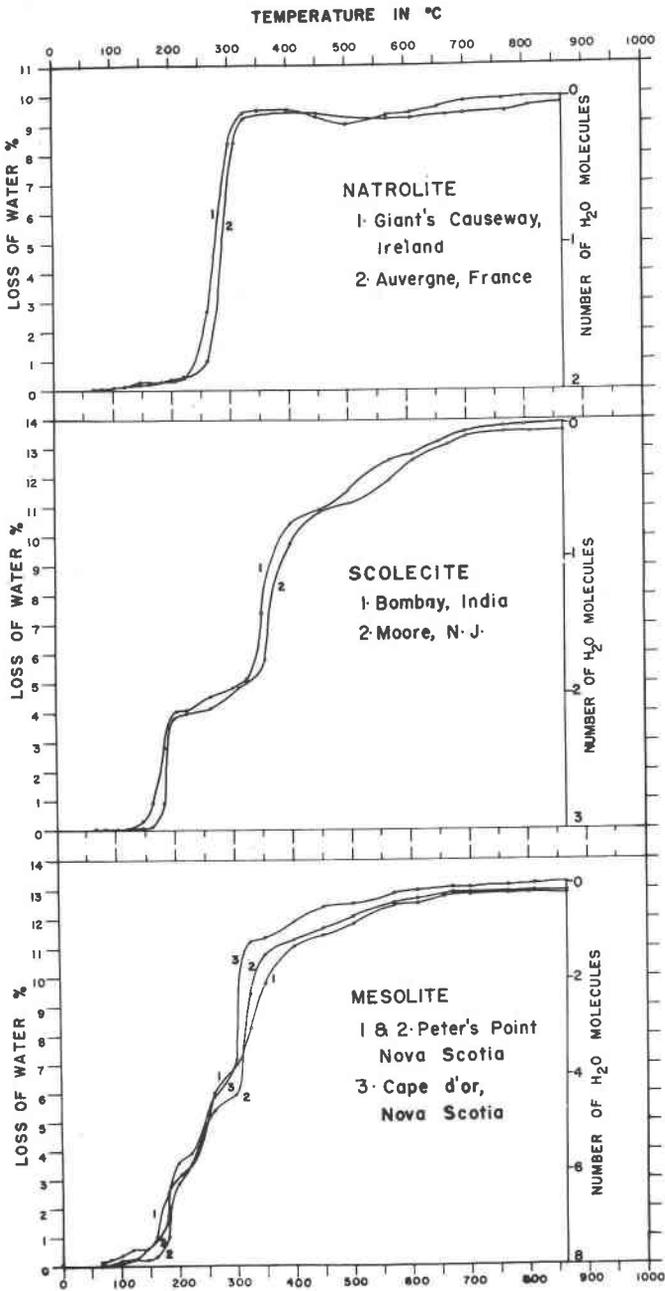


FIG. 1. Dehydration curves of natrolite, scolecite, and mesolite.

TABLE 2. DEHYDRATION DATA OF NATROLITE, SCOLECITE, AND MESOLITE  
(Percentage of water lost up to temperature stated)

Temperature in C.	Natrolite		Scolecite		Mesolite		
	1	2	1	2	1	2	3
67°	0.08	0.02	0.02	0.01	0.01	0.03	0.13
82°	0.04	0.05	0.05	0.01	0.02	0.07	0.27
101°	0.11	0.13	0.05	0.06	0.22	0.15	0.41
121°	0.14	0.16	0.05	0.09	0.22	0.23	0.59
147°	0.30	0.19	0.33	0.10	0.62	0.25	0.62
162°	0.30	0.24	0.94	0.12	1.01	0.31	0.93
184°	0.30	0.32	2.84	0.94	2.57	1.03	1.79
200°	—	0.42	—	3.80	—	2.89	3.61
205°	0.36	—	4.06	—	3.23	—	—
222°	0.48	0.50	4.07	3.99	3.52	3.58	3.96
262°	2.70	1.00	4.56	4.15	6.00	5.41	5.92
300°	8.40	—	4.89	—	7.02	—	—
310°	—	8.47	—	4.85	—	5.94	7.21
325°	9.45	9.28	5.14	5.04	8.30	9.46	11.27
350°	9.50	9.01	7.40	5.82	9.81	10.82	11.36
400°	9.55	—	10.47	9.79	11.10	11.30	11.92
450°	9.31	9.42	10.90	10.88	11.48	11.69	12.44
500°	9.07	—	11.59	10.99	11.83	12.11	12.49
570°	9.36	9.21	12.61	11.94	12.48	12.54	12.90
610°	9.45	9.24	12.84	12.62	12.51	12.71	12.99
655°	9.62	—	13.23	—	12.74	—	—
670°	—	9.34	—	13.16	—	12.86	13.08
700°	9.81	9.41	13.58	13.41	12.82	12.86	13.04
765°	9.88	—	13.75	—	12.84	—	—
770°	—	9.43	—	13.53	—	12.90	13.13
800°	9.92	—	13.81	—	12.85	—	—
810°	—	9.63	—	13.56	—	12.92	13.19
865°	9.92	9.72	13.83	13.59	12.85	12.96	13.23

Natrolite: 1. Giant's Causeway, Ireland; 2. Auvergne, France.

Scolecite: 1. Bombay, India; 2. Moore, N. J.

Mesolite: 1. Peter's Point, Nova Scotia; 2. Same as 1; 3. Cape d'Or, Nova Scotia.

gree and may be explained as being due to the relatively small differences in volatility between the water molecules given off in the three stages so that the shoulders are not always well defined and sometimes may even fail to show up.

