LETTER

A P_{H_2O}-dependent structural phase transition in the zeolite natrolite

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ABSTRACT

The crystal structures of natrolite and its dehydrated high-temperature phases (α1- and α2-metanatrolite) have been determined from powder X-ray diffraction measurements as a function of temperature and partial pressure of water (P_{H_2O}) to characterize the phase transition behavior. The evolution of crystal structure as a function of temperature shows two different phase transitions, depending on the P_{H_2O}, with α1-metanatrolite occurring at elevated P_{H_2O} and α2-metanatrolite occurring at low P_{H_2O}. Our discovery of α2-metanatrolite implies the existence of more than one transition mechanism, which we correlate with the migration of Na$^+$ ions and the *rate* of evolution of H$_2$O molecules. The transition behavior is rationalized in terms of two cooperating mechanisms: (1) dehydration-induced processes, which determine the phase transition temperature; and (2) thermally induced processes, which determine how the framework and its extraframework cations are modified.

Keywords: Phase transition, natrolite, crystal structure, Rietveld refinement, TGA

INTRODUCTION

Recently, many advances in our understanding of phase transitions originally developed in the fields of solid-state physics and chemistry have begun to have an impact in mineralogy and mineral physics. A tradition of studying transformation processes in minerals has evolved from the need to understand the physical and thermodynamic properties of minerals in the Earth and at its surface. Accordingly, this contribution involves a detailed study of thermally induced phase transitions in the zeolite natrolite. For the first time, we demonstrate that the P_{H_2O} (i.e., relative humidity, RH) determines not only the temperature but the nature of the high-temperature phase. Natrolite [orthorhombic *Fdd*2, Na$_{16}$Al$_{16}$Si$_{24}$O$_{80}$·16H$_2$O; *a* = 18.2915(3) Å, *b* = 18.6324(3) Å, *c* = 6.5856(1) Å, *V* = 2244.5(1) Å^3] is a common framework silicate containing elliptical structural channels occupied by H$_2$O molecules and charge-balancing Na$^+$ ions (Fig. 1a) that create a microporous structure. Various authors (e.g., van Reeuwijk 1974; Alberti and Vezzalini 1983; Belitsky et al. 1992; Joswig and Baur 1995; Baur and Joswig 1996) have shown that the framework of natrolite is collapsible, converting to so-called α-metanatrolite between 250 and 400 °C, and on exposure to moist air α-metanatrolite readsorbs H$_2$O and reconverts to natrolite (the name α-metanatrolite was first used by van Reeuwijk 1974). Under high water pressures, natrolite can even transfer to an overhydrated structure similar to paranatrolite. Belitsky et al. (1992) suggested that "x-metanatrolite" exists as an intermediate metahydration phase that appears simultaneously with α-metanatrolite and transforms to α-metanatrolite after further dehydration in vacuum, but they did not provide any structural model or further discussion about the nature of "x-metanatrolite." Thus, the combined effects of temperature and RH on the phase transition have not been investigated or separated, resulting in an incomplete picture of the phase transition behavior in natrolite. We show here the results of in-situ powder X-ray diffraction

(XRD) measurements made with thin-layer slurry mounts in controlled-RH environments from ~0% to ~87% RH (at 23 °C) at ~1 bar and at ~0.15 mbar P_{total} (roughing pump vacuum) with stepwise heating from 23 to 400 °C. We provide the first illustration of how a combination of thermally induced and dehydration-induced mechanisms controls the phase transitions in natrolite. Similar mechanisms can be expected in other hydrous framework minerals.

WHAT'S NEW?

