

## PHASE TRANSITIONS OF NATURAL SCOLECITE

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Received June 9th, 1985

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Based on DTA and TGA, the natural zeolite scolecite (Teigarhorn, Iceland) was subjected to decomposition at temperatures of 20, 250, 300, 400, 450, 500, 590, 720 and 1 000°C; the decomposition products were identified by powder X-ray diffraction analysis and infrared spectroscopy. The crystal structure of scolecite remains stable up to 200°C only; then it begins to transform into a metaphase and at temperatures above 350°C, into an amorphous phase from which anortite and the high-temperature quartz modification form at 700–1 000°C. Dehydration of scolecite occurs in four steps. A considerable weakening of the O—H stretching vibrations and vanishing of the water bending vibrations occur at 450°C. The remaining water splits heterolytically and forms structural O—H groups which persist up to 1 000°C.

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Scolecite, a calcium structure form of natrolite, is monoclinic (space group Cc) and belongs to zeolite structure group 5 (ref.<sup>1</sup>). Similarly as in natrolite, the structure of scolecite contains small cavities and channels in which cations coordinated by molecules of water are located. Each calcium ion is coordinated by three water molecules and four oxygen atoms from the Al—O<sup>(-)</sup>—Si bridge of the framework. The silicon and water contents of the structure framework as well as the strength of the bonds have a great effect on the stability of the mineral in natural conditions. For this reason, conditions of its dehydration at elevated temperatures and the associated structure changes are attracting interest.

The TGA and DTA curves of natural scolecite were scanned and its X-ray diffraction patterns obtained in the recent studies<sup>2-5</sup>, where, however, no calculation of the shifts of the lattice parameters with increasing temperature was made, nor the infrared spectra of the scolecite decomposition products were studied which would enable the behaviour of the "zeolite water" with increasing temperature to be investigated. Also, the measurements were performed in the dynamic mode, which does not leave time enough even for the metastable phase equilibrium to establish.

In the present work, measurements were therefore performed in the isothermal mode for 3 hours; the decomposition products were identified by X-ray diffraction analysis and the variations in the lattice parameters were calculated, so that the contraction of the elementary cell could be evaluated. Infrared spectroscopy was also employed for gaining insight into the behaviour of the "zeolite water".

TABLE I  
Results of DTA and TGA of scolecite

Measurement	Temperature of maximum, °C							
DTA		286	306	445	465	534	625	
TD <sup>a</sup>	20	250	300	400	500	590	720	1000
TGA	20	275		405	457	570	670	1000
H <sub>2</sub> O <sup>b</sup>		5.0	6.0		9.5	11.9	12.6	13.1

<sup>a</sup> Chosen temperature of decomposition; <sup>b</sup> total mass loss, %.

FIG. 1  
TGA curve of natural scolecite

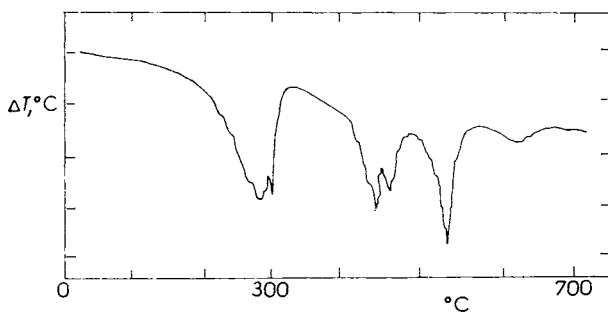
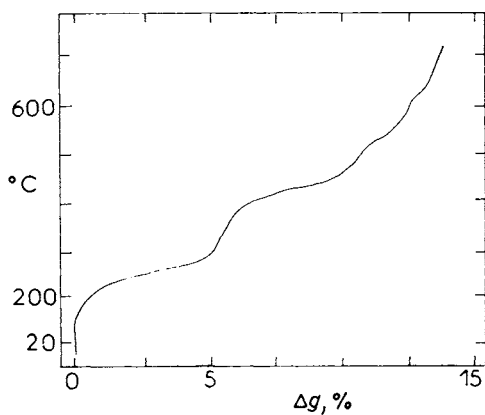