### (B) Differential Thermal Analysis

The only published *DTA* data for zeolites are the study of natrolite by Sveshnikov and Kuznetsov (1946), but no details of their work are available. In the present investigation, four specimens of natrolite and

three each of scolecite and mesolite from different localities have been examined by the *DTA* method. The specimens were fractionated into three particle-size groups: (1) minus 80 mesh, (2) minus 80 and plus 200 mesh, and (3) minus 200 mesh. The *DTA* curves of the three fractions of each specimen are essentially identical (Fig. 3 and Fig. 4). Some endothermic peaks showed a small shift in peak temperature, but the variations are so irregular that it would be impossible to state definitely

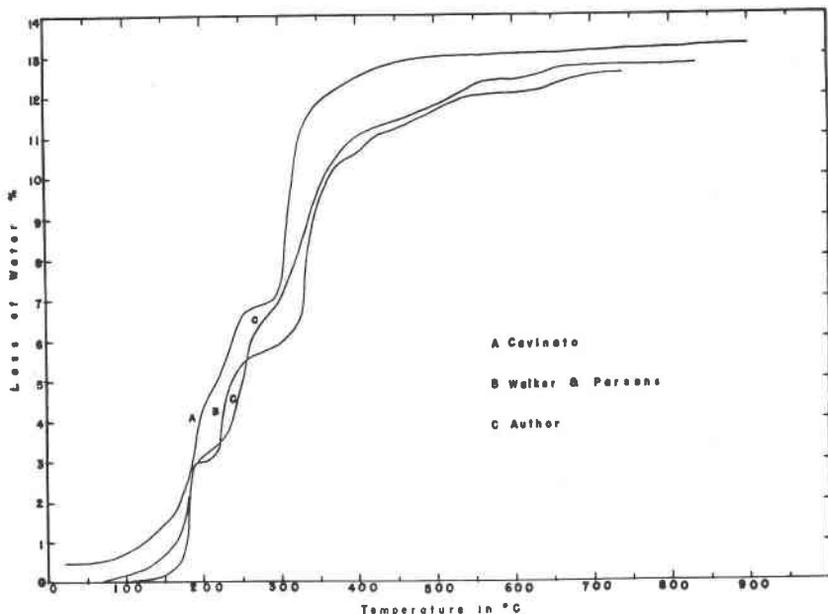


FIG. 2. Dehydration curve of mesolite.

whether they are due to the factor of particle size or not. However, the effect of grain size on the sharpness of an endothermic peak is more distinct, since almost all endothermic peaks shown by the minus 200 mesh fractions are sharper than the coarser ones. Furthermore, the endothermic doublets were also only shown by the finer fractions. Since particles of smaller grain-size should react thermally more uniformly, the sharpness of the endothermic peaks seems to be expected.

The *DTA* curves of both natrolite and mesolite show a high-temperature exothermic peak just above 1000° C. but experimental work showed that this peak on both curves varied considerably in shape and peak temperature. The exothermic reaction on the natrolite curve has a very small intensity and was shown only by the minus 80 mesh fractions. It results from recrystallization, but the small intensity clearly indicates

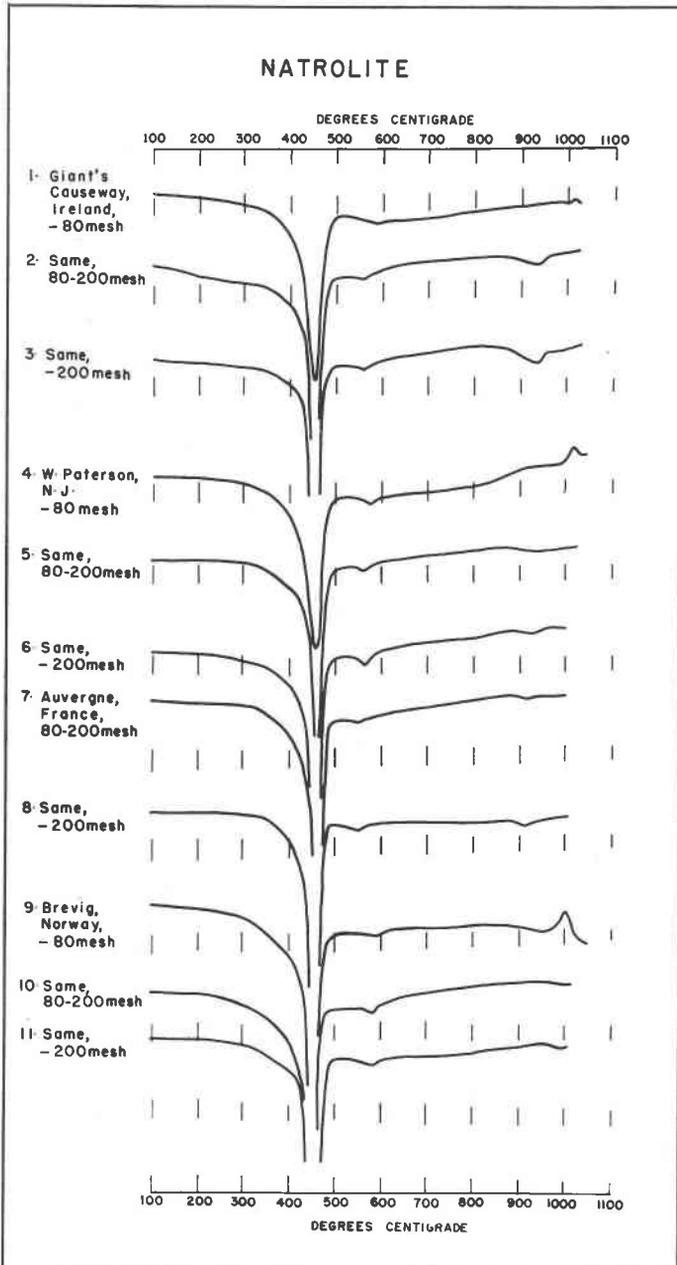


FIG. 3. Differential thermal analysis curve of natrolite.