The natrolite-to-α-metanatrolite-to-natrolite phase transition is reversible and has long been considered first-order in character, with a discontinuous change in structure, entropy, and latent heat at the transition temperature. It is well known that reactions involving gas [H$_2$O$_{(g)}$] are influenced by the partial pressure of the gas involved (e.g., the effect of CO$_2$ partial pressure on CaCO$_3$ decomposition), and this effect causes the reported phase transition temperatures in natrolite to vary. For example, the phase transition to α1-metanatrolite (previously known as α-metanatrolite) occurs at 175 °C at a P_{H_2O} of 1.84(1) µbar [controlled at 42.5(3)% RH, 23.5 °C, and ~0.15 mbar P_{total}], it increases to 200 °C when P_{H_2O} is 0.09(5) mbar [controlled at 0.36(2)% RH, 21.6 °C, 1 bar P_{total}], and it increases to 325 °C when P_{H_2O} is 22.24(2) mbar [controlled at 87.21(8)% RH, 21.4 °C, 1 bar P_{total}]. The high-temperature, dehydrated phase, α-metanatrolite has been considered monomineralic since the work of Rinne (1890). However, our powder XRD data show that under controlled P_{H_2O} conditions, different rates of dehydration result in two different phase transitions to two distinct high-temperature phases. When measurements were made at 1 bar P_{total} and high-RH conditions (30–87% RH) with stepwise heating from 23 to 400 °C, only one dehydrated phase formed, namely the originally described phase that we call α1-metanatrolite [Figs. 1b and 2a and Table 1a; *F*112, *a* = 16.167(1) Å, *b* = 16.938(1) Å, *c* = 6.4380(4) Å, γ = 89.680(2)°, *V* = 1764.0(2) Å^3]. This phase is the material described by Alberti and Vezzalini (1983) and Baur and

Joswig (1996) (to facilitate comparison with previous work, we adopt the original non-standard setting of space group $F112$ for α1-metanatrolite. The standard setting is $C2$). Surprisingly, when measurements were made at lower RH (~0–20% RH), a different phase transition occurred (Fig. 2b). For example, the observed XRD pattern measured at ~0.15 mbar P_{total} showed an additional non-α1-metanatrolite phase coexisting with α1-metanatrolite at temperatures >175 °C (Figs. 2b–2c; star symbol). These non-α1-metanatrolite reflections remained essentially at fixed d-spacings (including consideration of thermal expansion) and gradually decreased in intensity with increasing temperature. At about 350 °C, all non-α1-metanatrolite reflections disappeared and the material was single-phase α1-metanatrolite. Accompanying this phenomenon, the intensities of the α1-metanatrolite reflections progressively increased and reached a maximum at temperatures >350 °C (Fig. 2b). It is now apparent that a new phase forms, which we call α2-metanatrolite [Fig. 1c and Table 1b; $Fdd2$, a = 17.574(1) Å, b = 18.161(1) Å, c = 6.3674(3) Å, V = 2032.3(2) Å³], when natrolite is heated under low-P_{H_2O} conditions. These refined unit-cell parameters and our observed diffraction data for α2-metanatrolite are close to those of the "x-metanatrolite" phase of Belitsky et al. (1992). Similar behavior was observed under other low-RH conditions (e.g., ~0–20% RH at 1 bar P_{total}, Figs. 2d–2f). α2-metanatrolite formed at slightly lower temperatures than α1-metanatrolite, especially when heated under extremely dry conditions (e.g., Figs. 2c–2d). For intermediate-P_{H_2O} environments (e.g., Figs. 2e–2f), α1- and α2-metanatrolite occurred almost simultaneously upon dehydration. Crystal structure analyses using XRD data collected from cavity mounts show that α1- and α2-metanatrolite have different degrees of distortion of the tetrahedral Si/Al framework around the shared oxygen vertex, coupled with different Na⁺ ion positions. Structure models for α1- and α2-metanatrolite were determined through indexing and rigid-body, distance least squares, and Rietveld refinements. Difference-Fourier maps were used to locate the Na⁺ ion in each high-temperature polymorph.[1] Illustrations of the tetrahedral framework topologies of natrolite, α1-, and α2-metanatrolite are shown in Figure 1.

RESULTS

Structural details of α1- and α2-metanatrolite and their relationships to natrolite