FIG. 2  
DTA curve of natural scolecite

TABLE II  
Infrared spectra of scolecite thermal decomposition products; band positions in  $\text{cm}^{-1}$ , relative

Vibration	20°C	250°C	300°C	400°C
$\nu(\text{OH})$	3 600 m 3 520 m 3 330 m 3 220 s	3 550 m 3 440 w 3 330 m 3 220 s	3 600 sh  3 320 sh 3 200 sh	3 600—3 320 br
$\delta(\text{OH})$	1 665 w	1 665 sh	1 670—1 640 br	1 670—1 640 vw
$\nu_{\text{as}}[\text{Si}(\text{Al})-\text{O}]$	1 210 sh 1 180 vw 1 165 sh 1 100 sh 1 050 sh	1 150—880 vs, br	1 180—900 s, br  1 150 m	1 180 sh 1 150 w
	1 015 m 985 w 950 vw 930 m 890 sh	1 015—930 s	1 015—930 s	990—930 vs
$\nu_{\text{s}}[\text{Si}(\text{Al})-\text{O}]$	770 sh 720 s	770 sh 720 s	770 sh 720 s	770 sh 720 s
$\text{H}_2\text{O}$ libration	680 sh 665 vw	680 m 670—640 br		
$\text{Al}-\text{O}-\text{Si}$ torsion	625 m 595 vw	635 m 600 m 560 w 515 vw 500 m		
$\delta[\text{O}-\text{Si}(\text{Al})-\text{O} + \text{Si}-\text{O}-\text{Al}]$	490 m 427 w	435 vw	430 m	460 m

<sup>a</sup> Structure observed.

## EXPERIMENTAL

Powder samples of natural scolecite (Teigarhorn, Iceland), needle crystal aggregates (twinning) occurring as cavity fillings in basaltic rocks, were used. Their wet chemical analysis was performed in the Laboratory of Analytical Chemistry of our Institute. For  $\text{Ca}_8\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\cdot 24\text{H}_2\text{O}$  calculated: 43.62%  $\text{SiO}_2$ , 31.19%  $\text{Al}_2\text{O}_3$ , 13.57%  $\text{CaO}$ , 11.67%  $\text{H}_2\text{O}$ ,  $\text{Si}/\text{Al} = 1.40$ ,  $\text{Si}/(\text{Si} + \text{Al}) = 0.583$ ; found: 44.53%  $\text{SiO}_2$ , 25.74%  $\text{Al}_2\text{O}_3$ , 0.24%  $\text{Na}_2\text{O}$ , 0.10%  $\text{K}_2\text{O}$ , 14.23%  $\text{CaO}$ , 0.024%  $\text{MgO}$ , 0%  $\text{SrO}$ , 0.004%  $\text{MnO}$ , 0.18%  $\text{Fe}_2\text{O}_3$ , 0.12%  $\text{P}_2\text{O}_5$ , 0.008%  $\text{TiO}_2$ , 13.25%  $\text{H}_2\text{O}$  (total: 98.43%),  $\text{Si}/\text{Al} = 1.73$ ,  $\text{Si}/(\text{Si} + \text{Al}) = 0.634$ , crystallochemical formula  $\text{Na}_{0.22}\text{K}_{0.06}\text{Ca}_{8.10}\cdot\text{Mg}_{0.03}\text{P}_{0.03}(\text{Al}_{16.08}\text{Fe}_{0.06})\text{Si}_{23.65}\text{O}_{80}\cdot 23.45\text{H}_2\text{O}$ .

TABLE II

intensities: vs very strong, s strong, m medium, w weak, vw very weak; br broad, sh shoulder

450°C	500°C	590°C	720°C	1 000°C
3 600—3 320 br	3 600—3 320 br			
1 180 sh 1 150 w	1 180 sh 1 150 w	1 180 sh 1 150 w	1 180 sh 1 165 sh 1 150 w	1 180 sh
990—930 vs	980—920 vs	980—920 vs	1 080 sh 980 m	1 080—820 m, br <sup>a</sup>
770 sh 720 s	770 sh 725 s	770 sh 725 s	770 sh 720 s	770 sh 765—710 w, br
				630—530 m, br
460 m	450 m	450 m	450 m	

The DTA and TGA curves of the powder samples (50 mg) were run in air on a Netzsch instrument using a temperature program of 10°C/min.