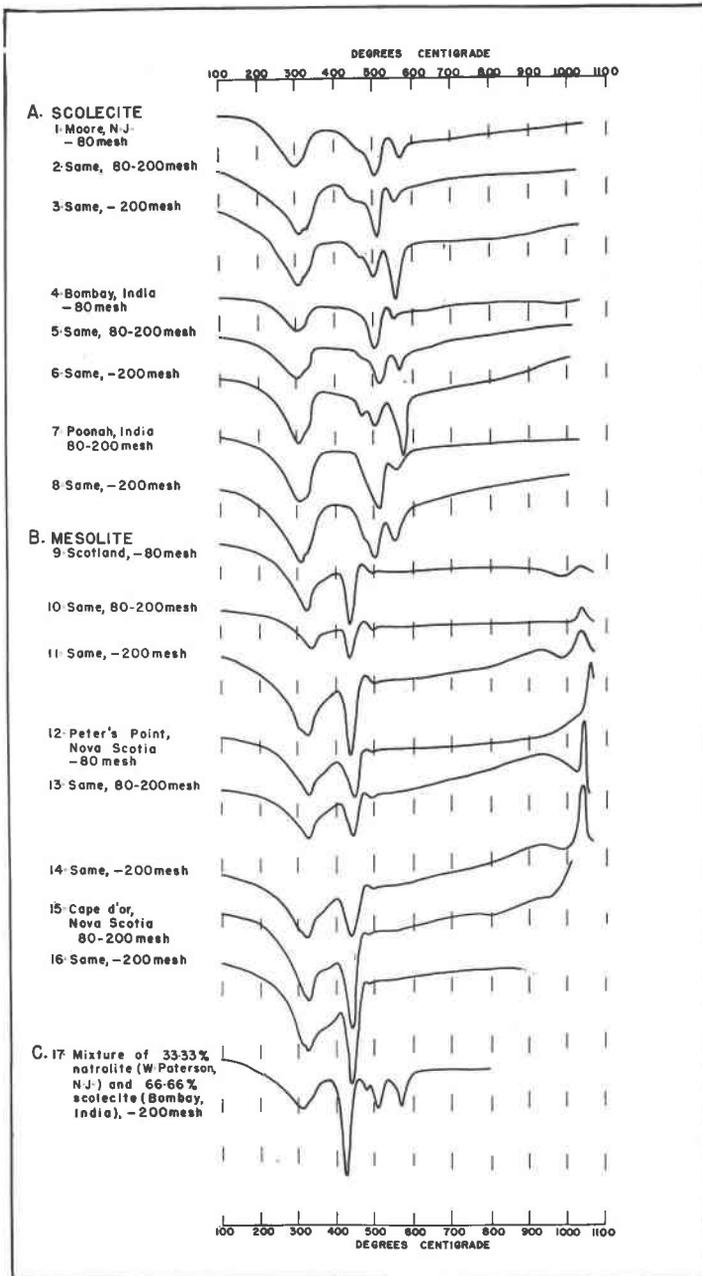


FIG. 4. Differential thermal analysis curves of scolecite and mesolite.

that the thermal effect must not be strong. In other words, the reaction may be a simple and easy one so that not much heat is evolved. Since finer particles should facilitate recrystallization, then this weak thermal effect may have been so subdued in the fractions of smaller grain sizes as to be unable to show up on the *DTA* curves.

The exothermic peak on the mesolite curve is a sharp and strong one. While it appeared at a constant peak temperature but showing increasing sharpness with decreasing particle size on the curves of the Scotland specimen, it occurred at a higher temperature on the curve of the coarse fraction of the Peter's Point specimen than on the curves of its finer fractions. Since the results are not consistent, the evidence for the effect of grain size on the exothermic peak does not seem conclusive.

Other factors may have also contributed to the variations of the reaction peaks. A reaction may be delayed if the sensitivity and position of the thermocouple head in the sample hole cannot be maintained reasonably constant in comparative runs, as often occurred in the present work as previously pointed out. Any change in the sample packing conditions in the sample holes may also impose some irregularities on the peak shape and temperature of reactions. Since limited ionic substitutions are known for the zeolites as discussed in an early section, shift of reaction peaks due to the presence of certain "impurities" is thus possible.

In spite of the aforesaid variations, the *DTA* curves of the three zeolites are as consistent and distinguishing as their dehydration curves. Each of the curves consists of a series of thermal reaction peaks due to loss of water and/or structural changes, but the intensity and temperatures at which they take place are markedly different for the three silicates. Further, those endothermic effects due to loss of water can be well correlated with the shoulders of corresponding dehydration curves, although they are found at higher temperatures for the reasons previously discussed. Also, the sharpness of these reaction peaks and their relative high temperatures indicate that the water is relatively firmly bound in the structures of the zeolites.

The *DTA* data and interpretations of the thermal reactions are given below:

#### (1) *Natrolite*

The natrolite curve is characterized by an extremely sharp and strong endothermic peak at 455° C. Sveshnikov and Kuznetsov (1946) reported the peak as at 350° C., but there is no way to determine the cause of their lower peak temperature because of lack of detailed information. The reaction starts at about 300° C. and ends abruptly at 490° C. It is obviously consistent with the sharp break on the dehydration curve of

the zeolite and both are due to the release of the two water molecules. The dehydrated material showed little changes in appearance and optical properties, but there was some lattice expansion (Table 3).