Natrolite has five independent O atoms, of which O2, O3, and O4 form the channel edge, coordinate with Na⁺ ions, and control the degree of rotation of chains around the O2 hinges, and the O1 and O5 atoms control the rotation of the central Si1-tetrahedron and link with the O3 and O4 atoms (Fig. 1a). A change in position of any of these (O1, O5, O3, and O4) will cause twisting *within* the chain. The rotation angle (ψ) of the chain around the c axis in natrolite (24.1°) is in agreement with the value of 24.2° obtained

by Pauling (1930) and 24.0° calculated by Alberti and Vezzalini (1981). The two independent chains in α1-metanatrolite rotate by 34.7° around the c axis (Fig. 1b), whereas the single type of chain in α2-metanatrolite rotates only 28.2° (Fig. 1c). The larger chain rotation in α1-metanatrolite leads to a greater contraction in the a and b axes and causes the largest changes in T-O2-T angles and the smallest channel size (Fig. 1b, Table 1a).
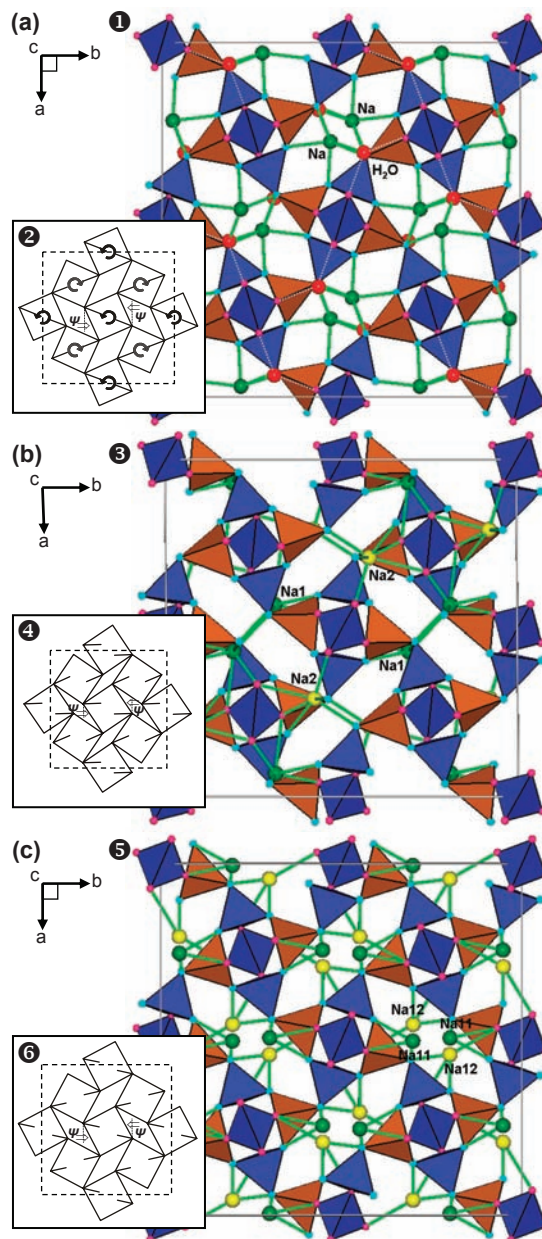
FIGURE. 1. Refined crystal structure of (**a**) natrolite; (**b**) α1-metanatrolite; and (**c**) α2-metanatrolite. Pictures 2, 4, and 6 are schematic projections on (001) of natrolite and the α1- and α2-metanatrolite structures in their real symmetry, respectively; chains rotated (ψ) by 24.1° in natrolite, 34.7° in α1-metanatrolite, and 28.2° in α2-metanatrolite. Pictures 1, 3, and 5 are viewed down the cross-linked chains. Si tetrahedra = blue; Al tetrahedra = orange; oxygen atoms are small light blue spheres (O2, O3, and O4) and pink spheres (O1 and O5). Na⁺ ions (green and yellow) and H_2O (red) are indicated on the figure.

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[1] Deposit item AM-08-041, information on materials and methods. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 1a. The α1-metanatrolite structure ($Na_{16}Al_{16}Si_{24}O_{80}$) at 400 °C, 0.15 mbar P_{total}

