

HIGH-TEMPERATURE PHASES OF ZEOLITES OF THE NATROLITE GROUP

L. P. VAN REEUWIJK, *Department of Soil Science, State Agricultural
University, Wageningen, The Netherlands*

ABSTRACT

The thermal changes occurring in zeolites of the natrolite group have been investigated by DTA, TGA, and continuous-heating X-ray photography. This combination of techniques facilitated a better description of the dehydration phenomena. Several as yet unknown metaphases have been recorded, and stability ranges have been reassessed. Structurally, upon heating natrolite behaves entirely differently from its isotypes mesolite and scolecite which are mutually similar in behavior. Thomsonite and gonnardite also show similar X-ray diffraction powder patterns, with aspects of both natrolite and mesolite/scolecite. Edingtonite shows an individual pattern and is the only member of the group where heating does not result in a phase amorphous to X-rays (X-amorphous).

The only feature common to all members of the group is that the room temperature phase reacts upon heating by a considerable contraction along the *a* and *b* axes and a slight expansion along the *c* axis, in accordance with the general structure of the group.

INTRODUCTION

The thermal properties of few natural zeolites have been studied as extensively as those of the members of the natrolite group. This applies particularly to the species natrolite, mesolite, and scolecite and to a lesser extent thomsonite, whereas gonnardite and edingtonite have received very little attention.

As has been pointed out in an earlier communication (van Reeuwijk, 1971), previous studies could not possibly give accurate information about the physical changes zeolites undergo upon thermal dehydration, due to the employment of inadequate methods and techniques.

The purpose of this report is to give an account of the thermal behavior of all members of the natrolite group as obtained by a combination of dynamic thermal analysis methods, *viz.*, differential thermal analysis (DTA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and continuous heating X-ray diffraction techniques.

MATERIALS

A representative specimen of each species was selected from our collection under study to illustrate the characteristic properties. The Guinier De Wolff X-ray photographs (Co-K α radiation) are given in Figure 1, the chemical analyses in Table 1.

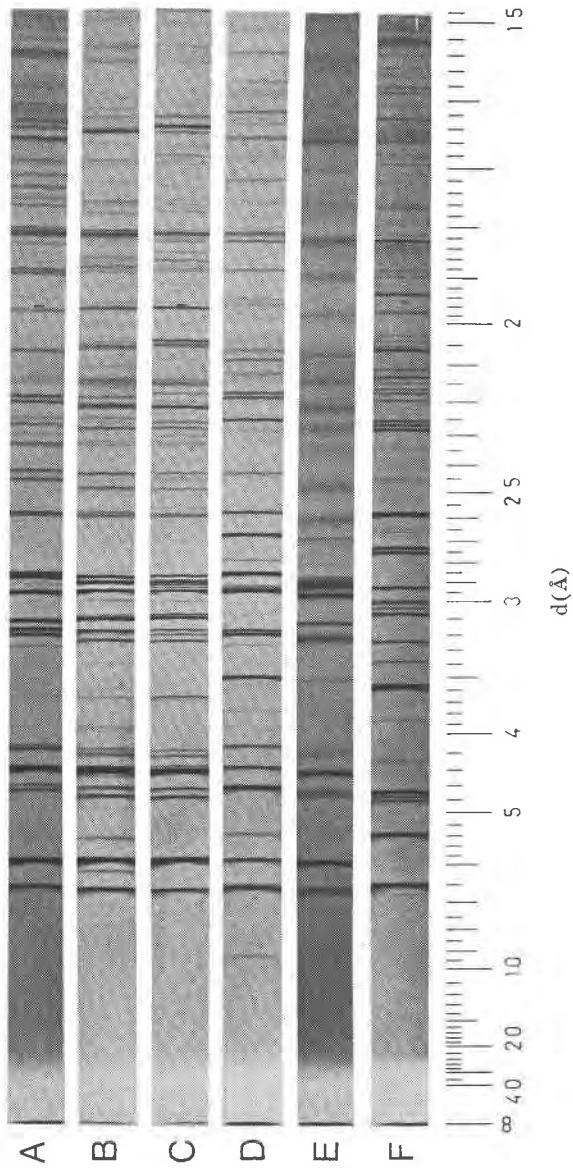


FIG. 1. Guinier X-ray photographs of zeolites of the natrolite group. A. natrolite, B. mesolite, C. scolecite, D. thomsonite, E. gonnardite, F. edingtonite.