TABLE 3. INTERPLANAR SPACING FOR NATROLITE AND ITS MODIFICATIONS,  $\lambda_{CuK_{\alpha 1}}=1.5405 \text{ \AA}$

Line No.	Natrolite		Anhydrous natrolite, at the first endothermic peak temperature (455° C.)		Metanatrolite, at the second endothermic peak temperature (565° C.)	
	<i>d</i> (Å)	<i>I</i> .	<i>d</i> (Å)	<i>I</i> .	<i>d</i> (Å)	<i>I</i> .
1	6.44	10	6.46	8	6.38	8
2	5.81	10	5.85	8	5.79	10
3	4.57	3	4.62	3	4.42	2
4	4.32	10	4.35	8	4.30	10
5	4.10	6	4.14	5	4.09	4
6	3.48	1	3.48	.5	—	—
7	3.18	10	3.18	7	3.13	10
8	—	—	3.14	5	—	—
9	—	—	3.09	2	—	—
10	2.93	4	2.94	4	2.93 D	3
11	2.83	10	2.85	10	2.83	10
12	2.66	1	—	—	—	—
13	2.57	3	2.57	3	2.56	3
14	2.43	3	2.44	1	2.42	2
15	2.41	2	2.41	1	—	—
16	2.32	2	2.32	.5	2.32	1
17	2.25	2	2.25 In	1	2.24 D	.5
18	2.17	6	2.18	5	2.18	2
19	2.06	1	2.06	.5	2.05 In	.5
20	1.96	1	1.96	.5	1.96 In	.5
21	1.87	2	1.93	1	1.88	1
22	1.80	4	1.80	4	1.80	3
23	1.75	1	—	—	—	—
24	1.73	1	1.72	.5	—	—
25	1.70 In	1	1.70 In	.5	—	—
26	1.68 In	1	1.68	.5	1.69	.5
27	1.65 In	1	1.65	.5	—	—
28	1.62 In	1	1.62	.5	—	—
29	1.60 In	1	1.60	.5	1.60 In	.5
30	1.57 In	1	1.57	.5	1.57 In	.5
31	1.53 In	2	1.53	1	1.53 In	1
32	1.46	4	1.46	3	1.45 In	1
33	1.42	1	1.42	.5	1.42	.5
34	1.39	2	1.39	1	1.39	1
35	1.37	.5	1.37 In	.5	—	—
36	1.35	.5	1.34 In	.5	1.35	.5
37	1.32	.5	1.33 In	.5	1.32 In	.5
38	1.31	2	1.31	1	1.30 In	.5
39	1.29	.5	—	—	—	—
40	1.27	.5	—	—	—	—
41	1.24	.5	—	—	—	—
42	1.22	3	1.22	2	1.22 In	1
43	1.19	1	1.19 In	.5	1.19 In	.5
44	1.16	.5	—	—	—	—
45	1.14	.5	1.14 In	—	—	—

In—Indistinct; D—Diffuse.

At 565° C. there is a very small but persistent endothermic peak. Optical and *x*-ray diffraction data of the Giant's Causeway specimen heated up to that temperature indicate the presence of a new phase which may correspond to Rinne's metanatrolite (1890) and hence, the endothermic reaction may represent the transformation.

After the 565° C. endothermic effect, the curve is almost level until between 910° and 940° C. where there is a small rounded endothermic trough with an immediately preceded small hump. Since the *x*-ray powder photograph of the materials heated to that temperature showed only a few diffuse bands, the thermal reaction may be properly identified with structural destruction.

The zeolite shows a small exothermic reaction peak at about 1010° C. as mentioned previously. Samples heated up to the peak temperature were essentially isotropic but with scattered weakly birefringent granules. Nevertheless, they all gave a distinct *x*-ray powder pattern. Most lines are those of nepheline, although some could not be accounted for (Table 4). It is thus clear that the exothermic reaction must be caused by recrystallization of fused natrolite into nepheline and probably another phase, although glass is still dominant at that temperature. The formation of nepheline and glass from natrolite was reported by C. Doelter long ago (1890) and the exothermic reaction was also noted by Sveshnikov and Kuznetsov (1946), but the latter did not identify the products and the peak temperature given by them is much lower, namely, between 895° and 960° C.

## (2) *Scolecite*

The *DTA* curve of scolecite shows three sharp endothermic peaks. The first reaction starts at about 170° C. and produces a broad V-shaped peak at 310° C. But the large breadth of the peak and its strange change in slope on the high-temperature side suggest that it may be a doublet with a small and poorly defined subsidiary peak at about 320° C. (Fig. 4). The major peak may be well correlated with the first shoulder on the dehydration curve of the zeolite ending around 200° C., if about 100° is allowed for the temperature difference between these two kinds of thermal curves. Thus it would represent a loss of one of the three water molecules in the mineral. The possible small subpeak may be due to the transformation of the mineral to metascolecite, which has long been recognized as a high-temperature form resulting from the removal of one water molecule from the zeolite (Rinne, 1890; Cavinato, 1927; Hey & Bannister, 1936). It seems probable that since these two reactions, partial dehydration and phase transition, are so closely related, their thermal effects may overlap and hence cannot be well separated on the *DTA* curve.

TABLE 4. POWDER DIFFRACTION DATA FROM NATROLITE HEATED TO 1010° C. AND NEPHELINE,  $\lambda_{\text{CuK}\alpha 1} = 1.5405 \text{ \AA}$

