

SOME CONTRIBUTIONS TO THE KNOWLEDGE OF ZEOLITES

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INTRODUCTION

Of the 20 or so species of zeolite minerals lately investigated by the present author, rigorous structure determinations on unheated samples have been carried out recently for the following: laumontite [COOMBS, 1952], harmotome [SADANAGA et al., 1955], gmelinite, levyne [H. STRUNZ, 1956], faujasite [BERGERHOFF et al., 1958], natrolite [MEIER, 1960], stilbite [GALLIET al., 1960], ptylolite [J. BAUER et al., 1962], phillipsite [STEINFINK, 1962], gismondite [K. FISCHER, 1963], brewsterite [PERROTA et al., 1964]. Furthermore, the structure of dehydrated natrolite was determined by FANG [1963] and that of dehydrated and chlorinated chabasite by J. V. SMITH [1962]. These workers have determined by electron density measurements and Fourier analysis the atomic distances and the accurate atomic coordinates as well as the dimensions of the unit cells. Moreover, besides establishing the lattice structure, they provided information also about the positions of the cations and in some cases of the water molecules. However, several questions remained unanswered:

A) I. The temperatures at which zeolites heated to 1000 °C become amorphous roentgenographically.

II. The nature of the crystalline phases and structure variants, formed as a result of heating to lower temperatures.

III. Whether in the course of thermal decomposition up to 1000° C a new crystal lattice comes to exist, and if so, how, and what is the new mineral thus formed.

To answer these questions, the author has performed X-ray diffractometry on unheated zeolite samples and on samples heated to characteristic temperatures (the temperature of exo- and endothermic peaks on the DTA graphs).

B) Up till the last decade, the water content of zeolites was considered a function of ambient water vapour pressure, whose removal from the mineral caused no structural change and whose distribution within the structure was random. Water of this kind was called zeolite water. In most recent literature, however [AVERBUCH et al., 1950, J. V. SMITH, 1962, 1964, ROSHKOVA et al., 1962] it is stated as a result of research by the most up-to-date techniques that not all zeolites contain zeolite water and not all the water held in zeolites is zeolite water. It was KOIZUMI [1953] and PENG [1955] who, first applying the DTA method to the water content of zeolites, obtained some important results concerning the nature of zeolite water. Rigorous structure analysis [MEIER, 1960, J. V. SMITH, 1962] has shed light in some cases also

on the nature of the water bond, but these investigations did not establish the water loss *vs.* temperature relationship, and its correlation with structural changes, nor the precise nature of the initial and final phases and of the intermediate phases formed during the experiments. The complex approach resorted to in the present author's investigations (chemical analysis complemented with spectroscopy, X-ray diffractometry, infrared spectroscopy, DTA, dehydration, devolatilization analysis, derivatography and regeneration methods applied to the initial zeolite phase as well as to phases heated to the characteristic temperatures) made it possible to clean information as to the nature and the manifold aspects of water in zeolites.

C) Zeolites were first classified on the basis of morphological features; consequently,

1. fibrous, platy and cubic zeolites were distinguished, at first.

2. DEER's classification [1963] essentially rested on this basis, but also took into account whether the bond strengths of the (SiAl)O₄ tetrahedra in the tectosilicate lattice are stronger in one or two directions or equally strong in all three directions. DEER could thus distinguish the natrolite, heulandite and harmotome groups.

3. In his structural system, J. V. SMITH [1962] chose the number of interlinked tetrahedra and the mode of linkage as a basis. He distinguished the following main groups: 1. analcite, 2. sodalite, 3. chabasite, 4. natrolite, 5. phillipsite, 6. mordenite, 7. bikiatite, 8. zeolites of unknown structure.

4. Studying the escape of water from the zeolites, KOIZUMI [1953] classified them on the basis of their dehydration in to 1. natrolitic, 2. analcitic, 3. combinations of the two, and 4. zeolites belonging to neither of these types.

EXPERIMENTAL

A) I. Heating some natural zeolites, KOIZUMI [1960] observed the transitions

phillipsite	→ wairakite + H ₂ O	at 260° C
scolecite	→ wairakite + H ₂ O + anorthite	300° C
laumontite	→ wairakite + H ₂ O	410° C
heulandite	→ wairakite + H ₂ O + SiO ₂	320° C
epistilbite	→ wairakite + H ₂ O + SiO ₂	350° C
wairakite	→ anorthite + H ₂ O + SiO ₂	465° C

at the temperatures listed on the right side. He found that the five natural zeolites listed above decomposed to wairakite at relatively low temperatures. On heating to higher temperatures (1000° C), it is known by common results of several researches that zeolites transform into feldspars.