Table 1. CHEMICAL ANALYSES OF MINERALS OF THE NATROLITE GROUP.

	A	B	C	D	E	F
SiO ₂	47.06	46.21	45.97	38.62	42.83	35.14
Al ₂ O ₃	26.66	26.02	25.69	31.04	28.79	20.12
Na ₂ O	15.36	5.08	0.26	4.26	8.02	-
CaO	0.27	10.40	14.21	12.81	7.56	-
BaO	-	-	-	-	-	31.18
H ₂ O	9.76	13.34	14.44	13.48	13.78	13.16
Total	99.06	101.05	100.57	100.21	100.98	99.60

A. Natrolite, Na_{15.23}Ca_{0.15}Al_{16.09}Si_{24.08}O₈₀ · 16.58 H₂O (Auvergne, France)

B. Mesolite, 3(Na_{5.09}Ca_{5.76}Al_{15.86}Si_{23.95}O₈₀ · 24.04 H₂O), (Oregon, U.S.A.)

C. Scolecite, Na_{0.26}Ca_{7.96}Al_{15.84}Si_{24.09}O₈₀ · 25.22 H₂O, (Teigarhorn, Iceland)

D. Thomsonite, Na_{4.40}Ca_{7.31}Al_{19.50}Si_{20.62}O₈₀ · 23.99 H₂O, (Kilpatrick, Scotland)

E. Gonnardite, Na_{8.15}Ca_{3.15}Al_{17.79}Si_{22.49}O₈₀ · 24.12 H₂O, (Auvergne, France)

F. Edingtonite, $\frac{1}{4}$ (Ba_{8.27}Al_{16.05}Si_{23.82}O₈₀ · 29.74 H₂O), (Böhlet, Sweden)

PROCEDURES

DTA, TGA, and DSC were performed according to the methods described earlier (van Reeuwijk, 1971) with the only difference that in the present study a heating rate of 10°C/min. was used for DTA and TGA. Continuous heating X-ray diffraction patterns were recorded using a Guinier-Lenné camera with an average heating rate of ca. 0.3°C/min. and a filmspeed of 2 mm/hr. Here, Cu-K α radiation was used.

RESULTS

The DTA and TGA curves are presented in Figure 2 and the results of the DSC in Table 2. The continuous heating X-ray diffractograms are given in Figure 3.

Natrolite

The DTA and TGA traces of natrolite are the simplest of the group. Dehydration occurs, with an initial temperature of ca. 240°C, in a single process in which all 16 molecules H₂O are given off. Variation within the group of available samples was negligible. The heating X-ray diffractogram (Fig. 3A) shows the corresponding transition to metanatrolite to take place at 280°C, again clearly illustrating that peak maxima in DTA curves (cf. Fig. 2A) cannot be used in deter-