Line	Nepheline (A.S.T.M.)		Natrolite heated to 1010° C.		Nepheline, Magnet Cove, Ark.	
	<i>d</i> (Å)	<i>I.</i>	<i>d</i> (Å)	<i>I.</i>	<i>d</i> (Å)	<i>I.</i>
1	—	—	8.694	7	—	—
2	—	—	4.989	7	4.958	1
3	—	—	—	—	4.634	1
4	4.210	8	4.256	10	—	—
5	—	—	4.141	10	4.187	8
6	3.83	8	3.830	10	3.839	10
7	3.59	4	—	—	3.644	1
8	3.27	7	3.260	10	3.267	9
9	3.17	2	—	—	—	—
10	3.01	10	2.999	10	3.019	10
11	2.87	7	2.876	6	2.888	8
12	2.58	6	2.567	6	2.582	6
13	2.48	4	2.486	4	2.502	4
14	2.38	4	—	—	2.405	3
15	2.34	8	2.336	10	2.356	6
16	2.29	7	—	—	2.316	3
17	2.11	2	—	—	2.175	1
18	—	—	—	—	2.132	1
19	2.08	6	2.077	8	2.105	3
20	2.03	2	2.026	1	—	—
21	1.98	4	1.974	1	1.980	1
22	1.93	6	1.923	4	1.931	3
23	1.88	4	1.881	1	1.896	2
24	1.84	2	—	—	1.850	1
25	1.81	6	1.791	1	1.810	2
26	—	—	1.786	1	1.775	1
27	1.76	4	1.753	1	—	—
28	1.72	6	1.704	4	1.704	2
29	1.69	4	—	—	—	—
30	1.64	2	1.663	1	1.643	1
31	1.62	6	1.629	1	1.627	2
32	1.60	2	1.612	4	1.610	1
33	—	—	1.595	1	—	—
34	1.56	6	1.557	8	1.573	6
35	1.53	6	1.523	2	1.535	1
36	1.47	5	1.467	3	1.478	2
37	1.46	7	1.455	1	1.468	1
38	1.43	6	1.426	6	1.440	3
39	1.39	8	1.380	8	1.393	5
40	1.38	4	1.370	1	1.384	1
41	1.35	4	1.335	1	1.355	1
42	1.35	2	—	—	—	—
43	1.32	4	1.312	6	1.325	2
44	1.31	2	—	—	—	—
45	1.28	7	1.278	7	1.288	3
46	1.26	4	1.265	1	1.276	1
47	1.26	5	1.263	1	1.266	2
48	1.25	2	—	—	—	—
49	1.24	4	1.233	1	1.244	1
50	1.22	6	—	—	1.227	1
51	1.21	7	1.218	1	1.213	2
52	1.19	8	1.201	6	1.195	3
53	1.18	2	1.182	7	1.163	1
54	1.16	4	1.151	1	1.148	1
55	1.14	6	1.137	—1	1.141	1
56	—	—	1.028	—1	—	—

The second endothermic effect starts at about 440° C. and forms a doublet with a small auxiliary peak at about 470° C. and a sharp major peak at 500° C. It may be correlated with the final shoulder on the dehydration curve due to the liberation of the other two water molecules. Its doublet form also seems to be in accord with the appearance of the shoulder which has a secondary break and both suggest differing volatilities of the two water molecules.

The third endothermic peak merges with the second doublet at about 525° C. and reaches its maximum at about 560° C. The powder *x*-ray diffraction photograph of the Bombay specimen heated up to that temperature gave only a few diffuse lines, thus indicating the reaction as a result of structural disintegration (Table 5).

Then the curve levels off until the final firing temperature at 1050° C. used in the present study. Heated samples were a porous porcellaneous mass, isotropic between crossed nicols, and yielded no diffraction lines. Hence, melting of the zeolite resulting in glass and anorthite as reported by Doelter (1890) cannot be proved.

### (3) *Mesolite*

The *DTA* curve of mesolite features two major and one minor endothermic reactions and two exothermic peaks. As in the case of scolecite, thermal decomposition of this zeolite starts at a relatively low temperature, probably in the neighborhood of 150° C. and then proceeds slowly until it reaches the first endothermic peak. The latter is a doublet with a minor subpeak at about 310° C. and a major one at 325° C., but the minor subpeak is not always developed. The second endothermic reaction takes place sharply at 400° C. and reaches its peak at about 440° C. It is a strong symmetrical peak, but the base line shifts to higher level on the high temperature side, probably due to a change in the thermal conductivity and specific heat of the material.

As demonstrated by the dehydration curve presented above, mesolite gives off its water successively in three stages with 2, 2, and 4 molecules respectively. If about 100° is assumed as the temperature difference between the two kinds of thermal data, the first endothermic doublet would be correlative with the first two shoulders on the dehydration curve and the second sharp endothermic peak with the last large shoulder. Then, it would follow that the first and second endothermic reactions may be attributed to the loss of (2+2) and 4 water molecules respectively. Samples heated up to the peak temperatures of the two thermal effects showed an increase in the refractive indices, but little changes in appearance. The heated material just after the first endothermic peak, like natrolite, had an expanded lattice, but after the second endothermic peak it showed some contraction (Table 6).

TABLE 5. INTERPLANAR SPACING FOR SCOLECITE AND MODIFICATIONS AT VARIOUS PEAK TEMPERATURES,  $\lambda\text{CuK}\alpha_1=1.5405 \text{ \AA}$