Heating our zeolites we have determined their temperatures of decomposition or transformation. Listed according to J. V. SMITH's system, these are as follows.

1. Zeolites of the analcite type:	wairakite	465° C
2. Zeolites of the sodalite type:	faujasite	400° C
3. Zeolites of the chabasite type:	chabasite	700° C
4. Zeolites of the natrolite type:	natrolite	
	mesolite	500—600° C
	scolecite	
	thomsonite	350° C
	gonnardite	

5. Zeolites of the phillipsite type:
 phillipsite 400° C
6. Zeolites of the mordenite type in general
7. Zeolites of unestablished structure
- | | | |
|----------------|---|---------------|
| heulandite | } | 400° C |
| clinoptylolite | | above 1000° C |
| mordenite | | |
| laumontite | | 800° C |
- the stilbite family 350° C

The figures mean those temperatures at which the mineral can still be identified by a few $d(\text{Å})$ values but above which it turns roentgenographically amorphous.

A) II. We could prove the presence of wairakite, first produced by KOIZUMI [1960] after the heating of some of our zeolites: phillipsite, laumontite, heulandite, epistilbite, chabasite and desmine [É. PÉCSI-DONÁTH, 1965, 1966]. The transformation of stilbite produced, besides wairakite, also heulandite in some cases and clinoptylolite in others [É. PÉCSI-DONÁTH, 1965] could also be shown.

A) III. We have established that

1. On heating, the $d(\text{Å})$ values of the new substance appear in some cases beside those of the old one as the new crystal lattice starts to develop. (Chabasite, gmelinite, levyne, mordenite, harmotome, brewsterite).

2. Some other zeolites pass through a roentgenographically amorphous state into a new crystalline phase. This is the case with species of zeolite not mentioned above.

3. Heating to 1000° C invariably produces a feldspar or feldspathoid, with the single exception of clinoptylolite which has proved to be roentgenographically amorphous at that temperature. The new lattices are mostly well-formed, with well-defined $d(\text{Å})$ values, but some are poorly crystallized. The products of transformation obtained at 1000° C are as follows:

Zeolite	Feldspar	Feldspathoid	Other
wairakite	anorthite		
chabasite	anorthite		
gmelinite	oligoclase		
levyne	oligoclase		
natrolite	albite	+	nepheline
scolecite	anorthite		
mesolite	bytownite		
thomsonite	anorthite	+	nepheline
phillipsite			nepheline
harmotome	bytownite	+	$\text{BaAl}_2\text{Si}_2\text{O}_8 + \text{KAlSi}_3\text{O}_8$
gismondite	anorthite		
mordenite	—		
heulandite	bytownite		
clinoptylolite	—		
laumontite	oligoclase		
brewsterite	anorthite	+	celsian
stilbite	anorthite		
epistilbite	anorthite		
parastilbite	anorthite		

4. In some zeolites the fact that the mineral turns amorphous roentgenographically merely means that the new structure is cryptocrystalline. Scolecite becomes almost completely amorphous roentgenographically beyond 350° whereas the DTA graph exhibits a sharp endothermic peak between 500 and 550° C. This suggests that on heating above 350° C scolecite develops a cryptocrystalline structure not resolved by the diffractometer. For this reason we experimented with imbibition with glycerine, as usual in clay mineral research, and with silicon oil, applied by us for the first time to zeolites. Scolecite heated to 350° C after such treatment gave an X-ray structure differing by slight intensity decreases from the unheated one. The substance treated in this same way and heated at 400° C still gave identifiable $d(\text{Å})$ values in spite of intensity decreases. Samples heated to 500 and 700° C, respectively, gave no structure in spite of the treatment, and at 1000° C, we obtained the anorthite structure.

B) As regards the nature of water in zeolites, we have studied:

1. The temperatures of formation of some partly or entirely dehydrated zeolite species and the nature of water contained in them.