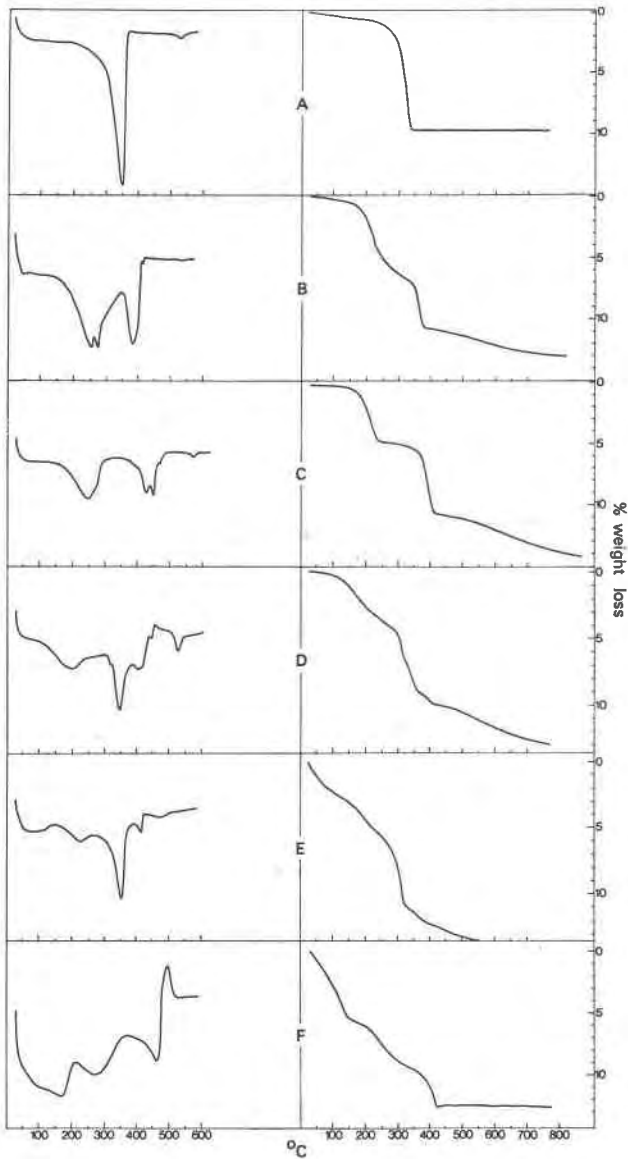


FIG. 2. DTA and TGA curves of zeolites of the natrolite group. A. natrolite, B. mesolite, C. scolecite, D. thomsonite, E. gonnardite, F. edingtonite.

TABLE 2. Heats of dehydration (ΔH) of minerals of the natrolite group

	Peak	number of molecules H ₂ O	ΔH (kcal/mole H ₂ O)		Peak	number of molecules H ₂ O	ΔH (kcal/mole H ₂ O)
Natrolite	350° C	16	21.3	Thomsonite	200° C	8	13.1
					350	8	15.5
					425	2	21.8
Mesolite	245	12	17.5	Gonnardite	75	5	4.4
	380	7	17.8		220	5	18.0
					450	9	23.8
Scolecite	225	8	19.5		420	2	7.9
	410	10	11.8	Edingtonite	160	12	7.2
					270	10	7.5
			450		7	9.5	

mining actual reaction temperatures. However, for the sake of comparison with previous work, peak maxima will be used to indicate reactions. Maxima for natrolites were found to occur at 350°C which is from 50 to 100°C lower than those usually reported by previous workers (Koizuma, 1953; Peng, 1955; Pécsi-Donáth, 1962). However, Sveshnikov and Kusnetzov (1946) are quoted by Peng to have found maxima at 350°C.

The photograph (Fig. 3A) reveals that a contraction along the *a* and *b* axes together with a slight expansion along the *c* axis precedes the transition to metanatrolite. In contrast to what was hitherto believed, metanatrolite is shown to consist of two phases, the second starting at 510°C accompanied by a small endothermic peak in the DTA due to heat of transition alone since no dehydration is involved. Metanatrolite as a single phase was described by Hey (1932); however, at this stage it cannot be decided to which of the two present phases his description applies.

Rehydration is possible until the structure becomes X-amorphous at 785°C. Peng (1955) and Pécsi-Donáth (1962) reported collapse of structure at temperatures well over 900°C.

At 900°C α -carnegieite is formed. This phase appears to exist over only a short temperature range as gradual transformation to nepheline is initiated already at 910°C and completed at 970°C.