Line	Scolecite		First endothermic peak (320° C.)		Second endothermic peak (500° C.)		Thrid endothermic peak (550°-570° C.)	
	<i>d</i> (Å)	<i>I</i> .	<i>d</i> (Å)	<i>I</i> .	<i>d</i> (Å)	<i>I</i> .	<i>d</i> (Å)	<i>I</i> .
1	6.53	3	6.52	3	6.41 B	4	Diffuse	Band
2	5.81	4	5.81	8	5.75 B	8		
3	4.69	3	4.61	5	4.64	1		
4	4.37	5	4.35	8	4.32	6		
5	4.19	1	4.16	1	4.16	1		
6	3.63	1	3.63	1	3.61	3	Diffuse	Band
7	3.15	2	3.17	5	3.16	3		
8	3.09	1	3.07	2	3.06	1		
9	2.86	10	2.87	10	2.86	10		
10	2.68	.2	—	—	—	—		
11	2.58	1	2.57 B	2	2.56 B	.5		
12	2.47	1	2.44	2	2.42 B	1		
13	2.42	1	—	—	—	—		
14	2.32	1	—	—	—	—		
15	2.26	1	2.25	.5	2.27	.5		
16	2.20	3	2.18 D	4	2.19	2		
17	2.17	.2	2.15 D	.5	—	—		
18	2.07	1	2.04	1	2.04 B	1		
19	2.03	.5	—	—	—	—		
20	1.99	2	1.96	2	1.95	1	Diffuse	Band
21	1.95	2	1.87	2	1.86	1		
22	1.90	.5	—	—	—	—		
23	1.86	1	—	—	—	—		
24	1.80 B	3	1.80	2	1.80 D	1		
25	1.75	2	1.75 B	1.5	1.75	.5		
26	1.72	.5	1.73 B	.5	—	—		
27	—	—	1.68	1	1.68	.5		
28	1.66 B	.5	1.66	.5	—	—		
29	1.64 B	1	1.63	3	1.63	.5		
30	1.61	1	1.62 In	.5	—	—		
31	1.60	.3	1.60	1	1.58 D	.5		
32	1.52	.5	1.51 In	.5	1.52 D	.5		
33	1.50	.2	—	—	—	—		
34	1.47	2	1.48	3	1.47 D	2		
35	1.43	1	1.43	1	1.43 D	.5		
36	—	—	1.40	1	—	—		
37	1.38	1	1.39	1	1.38 D	.5		
38	—	—	1.37	.5	—	—		
39	1.33	1	1.33	1	1.33	.5		
40	—	—	1.31 B	2	1.31	.5		
41	1.31	1	1.29	.5	1.27	.2		
42	—	—	1.28 In	.5	1.24	.5		
43	1.27	.5	—	—	—	—		
44	1.24	2	1.23	.5	—	—		
45	1.22	.5	—	—	1.21	.5		
46	1.21	.5	1.21 In	.5	—	—		
47	1.19	.5	1.19 In	.5	1.18	.5		
48	1.17	.5	1.17 In	.5	—	—		
49	1.15	.5	1.14	.5	—	—		
50	1.15	.2	—	—	—	—		

B—Broad; In—Indistinct; D—Diffuse.

TABLE 6. INTERPLANAR SPACING FOR MESOLITE AND ITS MODIFICATIONS AT VARIOUS THERMAL REACTION PEAK TEMPERATURES,  $\lambda\text{CuK}\alpha_1=1.5405 \text{ \AA}$ 

Line	Mesolite		First endothermic peak temperature, 325° C.		Second endothermic peak temperature, 440° C.		Third endothermic peak temperature, 490° C.	
	$d(\text{\AA})$	$I.$	$d(\text{\AA})$	$I.$	$d(\text{\AA})$	$I.$	$d(\text{\AA})$	$I.$
1	6.44 B	4	6.54	4	6.44	4		
2	5.79	7	5.81	6	5.81	6		
3	5.46	-1	—	—	—	—		
4	4.66	3	4.62	4	4.66	1		
5	4.35 B	5	4.37 D	6	4.33 D	4	Diffuse	Weak
6	4.16	1	4.17	2	4.09	2		
7	3.89	-1	3.66	-1	—	—		
8	3.18 D	3	3.18 D	4	—	—		
9	3.08 D	2	3.09	2	3.07	2		
10	2.86	10	2.88	10	2.85 D	10	Diffuse	Weak
11	2.57 D	1	2.58	2	2.55 B	-1		
12	2.47	1	2.48 B	2	2.41 D	-1		
13	2.41	1	2.44	2	—	—		
14	2.34	-1	2.33	-1	—	—		
15	2.27	-1	2.27	-1	—	—		
16	2.19 D	3	2.21	3	2.18 D	-1		
17	—	—	2.09	-1	2.06 D	-1		
18	2.05	-1	2.05	1	—	—		
19	—	—	2.00	-1	—	—		
20	1.95	-1	1.96	1	—	—		
21	1.86	-1	1.86	2	—	—		
22	1.81	3	1.81 D	2	1.81 D	2		
23	1.75	1	1.76 D	2	—	—		
24	1.72	-1	1.73 D	-1	—	—		
25	1.68	-1	1.69	-1	—	—		
26	—	—	1.67	-1	—	—		
27	1.64	1	1.64	2	1.64 D	-1		
28	1.59	-1	1.60	-1	1.61 D	-1		
29	1.54	-1	1.55 D	-1	—	—		
30	1.52	-1	1.53	-1	—	—		
31	1.47	3	1.48	2	1.47	-1		
32	1.43	1	1.44	1	—	—		
33	1.40	1	1.41	-1	—	—		
34	1.39	1	1.39	1	1.38 D	-1		
35	1.35	-1	1.37 D	-1	—	—		
36	—	—	1.35 D	-1	—	—		
37	—	—	1.33	1	1.31 D	-1		
38	1.30	-1	1.32	1	—	—		
39	—	—	1.30	-1	—	—		
40	—	—	1.28	-1	—	—		
41	1.24 B	1	1.24	1	—	—		
42	1.21	-1	1.22	-1	—	—		
43	1.19	-1	1.19	-1	—	—		
44	—	—	1.18 D	-1	—	—		
45	1.15	-1	1.16	-1	—	—		
46	1.15	-1	1.15	-1	1.13 D	1		
47	1.15	-1	—	—	1.10	1		

B—Broad; In—Indistinct; D—Diffuse.

Another endothermic peak occurs at 490° C. and is of small intensity. Since the Peter's Point specimen heated to that temperature gave no distinct diffraction lines, the reaction is interpreted as a structural breakdown. Just prior to this peak there is a very small swell at 470° C. indicative of a weak exothermic reaction, but its explanation is not clear.

