

## A STUDY OF THE STRUCTURE STABILITY OF NATROLITE DURING ITS LONG-RUN HEATING

Drahoš RYKL and František PECHAR

*Institute of Geology and Geotechnics,  
Czechoslovak Academy of Sciences, 182 09 Praha 8*

Received April 15th, 1986

The structure stability of natrolite heated at 310, 350, 400, and 500°C for a time from 7.5 min to 8 192 h was studied by weight loss measurements, infrared spectroscopic investigation and evaluation of powder X-ray diffraction data. No substantial structure changes other than partial dehydration were observed. The dehydration process is only associated with the formation of structural hydroxide groups and with short-range changes in the crystal structure arrangement.

The stability of minerals at elevated temperatures can be examined in two modes, *viz.* the dynamic mode, where the DTA and/or TGA curves are scanned in various heating regimes<sup>1</sup>, and the isothermal mode, where the sample is heated at a pre-selected temperature for various time periods<sup>2</sup>. The two methods are usually complementary, and measurements by the former method are necessary for finding suitable temperatures for experiments by the latter method. For establishing structure changes during the heat treatment of crystalline phases, the measurements have to be supplemented with X-ray diffraction analysis and infrared spectroscopic examination of the decomposition products<sup>2,3</sup>.

The aim of the present work was to study the stability of the zeolite natrolite during its isothermal heating at 310–500°C for periods of time increasing in a geometric series from 7.5 min to 8 192 h. The results of this study served for the determination of the limits of stability of the crystalline phases and the degree of dehydration in dependence on the temperature and time of heating.

### EXPERIMENTAL

Samples of natrolite from a locality at Těchovice near Děčín were ground in an agate mill and isothermally heated in an electric resistance furnace, controlled by means of a pulse controller enabling the temperature to be held constant to within  $\pm 1^\circ\text{C}$  for any time of the experiment.

The furnace contained a ceramic tube 60 mm in diameter, fitted with outer double resistance winding made of kanthal. The maximum input possible was 1 kW *per* winding; however, owing to the good insulation of the furnace with ground asbestos, the overall working input was as low as 200 W at 400°C. The overdimensioned resistance winding then ensured a long-term trouble-free service of the equipment.

The furnace was fitted with a metallic block with eight drillings 10 mm in diameter for accommodating test tubes with samples and two thermocouples, a control and a measuring ones. The block was aluminium for measurements up to 400°C and titanium for measurements at higher temperatures.

The test tubes for the samples were made of Simax glass, 10 mm in diameter. Their length was such that they protruded at least 50 mm above the top of the furnace. The sample weight was typically about 0.3 g.

The heat treatment time periods were chosen in a  $2^n$  h series with  $n$  running from  $-3$  to  $+12$  or  $+13$ , *i.e.*, from 7.5 min to 8 192 h. Each experiment was performed at least in duplicate.

Immediately after the heat treatment the test tubes were sealed up in order to prevent rehydration, allowed to cool down and weighed in.

For infrared spectroscopic measurements the samples were ground into Nujol mulls. The spectra were run on a Perkin-Elmer 325 grating spectrophotometer over the region of 4 000 to 600  $\text{cm}^{-1}$ .

The X-ray diffraction patterns of the powder samples were obtained on DRON II and DRON UM diffractometers using  $\text{CuK}_\alpha$  radiation over the  $2\theta$  angle region of 5–60°.  $\text{Al}_2\text{O}_3$  was used as the internal standard. The  $2\theta$  values corrected for the standard were entered as input data for MPIN processing<sup>3</sup> by the least squares method and calculation of the lattice parameters along with the respective standard deviations.

## RESULTS

### *Weight Loss of Natrolite Subjected to Isothermal Heating at 310–500°C*

The natrolite weight losses, arising from the gradual dehydration of the mineral, are shown in Fig. 1 in dependence on time for various heating temperatures. By analysis of sample prior to the heat treatment, the amount of bonded water in cavities of the mineral was 10.92 wt. %. The time and temperature dependences of the