According to the known phase relations the formation of nepheline from carnegieite by heating is an unusual sequence (Smith and Tuttle, 1957; Levin *et al.*, 1969).

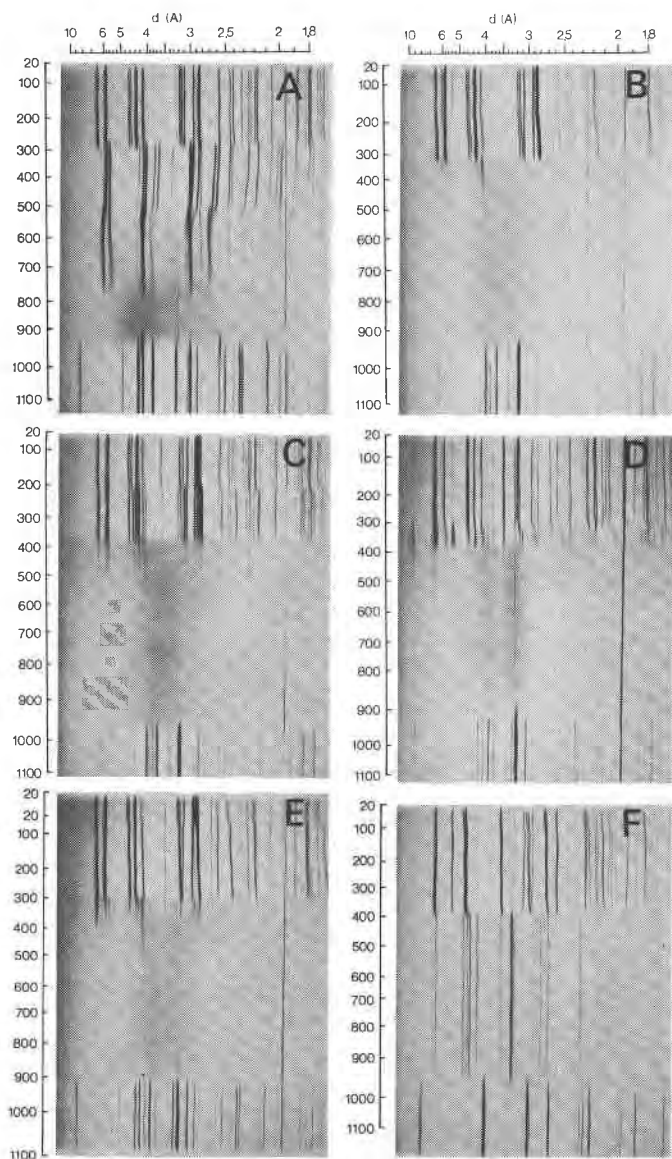


FIG. 3 Continuous heating X-ray photographs of zeolites of the natrolite group. A. natrolite, B. mesolite, C. scolecite, D. thomsonite, E. gonnardite, F. edingtonite. The continuous reflections from top to bottom of the photographs are due to the Pt sample grid.

From the reaction equation



appears that about 17 percent of the material at high temperatures consists of silica, however, up to 1150°C (maximum temperature of the camera) no crystalline silica phase can be detected.

The occurrence of albite as a heating product of natrolite (Pécsi-Donáth, 1968) has not been observed in any of the samples.

Mesolite

The dehydration of mesolite occurs in two main steps, the first of which is a double reaction with peak maxima in the DTA trace at 255° and 275°C (Fig. 2B). During this reaction 2×6 molecules of H₂O are lost (per 80 oxygens). The heating X-ray diffractogram (Fig. 3B) shows that the transition to metamesolite is initiated at *ca.* 175°C and entails merely a contraction of the crystal lattice along the *a* and *b* axes. The (111) and (511) reflections at 6.13 and 5.42 Å disappear above 200°C but reappear upon rehydration.