A strong exothermic reaction takes place at about 1040° C., giving rise to a sharp peak with an immediately preceding dip. It is associated with recrystallization of fused mesolite, since specimens heated to the peak temperature comprised a mixture predominantly of glass with some cryptocrystalline plagioclase, probably labradorite, as shown by the diffraction pattern (Table 7).

It has been well established that the three zeolites are independent species but isostructural and mesolite is not an intermediate mixture (Gorgey, 1909; Bowman, 1909; Winchell, 1925; Cavinato, 1926; Hey & Bannister, 1932-33-36; Taylor *et al.*, 1933; Wyart, 1933; Berman, 1937). This is fully confirmed by the present study. Both their dehydration and *DTA* curves are distinctive and the *DTA* curve of mesolite does not appear to be a combination of the natrolite and scolecite curves. Additional evidence is provided by the *DTA* curve of an artificial mixture of one part of natrolite and two parts of scolecite proportional to the composition of mesolite (Fig. 4, No. 17). It produced a typical composite curve of the two components showing no resemblance whatever to the mesolite curve. However, although the overall shape of the mesolite curve is characteristic, its first endothermic peak well matches the first endothermic peak of scolecite and its second endothermic peak falls almost within the same temperature range as the intense endothermic peak of natrolite. Since all of the peaks mainly result from dehydration, it appears that the water molecules in the three zeolites released during corresponding endothermic reactions may be structurally of the same type so that upon heating they behave in the same manner.

#### CRYSTAL STRUCTURE AND THERMAL BEHAVIOR

The fundamental cause of thermal decomposition of a mineral is the disruption of certain bonds within its crystal structure. Since the bonds which hold atoms to their lattice positions have specific energy values, a definite activation energy is required for their dislocation. Hence, the decomposition temperature may be regarded as a measure of the bond strengths involved. On this account, the thermal behavior of a mineral may be better understood in terms of structural concepts and thermal analysis data in turn should provide useful information on the structure.

According to both Pauling (1930) and Taylor *et al.* (1933), scolecite and mesolite have essentially the same framework structure as that of

TABLE 7. POWDER DIFFRACTION DATA FROM MESOLITE HEATED TO 1040° C.  
 AND LABRADORITE,  $\lambda\text{CuK}\alpha_1 = 1.5405 \text{ \AA}$ 

Line	Labradorite (A.S.T.M.)		Mesolite heated to 1040° C.		Labradorite, Labrador	
	$d(\text{\AA})$	$I.$	$d(\text{\AA})$	$I.$	$d(\text{\AA})$	$I.$
1	—	—	—	—	6.488	1
2	—	—	—	—	4.689	1
3	4.07	4	3.975	7	4.038	5
4	—	—	—	—	3.885	1
5	3.77	1.3	3.678	6	3.763	5
6	3.64	1.1	—	—	3.683	4
7	—	—	3.378	-1	3.488	1
8	—	—	—	—	3.365	1
9	3.20	10	3.163	10	3.215	10
10	3.00	1.1	—	—	3.020	1
11	2.92	1.1	2.888	-1	2.940	3
12	2.84	0.5	2.787	-1	2.845	2
13	2.64	0.5	2.649	-1	2.660	2
14	2.53	2.7	2.498	-1	2.500	3
15	2.40	1	2.401	-1	—	—
16	2.29	5	—	—	2.300	1
17	2.21	1	—	—	—	—
18	2.12	0.7	2.130	4	2.128	1
19	2.01	0.5	—	—	2.025	1
20	—	—	1.999	1	1.996	1
21	1.92	0.4	1.912	2	1.925	1
22	—	—	—	—	1.890	1
23	1.83	0.7	1.829	4	1.835	3
24	—	—	—	—	1.800	1
25	1.77	0.5	1.765	4	1.765	2
26	—	—	—	—	1.750	1
27	1.71	0.3	1.708	-1	1.725	1
28	1.62	0.3	1.605	-1	1.608	1
29	1.56	0.1	1.560	-1	1.545	1
30	1.53	0.1	1.525	-1	—	—
31	1.48	0.4	1.480	2	1.463	2
32	1.37	0.1	—	—	1.388	1
33	1.35	0.4	1.350	4	1.355	2
34	1.32	0.1	1.319	-1	1.328	1
35	1.29	0.1	—	—	—	—
36	1.27	0.2	1.271	-1	1.272	1
37	1.25	0.1	1.253	-1	—	—
38	1.21	0.4	1.219	-1	1.224	1
39	1.16	0.3	—	—	—	—
40	1.13	0.3	—	—	1.135	1
41	1.07	0.1	—	—	—	—

natrolite, probably with the same cavities filled. But since they have different water contents and cations, they must differ in certain details of their arrangements. These structural differences are believed to be chiefly responsible for the differing thermal behavior of the zeolites.

The diagnostic feature of the thermal behavior of natrolite is the intense endothermic effect at 455° C. with its two water molecules removed at the same time. Evidently, the two must occupy equivalent lattice positions so that they have the same volatility. This is in perfect agreement with the structure suggested by Taylor *et al.* (Fig. 5a). After dehydration the structure is essentially preserved and will not break down until about 940° C.