Infrared spectra of Nujol mulls were scanned on a Perkin-Elmer 325 grating spectrophotometer over the 4 000 — 400 cm<sup>-1</sup> region.

The X-ray diffraction patterns of the scolecite decomposition products were obtained with a Guinier chamber using CuK<sub>α</sub> radiation; synthetic α-Al<sub>2</sub>O<sub>3</sub> served as the internal standard. The film records were evaluated on a Joyce-Loebl III densitometer. The interplanar distances ( $d_{hkl}$ ) were indexed by means of X-ray diffraction patterns of the mineral according to Breck<sup>1</sup>, and the lattice parameters of the elementary cell of scolecite at temperatures of 20, 200, and 250°C were calculated and refined by MPIN computer program<sup>6,7</sup>. The isothermal decomposition was

carried out, with respect to the temperatures found from the DTA curves, in vacuum in an apparatus as described previously<sup>8</sup>. The samples were cooled in vacuum and embedded in Nujol for further experiments.

## RESULTS AND DISCUSSION

The results of analysis show that the  $\text{Si}/\text{Al}$  and  $\text{Si}/(\text{Si} + \text{Al})$  values for the scolecite sample do not differ appreciably from the theory<sup>1</sup>, which indicates a relatively high degree of ordering of the scolecite structure, approaching the ideal structure. Some changes in the occupation factors of the cation sites, where  $\text{Ca} \rightleftharpoons \text{Na}$  substitution takes place, and some disorder in the  $\text{Al}(\text{Fe})$  and  $\text{Si}$  distribution can only be expected. This is associated with a lowering in the amount of the "zeolite water" coordinated to cations. Increase in the silicon content, and the associated shortening of bonds in the tetrahedral sites, can bring about upward shift of the decomposition temperature.

### *Thermal Behaviour*

The results of thermal analysis are given in Table I and Figs 1 and 2. The dehydration of scolecite (Fig. 1) occurs in four distinct steps. The highest mass losses are observed

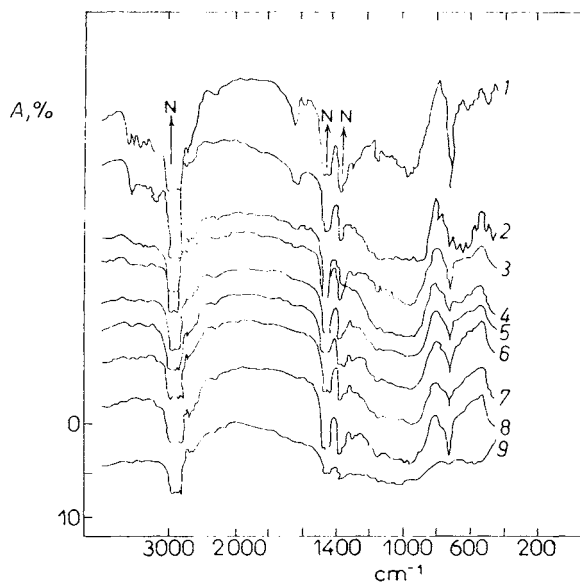


FIG. 3

Infrared spectra of thermally decomposed natural scolecite. Decomposition temperature: 1 20°C, 2 250°C, 3 300°C, 4 400°C, 5 450°C, 6 500°C, 7 590°C, 8 720°C, 9 1000°C. N — Nujol bands

at 100–290°C (5%) and at 405–570°C (6.9%); the other mass changes are less marked, particularly at higher temperatures, where the mineral loses mass continuously. According to analysis, 1.13% of the initial amount of water remains in the sample after dehydration.

The DTA curve has a complex shape (Table I, Fig. 2). No exo effects are observed, and six endo maxima can be distinguished. The most marked ones, at 286, 306, and 534°C, correspond to dehydration, the other endo maxima are indicative of gradual changes in the scolecite structure. The most pronounced maximum, at 534°C, is due to transformation of the structure into a different phase. Starting from 455°C, a gradual amorphization of the mineral phases takes place.