Atom	x	y	z	U_{iso} (Å²)	Occupancy
Si11	0.0000	0.0000	0.000	0.009(1)	1.0
Si12	0.2500	0.2500	0.250	0.009(1)	1.0
Si21	0.1356(3)	0.2335(3)	0.619(1)	0.009(1)	1.0
Si22	0.1122(3)	−0.0197(3)	0.370(1)	0.009(1)	1.0
Al11	0.0246(3)	0.1066(2)	0.615(1)	0.009(1)	1.0
Al12	0.2685(3)	0.1398(2)	0.863(1)	0.009(1)	1.0
O11	0.0420(3)	0.0674(3)	0.860(1)	0.020(2)	1.0
O12	0.2417(4)	0.1716(2)	0.112(1)	0.020(2)	1.0
O21	0.0390(3)	0.2078(2)	0.614(1)	0.020(2)	1.0
O22	0.2096(3)	−0.0400(3)	0.359(1)	0.020(2)	1.0
O31	0.0950(4)	0.0686(3)	0.437(1)	0.020(2)	1.0
O32	0.1476(4)	0.3044(4)	0.781(1)	0.020(2)	1.0
O41	0.0736(3)	−0.0785(3)	0.543(1)	0.020(2)	1.0
O42	0.1874(4)	0.1570(3)	0.693(1)	0.020(2)	1.0
O51	0.0707(3)	−0.0381(4)	0.146(1)	0.020(2)	1.0
O52	0.1682(2)	0.2584(4)	0.393(1)	0.020(2)	1.0
Na1	0.0683(5)	0.1911(4)	0.149(3)	0.051(2)	1.0
Na2	0.2912(6)	0.0793(4)	0.403(3)	0.051(2)	1.0

Notes: Monoclinic, space group *F*112; *a* = 16.167(1) Å, *b* = 16.938(1) Å, *c* = 6.4380(4) Å, γ = 89.680(2)°, *V* = 1764.0(2) Å³. (The e.s.d. values are in parentheses).

TABLE 1b. The α2-metanatrolite structure ($Na_{16}Al_{16}Si_{24}O_{80}$) at 400 °C, 0.15 mbar P_{total}

Atom	x	y	z	U_{iso} (Å²)	Occupancy
Si1	0.0000	0.0000	0.0000	0.009(1)	1.0
Si2	0.1448(3)	0.2189(3)	0.623(1)	0.009(1)	1.0
Al	0.0339(3)	0.0990(3)	0.606(1)	0.009(1)	1.0
O1	0.0325(5)	0.0673(3)	0.861(1)	0.020(2)	1.0
O2	0.0572(3)	0.1920(3)	0.611(2)	0.020(2)	1.0
O3	0.1020(4)	0.0513(3)	0.468(2)	0.020(2)	1.0
O4	0.1939(4)	0.1602(4)	0.757(1)	0.020(2)	1.0
O5	0.1798(2)	0.2204(4)	0.389(1)	0.020(2)	1.0
Na11	0.005(1)	0.198(1)	0.742(6)	0.051(2)	0.41(1)
Na12	0.207(2)	0.051(2)	0.264(8)	0.951(2)	0.59(1)