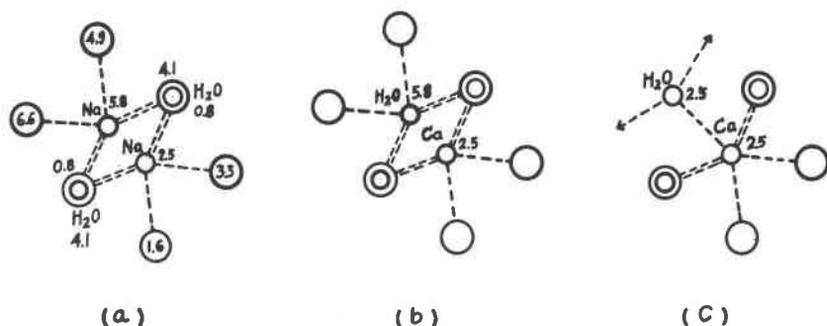


FIG. 5. The arrangement of cations and water molecules in natrolite by W. H. Taylor *et al.* (a), in scolecite by L. Pauling (b), and in scolecite by Taylor *et al.* (c). The large circles represent oxygen atoms in the SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra. The figures denote heights in Angstrom units above the plane of projection. (After W. H. Taylor *et al.* 1933)

The dehydration of scolecite proceeds discontinuously with one water molecule coming off during the 310° C. endothermic reaction and the other two in the 500° C. endothermic doublet, indicating that the former must be more loosely bound in the structure than the latter. This tends to bear out Pauling's arrangement of the water in the zeolite (Fig. 5b) in which one molecule is placed at 3.6 Å from the single cation of Ca while the other two are 2.5 Å away as in the natrolite structure. It is, however, at variance with the structure proposed by Taylor *et al.* (Fig. 5c) in which one water molecule is a little closer to the cation than the other two at distances of 2.3 Å and 2.5 Å respectively, and hence the single water molecule would come off later than the other two. But Hey (1936) found it satisfactory to explain his dehydration data of the zeolite. Another point brought up by the present study is that both the DTA and static curves suggest that even the other two water molecules may not occupy exactly the same lattice positions as they do in the structure suggested

either by Pauling or by Taylor *et al.*, since they are removed in a doublet reaction. Further structural study thus seems desirable.

While the natrolite structure persists up to about 940° C. as already discussed, scolecite begins to show signs of structural collapse after final dehydration at 500° C. and breaks down completely at 560° C. Their different structural stability cannot be explained by the nature of the cations, since Ca and Na ions are almost of the same size and the strength of the Ca-H<sub>2</sub>O bond (2/7) is even stronger than that of the Na-H<sub>2</sub>O bond (1/6) according to the structures of the two zeolites worked out by Taylor *et al.* It seems certain that the much lower stability of scolecite may result from the introduction of the extra water molecule into the natrolite structure, which, according to Pauling's suggestion (Fig. 5*b*), takes up one of the two Na positions in natrolite. Since it must be much more loosely bound to other ions than the corresponding Na ion in natrolite, the entire structure would be weakened accordingly. Furthermore, since it is more readily driven out upon heating than the other two water molecules, its removal would further damage the structure. But the other two water molecules are given off at slightly higher temperatures (about 500° C.) than the two in natrolite (at 455° C.) although they probably occupy similar lattice positions. This is explained as being due to the strength difference between the Ca-H<sub>2</sub>O and Na-H<sub>2</sub>O bonds.

No detailed *x*-ray analysis has yet been made of mesolite. Since its *x*-ray diffraction pattern is almost identical to that of both natrolite and scolecite and it has a composition corresponding to one natrolite and two scolecite molecules, Taylor *et al.* (1933) have suggested that the mesolite structure must be similar in all its essentials to that of the other two zeolites except that its cell size is three times as large. Further, 6 of the 8 water molecules occupy the general positions as in natrolite and the other two are more strongly tied to the Ca ions as in scolecite. Such an arrangement of the water molecules fails, however, to explain the mode of dehydration of the zeolites as revealed by their thermal curves, which show that 2 water molecules each are removed earlier in two closely spaced stages and the other 4 in a single higher-temperature reaction. It is thus indicated that the water in mesolite may comprise two volatile groups of two molecules each and one less volatile group of four. Further, as has been noted above, the two volatile groups come off in about the same temperature range as the first water molecule of scolecite and the less volatile one at about the peak temperature of the intense endothermic effect of natrolite. Then it may be reasonably assumed that only 4 of the 8 water molecules may occupy the general positions as in natrolite and the other 4 may be placed in similar positions as the extra water molecule in scolecite. In the absence of detailed structural data at present, however, it would be merely speculative to assign any specific positions to the water.

After final dehydration at 440° C. mesolite has already shown considerable optical and structural changes and breaks down completely at 490° C. The still lower stability of the zeolite may be similarly explained as for scolecite as being due to addition of extra water molecules to the natrolite structure. Thus, it appears that the higher the water content of a zeolite, the smaller is its stability range, which seems to be in line with the view of J. W. Gruner (1950) as to the reaction energies of silicates.

#### CONCLUSIONS

The distinctive shoulders on the dehydration curves and their corresponding endothermic peaks on the *DTA* curves of the three zeolites clearly indicate that the water must hold definite lattice positions. Although the three are isostructural, they give off their water at different temperatures and in different amounts. The conclusion is irresistible that the water occupies different positions in their structures. On the basis of their thermal data, it is suggested that natrolite contains a single group of two water molecules of equal volatility, scolecite has a volatile group of one molecule and another less volatile group of two, and mesolite comprises two groups of two molecules each of high and slightly different volatilities and a group of four molecules of equal and lower volatility. This confirms the validity of the methods to arrange water molecules in natrolite and scolecite proposed by Taylor *et al.* and by Pauling. But it is assumed by Taylor *et al.* that the water in mesolite consists of a group of six molecules and another group of two.

The physical properties of the three zeolites show marked changes during the course of dehydration and upon heating up to about 1050° C. They do not, however, undergo the same kind of changes at the same temperature. While natrolite shows only slight changes in the optical properties and crystal structure after complete dehydration at 455° C. and retains its structure until about 940° C, the structures of scolecite and mesolite are completely destroyed respectively at about 560° C. and 490° C. immediately after their final dehydration. Their stability ranges thus seem to depend upon the degree of hydration—apparently the higher the water content of the mineral, the lower is its stability.

The thermal curves of the three zeolites are so characteristic that they should prove to be a useful means of identification. Further, they may serve as an additional proof that the three do not constitute an isomorphous series but are independent species.

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