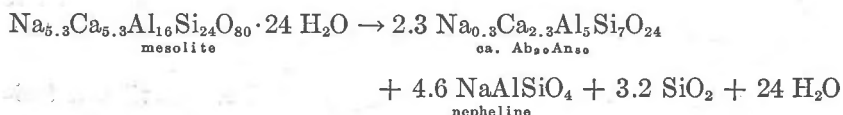
The second main step, when 7H₂O are given off occurs over a shorter temperature range than the first and is in most cases a double reaction as well at 380° and 410°C in the DTA trace. However, the magnitude of the second peak varies considerably from specimen to specimen and is usually much smaller than that of the first or may even be absent. Peng (1955) reported the first doublet at 310°C and the second peak as a single one at 440°C. Pécsi-Donáth (1962) analysed only one specimen which gave a single peak at 300°C and a double one at 410° and 440°C. The findings of Koizumi (1953) agree most closely with those reported here.

The photograph (Fig. 3B) shows that the metastructure is destroyed after dehydration at 320°C, and from then on only some diffuse reflections are discernible. Rehydration from beyond this transition is not possible. This implies that not all the water in this mineral is reversibly removable, the remaining water (if this is water as such) is gradually given off during further heating. The disappearance of the remaining reflections at 490°C is accompanied by a weak endothermic peak at 540°C in the DTA curve, which indicates a total collapse of the structure remnants.

At 910°C a high temperature feldspar phase is formed, which shows, when compared with a set of X-ray photographs of members of the albite-anorthite series, close resemblance to bytownite (Ab₂₀An₈₀).

Not all available material can be incorporated in this phase and from 975°C onwards a nepheline phase can be observed as well.

If all Na and Ca is incorporated in $Ab_{20}An_{80}$ and nepheline, then silica is left over as in the case of natrolite:



Again no crystalline form of silica could be detected, however.

Scolecite

The dehydration of scolecite is very similar to that of mesolite and also occurs in two main steps. The first reaction, initiated at *ca.* 160°C shows a single but non-symmetrical DTA peak with a maximum at 250°C (Fig. 2C).

During this reaction 8H₂O are removed. The second dehydration step, when another 10H₂O are lost, is in some cases a double reaction with peak maxima at 430° and 450°C followed by a smaller separate peak at 480°C whereas other specimens may show a real triple peak at 430°, 450°, and 470°C as shown in Figure 2C. This, however, is neither reflected in the TGA trace nor in the heating X-ray diffractogram (Fig. 3C).

This photograph shows that after the second dehydration step reflections of metascolecite continue, but they are much weaker and slightly shifted. Rehydration of this phase is not possible. As with mesolite, the remainder of the water is lost gradually upon further heating. At 490°C the material becomes X-amorphous corresponding with an endothermic DTA peak at 560°C. At 950°C high temperature anorthite is formed without any apparent accompanying phase, although according to the stoichiometry again silica is left over:



In addition to differences in temperatures of reaction, a diagnostic difference between mesolite and scolecite is the course of both the DTA and TGA curves between the two main dehydration steps. For mesolite this part is sloping, whereas for scolecite it is virtually horizontal.

Thomsonite

The dehydration of thomsonite appears to be somewhat more complex. During the first rather long range of dehydration initiated at

ca. 100°C and having a DTA maximum at 200°C (Fig. 2D) 8H₂O are lost accompanied by a slight but definite contraction of the lattice mainly along the *a*-axis and a still smaller expansion along the *c*-axis (Fig. 3D).

The next step is a double reaction with a small peak at 325°C and a large one at 350°C in the DTA trace during which another 8H₂O are removed and a distinct crystallographic metaphase is formed (Fig. 3D, at 290°C).

Upon further heating, yet another metaphase is formed at 325°C accompanied by a double endothermic DTA peak with maxima at 400° and 440°C, respectively, and during which the base line shifts to a higher level culminating in a small exothermic peak at 450°C. This corresponds with a temperature of 390°C on the heating X-ray diffractogram where a transition to a phase with very weak reflections occurs. Rehydration of this phase is not possible. Collapse of the structure is indicated by the endothermic peak at 520°C in Figure 2D. Milligan and Weiser (1937) and Koizumi (1953) reported no crystallographic changes during dehydration of thomsonite, however, they analyzed their samples after cooling in air.