Notes: Orthorhombic, space group *Fdd*2; *a* = 17.574(1) Å, *b* = 18.161(1) Å, *c* = 6.3674(3) Å, *V* = 2032.3(2) Å³. (The e.s.d. values are in parentheses).
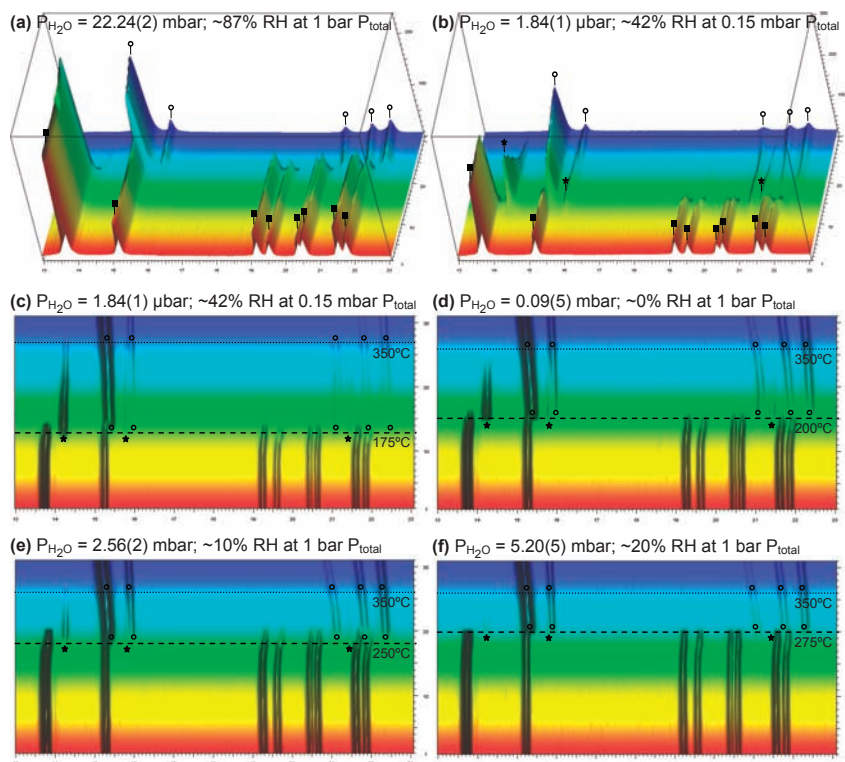
Twisting *within* the chain by movements of O1, O5, O3, and O4 shortens the *c*-axis length. As the tetrahedra cannot be compressed along the chain direction, shortening of the *c* axis results from tilting of the tetrahedra around the O1, O5, O3, and O4 atoms (Alberti and Vezzalini 1983). Twisting of two independent chains in α1-metanatrolite is in a clockwise fashion when viewed down the *c* axis (i.e., all central Si1-tetrahedra are rotated relative to the surrounding four-tetrahedra ring in a clockwise direction), reducing the symmetry from *Fdd*2 to *F*112. The sense of chain twisting in α2-metanatrolite, however, is similar to that in natrolite and the resultant structure obeys *Fdd*2 symmetry. The twisted chains in α1- and α2-metanatrolite shorten the *c* axis by 2.24% and 3.31%, respectively.

Baur and Joswig (1996) and Joswig and Baur (1995) discussed the unusually small Si-O2-Al angles in their α-metanatrolite structure, and we obtained similar results for our α1-metanatrolite structure (average Si21-O21-Al11 and Si22-O22-Al12 angles of 113.7°). Small bridging angles are energetically unfavorable in tectosilicates (values <128° are rare) and must be stabilized by additional interactions of O2 with the extraframework Na⁺ ions, as discussed by Joswig and Baur (1995). However, a different mechanism operates for α2-metanatrolite. The α2-metanatrolite framework has a larger channel size (i.e., the framework does not contract as much as in α1-metanatrolite), with its extraframework Na⁺ ions positionally disordered between two distinct sites close to the center of channels. The Si-O2-Al angle of α2-metanatrolite is 121.3°, near but still below the minimum possible values of pure T-O-T hinge angles (128°) for a stable configuration without bonds to any other ions such as Na⁺. This contrast with the α1-metanatrolite structure implies that when natrolite collapses to α2-metanatrolite, its framework retains a tendency not to form Si-O-Al angles less than the 128° minimum angle if the extraframework Na⁺ ions have not yet migrated closer to framework O atoms. α2-metanatrolite appears to be an intermediate/metastable structure between two global minimum low- and high-temperature phases (natrolite and α1-metanatrolite, respectively). α2-

FIGURE. 2. Temperature-resolved 3D-XRD patterns measured under different P_{H_2O} conditions, illustrating the distinct changes as a function of temperature: *x*, *y*, and *z* axes represent 13–23 °2θ, intensity (cps), and temperature (23–400 °C, no. 1–31), respectively. The square, circle, and star symbols represent reflections of natrolite, α1-metanatrolite, and α2-metanatrolite phases, respectively. (**a**–**b**) orthogonal view; (**c**–**f**) viewed down the *y*-axis. The comparatively moist environment employed on heating caused the initial dehydration temperature (dashed lines in **c**–**f**) to increase gradually. The α2-metanatrolite reflections (star) became weaker as P_{H_2O} was increased. At temperatures >350 °C, the α2-metanatrolite reflections disappeared and only α1-metanatrolite (circle) remained.

metanatrolite transforms to α1-metanatrolite on further heating, irrespective of the P_{H_2O} of the environment (i.e., >350 °C, all α2-metanatrolite reflections are absent).