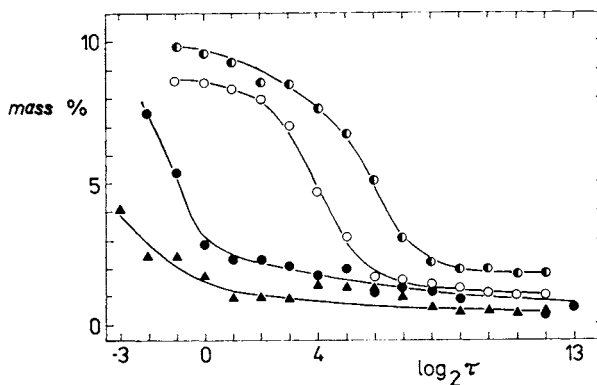


FIG. 1

Time dependence of natrolite weight loss (%  $\text{H}_2\text{O}$ ) in isothermal heating regime. Temperature (°C): ● 310, ○ 350, ● 400, ▲ 500. Time (h) in a logarithmic scale

weight loss indicate the occurrence of two dehydration steps. The first of them corresponds to a partial loss of the relatively weakly bonded water in the cavities of the mineral; liberation of this water is complete in 20 h at 310°C or in 8 h at 350°C. Additional loss of total water takes place in the second step, which is complete in 1 895 h at 310°C or in 64 h at 350°C. For higher temperatures, 400 and 500°C, the dehydration curves show a gradual loss of bonded water, commencing after 4 h at 400°C or after 1 h at 500°C. The curves also demonstrate that some residual water remains present even after the longest heating times; the amount depends on the heating temperature, making 1.82 wt. % at 310°C and 0.41 wt. % at 500°C.

#### *Infrared Spectra of Natrolite Subjected to Isothermal Heating at 310–500°C*

At all of the temperatures and time periods applied, changes in the intensities and shapes of bands of the antisymmetric and symmetric OH stretching vibrations occur, and a substantial intensity decrease is observed for the bands of the bending and torsional vibrations of water molecules (Fig. 2). These changes give evidence of a gradual dehydration and formation of hydroxide groups of Si—OH—Al type. Presumably, a fraction of water molecules in the mineral cavities undergo a hydrolysis reaction, and the free protons then attack oxygen atoms of the Si—O—Al bridges. No marked changes other than those in the intensity and shape of the bands also occur for the antisymmetric and symmetric stretching and bending vibrations of the Si(Al)—O, Si—O—Al and O—Si(Al)—O bonds, demonstrating that no substantial changes in the symmetry of the unit cell of the crystal lattice take place during the heating; only the short-range ordering of the tetrahedral bonds undergoes changes, and local thermal defects are created in the structure. The degree of disorder increases with

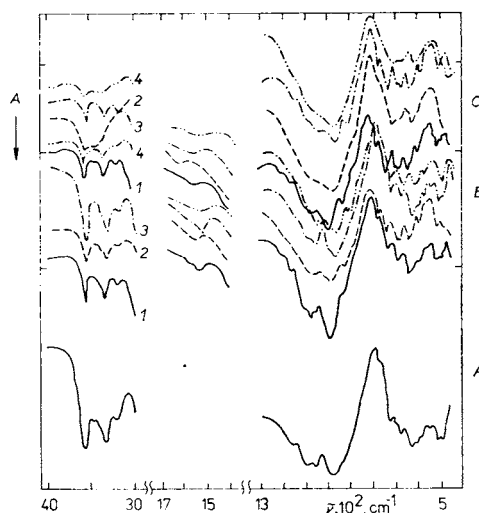


FIG. 2

Infrared spectra of natrolite after isothermal heat treatment. **A** initial sample, **B** after 32 h of heating, **C** after 4 096 h of heating. Temperature (°C): 1 310, 2 350, 3 400, 4 500

increasing temperature. The local changes concern particularly bonds in the Si—OH—Al bridges, which are subject to lengthening and weakening; as a consequence of thermal vibrations, bond breakdown can take place at these sites.