### *Infrared Spectra*

Broad bands and splittings are observed in the 3 600–3 200  $\text{cm}^{-1}$  range, belonging to the symmetric and antisymmetric OH stretching vibrations, at temperatures of 20–590°C (Table II, Fig. 3). The H—O—H bending vibrations at 1 670–1 640  $\text{cm}^{-1}$  remain preserved up to temperatures near 400°C. Hence, total dehydration takes place at a temperature as high as 450°C; water then undergoes heterolytic reaction with calcium ions and the protons released attack the oxygen atoms of the skeleton, forming structural —OH groups. The antisymmetric and symmetric Si(Al)—O stretching and O—(Al,Si)—O bending vibrations, appearing at 1 180–920, 790 to 700, and 490–430  $\text{cm}^{-1}$ , respectively, are observed for all reaction products; at 1 000°C only the  $\nu\delta$  O—Si(Al)—O vibrations were absent. These facts indicate that the tetrahedral coordination of the Al and Si atoms and the short-range structure arrangement remain unchanged over the entire temperature region.

### *X-Ray Diffraction Analysis*

The X-ray diffraction data (Tables III–VI) indicate that the scolecite structure is stable up to 150°C. At 200°C, the substance decomposes partly to metascolecite

TABLE III  
Lattice parameters ( $\text{nm} \cdot 10^{-4}$ ) of scolecite at different temperatures<sup>a</sup>

Parameter	20°C	200°C	250°C
<i>a</i>	6 532 (5)	6 550 (10)	6 608 (10)
<i>b</i>	18 966 (5)	18 490 (10)	18 458 (10)
<i>c</i>	9 778 (5)	9 779 (10)	9 781 (10)

<sup>a</sup> The parameters could not be calculated at temperatures above 250°C.

TABLE IV  
 Diffractograms of scolecite and metascolecite

<i>hkl</i>	scolecite <sup>a</sup>		metascolecite <sup>b</sup>	
	<i>d</i> <sub>0</sub> pm	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>0</sub> pm	<i>I</i> <sub>rel</sub>
120	659.0	90	652	3
11 $\bar{1}$	584.8	100	581	8
040	472.2	60		
200	460.8	50	461	5
21 $\bar{1}$	438.7	90	438.7	8
140	420.8	30		
220	414.4	20		
131	363.3	20	363	1
240	330.4	5		
051	322.1	30		
31 $\bar{1}$	318.1	30	317	5
211	315.1	30		
20 $\bar{2}$	307.8	20		
20 $\bar{2}$	307.8	20		
002	307.1	10		
160	298.7	10		
22 $\bar{2}$	292.9	60		
251	290.0	10		
33 $\bar{1}$	288.2	100	287	10
231	285.1	70		
14 $\bar{2}$	268.4	5		
260	260.8	5		
32 $\bar{2}$	257.8	15	257	2
122	254.9	5		
171	247.4	15		
41 $\bar{1}$	244.0	10		
310	241.6	15		
080	236.6	5		
400	231.5	10		
180	229.1	10		
16 $\bar{2}$	226.7	10	225	4
360			204	1
42 $\bar{2}$			196	2
			187	2
			180	2

<sup>a</sup> Ref.<sup>1</sup>; <sup>b</sup> ref.<sup>3</sup>

(Table IV), and at temperatures above 300°C an amorphous phase is formed. For a comparison with Tables III, V, and VI, Table IV gives the  $hkl$  indices and interplanar distances for scolecite<sup>1</sup> and metascolecite<sup>3</sup>. The decomposition of the scolecite structure is finished at about 500°C. In this temperature region, broad diffuse maxima are observed on a high background (Table V). Starting from 590°C, maxima of anortite at 403.8, 368.9, and 320.2 pm begin to appear in the amorphous phase in mixture with the undecomposed scolecite (maxima of scolecite at 652.8 and 581.2 pm are also present). At 720°C, a series of maxima of anortite are observed, and in addition, the high-temperature modification of quartz manifests itself by

TABLE V  
X-ray diffraction patterns of scolecite decomposition products (up to 590°C)