Dehydration behavior and structural phase transitions

Thermogravimetric (TG) data (e.g., van Reeuwijk 1974) illustrate that ~1.5% of the original weight of a specimen is lost at temperatures below the prominent weight loss; over this initial temperature range, the observed XRD patterns showed gradual changes in natrolite peak positions toward higher 2θ prior to the occurrence of the prominent first-order transition (Figs. 2c–2f). These responses are due to a minor framework modification characterized by a decrease in the natrolite *a* and *b* unit-cell parameters by 0.41% and 0.16%, respectively, accompanying a slight decrease in H_2O site occupancy from 1.0 to 0.84(1) and a total decrease in the unit-cell volume by 0.30% (a 0.26% increase in the natrolite *c* unit-cell parameter results from thermal expansion, e.g., see supporting material, Table 1). This transition is non-symmetry-breaking, leading only to disruption of the local environment of tetrahedrally coordinated H_2O molecules as a prelude to the prominent first-order phase transition, and a transition of this kind can be considered as a temperature-dependent second-order transition. Above a certain temperature, a sudden shift in XRD peak positions was observed, accompanied by an abrupt weight loss seen in TG data. Natrolite then loses all H_2O molecules, transforming to either α1- or α2-metanatrolite as discussed above. The reaction is thus a first-order phase transition, with the H_2O site occupancy going from 0.84(1) to 0.0 directly without presenting any partially hydrated intermediates. More importantly, this first-order phase transition exhibits marked P_{H_2O} dependence, yielding two different dehydrated structures dependent entirely on P_{H_2O}.

DISCUSSION

Differences in the *rate* of dehydration of natrolite under different P_{H_2O} conditions yield different reaction paths. Understanding the change in bonding configurations among H_2O molecules, Na^+ ions, and framework O atoms in the channel system of natrolite during dehydration is key to pinpointing the phase-transition mechanism(s) and to clarifying why and how the structural response is a function of P_{H_2O} and the *rate* of dehydration. The average kinetic energy of Na^+ ions and H_2O molecules in the channel system of natrolite is proportional to temperature, and the rate of $H_2O_{(g)}$ adsorption depends primarily on the P_{H_2O} of the environment. Therefore, the appearance of α2-metanatrolite and its relative proportions upon dehydration depend on the *rate* of evolution of H_2O molecules from the natrolite structure. If H_2O molecules evolve from the structure more rapidly (i.e., heating under dry conditions) and at lower temperatures than those required for Na^+ ions to migrate, the aluminosilicate framework cannot transform into α1-metanatrolite directly and goes first to α2-metanatrolite. In other words, the appearance of α2-metanatrolite and its proportions directly reflect the manner in which the aluminosilicate framework of natrolite responds to the migration of its extraframework cations. Conversely, heating under more-humid conditions leads to slower evolution of H_2O and transformation at higher temperatures, where Na^+ ions have sufficient energy to recoordinate to the bridging framework O atoms. This process makes a decrease in Si-O-Al

angles in the aluminosilicate framework possible, and the structure directly transforms into α1-metanatrolite without passing through α2-metanatrolite. Reaction to α1-metanatrolite with unusually small Si-O2-Al hinges wrapped around the Na^+ ions results from slow dehydration and can be considered as the equilibrium phase transition. α2-metanatrolite represents a metastable structure; the reaction passing from α2-metanatrolite to α1-metanatrolite is a result of rapid dehydration and can be considered a metastable phase transition.

This study demonstrates the remarkable conclusion that the *rate* of dehydration controls not only the temperature but the nature of structural phase transitions in natrolite. The dehydration-induced phase transition mechanism is the primary factor in determining the temperature at which the transition occurs and the thermally induced mechanism is a secondary factor relating to how much the framework and its extraframework Na^+ ions can change. Both mechanisms together determine the reaction path and which α-phase ultimately forms. Further studies using ^2D and ^{23}Na nuclear magnetic resonance (NMR) spectra as a function of dehydration state should provide direct information about the environment and internal mobility of H_2O/D_2O and Na^+ ions. Infrared spectroscopy to evaluate the possible formation of OH groups during dehydration should also clarify the behavior of H_2O molecules in the natrolite channel systems (Bish et al. 2006). We expect that our results can be applied to other hydrous materials that undergo phase transitions, particularly other natrolite-family zeolites (e.g., mesolite and scolecite) or cation-exchanged natrolite-type zeolites.

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