Just below 900°C a bytownite/anorthite phase is formed (about Ab₁₀An₉₀) followed by nepheline at 910°C.

Gonnardite

No detailed study of the structure of gonnardite has been made, but it is believed to be similar to that of thomsonite (Smith, 1963). This relation is expressed by the thermal behavior. The most important difference is the occurrence of an early dehydration step below 100°C (Fig. 2E) when 5H₂O are given off. This water loss induces a marked contraction of the lattice along the *a* and *b* axes as shown by Figure 3E. This shift, resulting in a merging of reflections, occurs just above room temperature and could only be shown clearly when the heating was started somewhat later than the film transport. The subsequent dehydration steps, where 5, 9, and 2 molecules H₂O are lost, respectively, are very similar to those of thomsonite except that double peaks in the DTA curve of the latter appear to be single ones here. During heating of the first metaphase, up to 300°C, contraction of the lattice along the *a* and *b* axes continues together with a slight elongation along the *c* axis. At 300°C there is a transition to a next metaphase (Fig. 3E) accompanied by a sharp endothermic peak at 350°C in the DTA curve (Fig. 2E). This phase disappears at 360°C on the photograph; from then on some weak reflections continue to about 500°C. No rehydration is possible beyond the 360°C trans-

formation. The occurrence of the weak endothermic peak at 460°C (Fig. 2E) indicates final collapse of the structure.

The subsequent high temperature phases are the same as those for thomsonite.

Edingtonite

A DTA curve of the Böhlet edingtonite has been reported by Pécsi-Donáth (1962) and differs from ours only in temperature measurement. It shows two rather broad and one sharper endothermic peaks at *ca.* 170°, 280°, and 465°, respectively (Fig. 2F). The corresponding steps in the dehydration curve indicate water losses of 12, 10, and 7 molecules, respectively. The TGA curve indicates that no more water is available so that edingtonite contains 29 H₂O per 80 oxygen atoms. Hey (1934) reports that edingtonite contains 32 H₂O per 80 oxygen atoms on grounds that air-dry material takes up more water on raising the water vapor pressure. As this feature is by no means restricted to this mineral, the argument does not apply. For this reason our powdered zeolites are stored and manipulated at the arbitrary but constant relative humidity of 51 percent at 25°C (Barrer and Langley, 1958).

Margaret Foster (1965) concludes from Koizumi's (1953) and Peng's (1955) dehydration curves that H₂O that is an intrinsic part of the structure does not begin to come off below 150°C and, therefore, she recommends that H₂O- be routinely determined in zeolites at 110°C. Our experiments also indicate adsorption of H₂O other than that incorporated in the structure, but a general rule that H₂O coming off below 150°C is not such incorporated water is incorrect, as is illustrated by gonnardite and edingtonite (Fig. 3E, F).

As with the other members of the group, dehydration of edingtonite effects a lattice contraction along the *a* and *b* axes together with an expansion along the *c* axis (Fig. 3F) resulting in a merging of a number of reflections. These shifts are completely reversible.

After the final dehydration reaction the DTA curve shows a relatively strong exothermic peak at 500°C, not due to lattice desintegration as suggested by Pécsi-Donáth (1962), but to the irreversible transformation to celsian and an unidentified phase with the following reflections: (*d* in Å, at room temperature) 5.60 (w), 4.74 (vs), 4.48 (s), 4.22 (vs), 3.58 (w), 3.55 (w), 2.68 (s), 2.30 (w). Remarkable is the small weight increase accompanying this reaction (Fig. 2F). When a TGA was carried out in a dry N₂ stream, transformation to celsian did not occur at the end of dehydration and no weight increase

was observed. Experiments to establish whether water or possibly oxygen is involved failed so far.