*Powder X-Ray Diffraction Patterns of Natrolite Subjected to Isothermal Heating at 310–500°C*

The refined lattice parameters of the unit cell of natrolite crystal for selected heating temperatures and times are given in Table I. Up to 400°C, the lattice parameters are

TABLE I  
Lattice parameters of natrolite in dependence on heating temperature and time

| Temperature<br>°C | Time<br>h | <i>a</i><br>nm | <i>b</i><br>nm | <i>c</i><br>nm | <i>b</i> – <i>a</i><br>nm |
|-------------------|-----------|----------------|----------------|----------------|---------------------------|
| 310               | 0.5       | 1.816(4)       | 1.868(5)       | 0.658(2)       | 0.052                     |
| 310               | 32        | 1.836(3)       | 1.864(3)       | 0.658(2)       | 0.028                     |
| 310               | 4 905     | 1.823(2)       | 1.859(3)       | 0.657(1)       | 0.036                     |
| 350               | 0.5       | 1.823(5)       | 1.873(5)       | 0.655(3)       | 0.050                     |
| 350               | 32        | 1.831(7)       | 1.868(7)       | 0.665(6)       | 0.037                     |
| 350               | 4 102     | 1.832(6)       | 1.878(9)       | 0.659(2)       | 0.046                     |
| 400               | 0.5       | 1.826(4)       | 0.864(6)       | 0.659(1)       | 0.038                     |
| 400               | 32        | 1.803(10)      | 1.858(10)      | 0.638(10)      | 0.055                     |
| 400               | 4 097     | 1.816(10)      | 1.862(10)      | 0.669(7)       | 0.040                     |
| 500               | 0.5       | 1.833(3)       | 1.872(6)       | 0.661(1)       | 0.039                     |
| 500               | 32        | 1.832(3)       | 1.859(5)       | 0.659(1)       | 0.027                     |
| 500               | 4 096     | 1.804(7)       | 1.883(10)      | 0.663(3)       | 0.079                     |

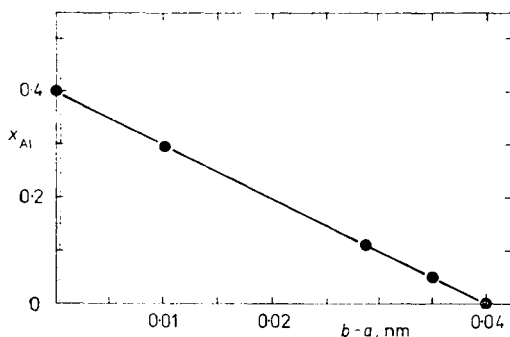


FIG. 3  
Dependence of the natrolite lattice parameter difference *b* – *a* (nm) on the fraction of Al atoms in tetrahedral sites ( $x_{Al}$ )

constant within the limits of experimental error, and so is the  $b - a$  difference which serves as a criterion of the natrolite structure disorder (Fig. 3). This confirms the conclusions drawn from the infrared spectra, namely, that the symmetry of the unit cell is not altered substantially during the dehydration; changes only occur in the occupation factors of the Si, Al atoms in the tetrahedral positions of the structure. The measurements did not reveal formation of any unstable phase during the dehydration<sup>2</sup>.

The variance of the lattice parameters was within the limits of error also for samples heated at 500°C for time periods up to 256 h, whereas for longer times (510–4 096 h), parameter  $a$  decreased slightly while parameter  $c$  increased and parameter  $b$  remained constant. The increase in the  $b - a$  parameter is indicative of the amount of Si atoms in the tetrahedral sites of the natrolite structure increasing on long-run heating at 500°C, particularly in the  $a, b$  plane of the unit cell (for a complete order in the structure, at Si : Al = 3 : 2, this parameter is 0.035 nm). This fact also gives evidence of structure disorder increasing with extending time of heating at 500°C.

In summary, the isothermal method, in contrast to the dynamic method<sup>2</sup>, does not reveal formation of metastable phases such as the monoclinic metanatlolite (300 to 500°C) during the long-run heat treatment of natrolite; only increasing disorder in the occupation of the structural tetrahedral sites by Si and Al atoms is observed for samples heated at 500°C for times longer than 30 h. Up to 500°C, the structure of the substance thus is evidently stable at any time of heating. Owing to this, natrolite can be employed as a suitable sorbent or molecular sieve at temperatures up to 500°C and recovered after use without structure breakdown.

#### REFERENCES

1. Pechar F., Rykl D.: *Report*. Institute of Geology and Geotechnics, Czechoslovak Academy of Sciences, Prague 1981.
2. Weiss Z.: *Report*. Coal Research Institute, Ostrava-Radvanice 1972.
3. Rykl D., Pechar F.: *Acta Montana* 63, 87 (1983).

Translated by P. Adámek.