$hkl$	20°C		250°C		300°C		400°C		590°C	
	$d_{\text{obs}}$ pm	$I_{\text{rel}}$	$d_{\text{obs}}$ pm	$I_{\text{rel}}$	$d_{\text{obs}}$ pm	$I_{\text{rel}}$	$d_{\text{obs}}$ pm	$I_{\text{rel}}$	$d_{\text{obs}}$ pm	$I_{\text{rel}}$
120	659.8	80	653.9	80	652.8	5	652.5	<sup>a</sup>	652.8	<sup>a</sup>
11 $\bar{1}$	584.9	100	588.0	100	581.1	10	581.1	<sup>a</sup>	581.2	<sup>a</sup>
040	473.2	40	472.1	50	461.1					
200	460.3	37	460.2	30	461.1	5				
21 $\bar{1}$	438.2	80	437.1	100	438.8	2				
140	420.1	20	422.1	20						
220	414.2	10	415.2	8	363.0	2	380.8	<sup>a</sup>	403.8 <sup>b</sup>	
131	363.9	15	363.7	10	363.0	2				
051	322.8	15	322.7	15						
31 $\bar{1}$	318.5	10	317.1	10	317.0	3				
211	315.7	10	315.6	15					368.9 <sup>b</sup>	10
202	307.5	5	308.6	10					320.2 <sup>b</sup>	25
002	306.5	5								
160	298.9	10	299.0	10						
22 $\bar{2}$	292.7	15	293.7	10						
251	290.0	15	290.7	10						
33 $\bar{1}$	288.4	10	289.3	10						
231	285.9	70	287.0	80	287.0	2				
14 $\bar{2}$	268.1	45	267.1	50						
071	247.9	10	247.8	15						
080	241.5	5	242.0	10						
180	229.8	5	227.8	10						
16 $\bar{2}$	226.1	20	225.2	25	225.1	3				
360	204.9	5	204.0	10	204.0	3				

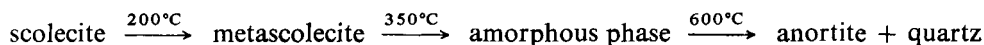
<sup>a</sup> Diffuse reflection; <sup>b</sup> anortite.



reflections at 342.8 and 288.5 pm. The mineral decomposition process is complete at 1 000°C, at which the two ultimate mineral phases, anortite and quartz, can be identified from the diffraction patterns.

### CONCLUSIONS

The structure of scolecite is found to be very unstable. At temperatures as low as 200°C the mineral transforms, during the dehydration, into the metastable phase and appreciable changes in the lattice parameters occur. This phase in turn transforms at 350°C into the amorphous phase from which anortite and quartz begin to form at 600°C. The transformation pathway thus is



The interaction of protons with the oxygen atoms during the dehydration gives rise to structural O—H groups which have a destabilizing effect on the scolecite structure.

TABLE VI

X-ray diffraction patterns of scolecite decomposition products (above 600°C)

<i>hkl</i>	720°C		1 000°C	
	<i>d</i> <sub>obs</sub> pm	<i>I</i> <sub>rel</sub>	<i>d</i> <sub>obs</sub> pm	<i>I</i> <sub>rel</sub>
022 <sup>a</sup>	468.5	2	468.5	10
202 <sup>a</sup>	403.9	8	403.9	15
112 <sup>a</sup>	392.8	6	392.8	20
130 <sup>a</sup>	378.8	6	378.9	30
203 <sup>a</sup>	368.9	15	368.9	20
101 <sup>b</sup>	342.8	5	342.8	5
040 <sup>a</sup>	321.5	15	321.5	18
204 <sup>a</sup>	320.5	45	320.6	60
004 <sup>a</sup>	318.1	30	318.7	90
— <sup>b</sup>	288.5	5	288.6	10
110 <sup>b</sup>	248.5	5	248.6	5
255 <sup>a</sup>	223.2	30	223.3	35
060 <sup>a</sup>	214.0	5	214.0	10
204 <sup>a</sup>			200.6	5
221 <sup>b</sup>			191.8	4

<sup>a</sup> Anortite; <sup>b</sup> quartz.

Due to this thermal instability, scolecite cannot be recommended for use as a catalyst support or for other applications at elevated temperatures.

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