At 925°C celsian is transformed to hexacelsian with the simultaneous disappearance of the unidentified phase. The transformation of edingtonite to hexacelsian is represented by the following equation:



hence again silica is left over. Unlike the reactions shown by other members of the group, this silica crystallizes as β -cristobalite at *ca.* 1050°C, indicated by some weak reflections on the original heating X-ray diffractogram (Fig. 3F). The co-existence of hexacelsian and β -cristobalite at such a relatively low temperature is not represented in the $\text{BaAl}_2\text{Si}_2\text{O}_8$ - SiO_2 phase diagram of Foster and Lin (1969).

CONCLUSIONS

Upon dehydration, all members of the natrolite group react by a contraction of the lattice along the *a* and *b* axes and often an expansion along the *c* axis. This is fully in accordance with the general structure of these minerals which consists of parallel chains of (Al, Si) O_4 tetrahedra in the *z* direction, less prominently linked together in *x* and *y* directions.

Although natrolite, mesolite, and scolecite are isotypes, the structural behavior of natrolite appears to deviate significantly from that of mesolite and scolecite which show a good mutual resemblance. Thomsonite and gonnardite, supposedly isotypes too, are very similar in thermal behavior and show, moreover, properties of both natrolite (350°C endothermic peak, more than one prominent metaphase) and mesolite/scolecite (*ca.* 200° and 400°C endothermic peaks, not all the water reversibly removable).

Apart from thermal expansion of the crystal lattice, the structural relationship of edingtonite with the group is not expressed by its thermal behavior. Unlike the behavior of the other members, after dehydration further heating produces an irreversible crystallographic transformation without going through an apparent X-amorphous phase.

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REFERENCES

- BARRER, R. M., AND D. A. LANGLEY (1958) Reactions and stability of chabazite-like phases. Part I. Ion-exchanged forms of natural chabazite. *J. Chem. Soc. (London)* 1958, 3804-3825.
- FOSTER, MARGARET D. (1965) Studies of the zeolites. *U.S. Geol. Surv. Prof. Pap.* 504-D.E.
- FOSTER, W. R., AND H. C. LIN (1969) Studies in the system BaO-Al₂O₃-SiO₂ II. The binary system celsian (BaAl₂Si₂O₈)-silica (SiO₂). *Amer. J. Sci.* 267-A, 134-144.
- HEY, M. H. (1932) Studies on the zeolites. Part III. Natrolite and metanatrolite. *Mineral. Mag.* 23, 243-289.
- (1934) Studies on the zeolites. Part VI. Edingtonite. *Mineral. Mag.* 23, 483-494.
- KOIZUMI, M. (1953) The differential thermal analysis curves and dehydration curves of zeolites. *Mineral J. (Tokyo)* 1, 36-47.
- LEVIN, E. M., C. R. ROBBINS, AND H. F. McMURDIE (1969) *Phase Diagrams for Ceramists*. The American Ceramic Society, p. 181-184.
- MILLIGAN, W. O., AND H. B. WEISER (1937) The mechanism of dehydration of zeolites. *J. Phys. Chem.* 41, 1029-1040.
- PÉCSI-DONÁTH, E. (1962) Investigation of the thermal decomposition of zeolites by the DTA method. *Acta Geol.* 6, 429-442.
- (1968) Some contributions to the knowledge of zeolites. *Acta Mineral. Petrogr.* XVIII, 127-141.
- PENG, C. J. (1955) Thermal analysis study of the natrolite group. *Amer. Miner.* 40, 834-856.
- SMITH, J. V. (1963) Structural classification of zeolites. *Mineral. Soc. Amer., Spec. Pap.* 1, 281-290.
- , AND O. F. TUTTLE (1957) The nepheline-kalsilite system. I. X-ray data for the crystalline phases. *Amer. J. Sci.* 255, 282-305.
- VAN REEUWIJK, L. P. (1971) The dehydration of gismondite. *Amer. Miner.* 56, 1655-1659.

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