a) On heating natrolite passes into metanattrolite, which is monoclinic as opposed to the original orthorombic structure. The unit cell dimensions, a_0 and b_0 , change and so does the space group (from Fdd2 to F112). The temperature of formation of the „meta” variety was given by several authors [F. RINNE, 1890, G. TAMMAN, 1897, F. ZAMBONINI 1906—08, more recently M. H. HEY 1952, ROSHKOVA et al., 1962] as 300° C. It was, however, pointed out already by PENG [1955] and KOIZUMI [1957] that there is a temperature gap of about 100° C between the escape of water and the transformation of the structure. This was proved by more recent observations also by ROSHKOVA et al. [1962] and É. PÉCSI-DONÁTH [1962]. Metanattrolite is not, however — as contrary to prior opinion — fully dehydrated, as has been proved particularly by infrared spectroscopy. After losing the crystal water between 300 and 400° C and transforming between 500 and 600° C into the monoclinic variety called metanattrolite, the mineral still contains some water which escapes gradually up to 1000° C. From 500 to 600° C, the infrared absorption bands characteristic of the bond Si-O-Al^(IV) disappear and are replaced by the absorption band of Si-O-Al^(VI) which proves that the small amount of water still present in metanattrolite is adsorbed water adhering to the lattice (cf. Table 1.).

b) The following up of the scolecite-metascolecite transformation has also provided some new evidence. According to F. RINNE [1896], there are two varieties of metascolecite: from 180 to 220° C, partial dehydration [produces metascolecite I, which, on further heating, assumes an orthorombic structure whilst retaining its pyroelectric property. According to M. H. HEY [1936], the metascolecite variety with 2H₂O occurs also as a natural mineral. According to KOIZUMI and ROY [1960], heating scolecite at 300° C produces anorthite and wairakite under the escape of water. Tracing the changes brought about by heating by means of the DTA method, the present author obtained the following results.

It could thus be established that the peak beginning at 170° C with its crest at 300° C, corresponding to a weight loss of 4,57 or 4,70 per cent, respectively (i.e. to the loss of one molecule of water), is the zone of formation of metascolecite I.

The further endothermic reaction with peaks given by KOIZUMI at 460, by PENG at 500° C indicates the formation of metascolecite II. We have found this peak to be double, with a total water loss of exactly, 4,57 and 4,70 per cent, respectively, indicating the escape of another molecule of water in two steps. As our sample was already amorphous roentgenographically at 500° C, the peaks at 540°

Table 1
Infrared absorption bands of natrolite (Fassa Valley, Tirol)

Unheated sample	Sample heated at		
	300° C	500° C	500° C
	in KBr		in nujol
wave number (cm ⁻¹)			
400—460	400—465	400—460	400—460
415	415	425	415
425	420		430
445	445	445	
	485	490	500
510	510	510	570
545	545	545	
580	580	580	
600	600	600	
625	625	630	630
675	675	680	
730	720	720	730
		750	
		770	
		790	
800—1500	800—1500	820—1500	
840	850	840	
	880		
940	940	900	
970	970	930	
980	980	—	—
		1000	
1040	1040		
1060	1060	1050	
		1080	
1090	1090	1090	
	1630		
1640	1650	1630	
1670			
3700—3000	3700—3000	3520—3000	3720—3500
	3330	3330	3330
3400			
3540	3540	3540	3550
4540			
5100			

Table 2

KOIZUMI [1953]	PENG [1955]	É. PÉCSI-DONÁTH [1962]	É. PÉCSI-DONÁTH [1966]
100° C end.			
170 end.	170° C end.		
	weak	200° C end.	
240 double	310	310	310° C big broad end.
275			
300 small			
460 big sharp	500	460	480 small sharp
		490	520 big sharp
550	560	540	570 small sharp
			770 flat end.
			950 weak ex.

and 570° C indicate the transition into the amorphous state, that is, the water escapes immediately thereafter. This water is presumably bound somewhat stronger as its escape gives rise to a small sharp endothermic peak. The water still left over in the lattice gradually escapes up to 1000° C, in two steps, but without giving rise to sharp endothermic peaks [É. PÉCSI-DONÁTH, 1966].

The transition scolecite → metascolecite can be traced also by means of infrared spectroscopy.

Table 3
Infrared absorption bands of scolecite (Attlitz Valley, Switzerland)

Unheated sample	Sample heated at			
	350° C	400° C	500° C	1000° C
wave number (cm ⁻¹)				
470—400	520—400	525—400	535—400	450—400
410	410	410	410	410
425	425	430	430	430
	450	445	445	440
	460			
	475			
540				535
585	585			570
625	635	625		
		645		650
690				
720	740	720	720	780
	780			
800—1400	1350—810	1350—820	1140—820	1600—800
	840	830		840
		860		
		880		880
910	920	910	920	920
			980	940
1020	1150	1000		
		1100	1080	1100
		1170	1180	
		1220		
1110				
1470		1650		
1600				
1670	1680			
2850				
2920				
2960				
3800—3000	3740—3000	3700—3100	3300—3700	3300—3700
3230	3220			
	3240			
3330	3450	3450		
3410			3580	
3510	3550	3570		
	3580			
3610				
3640	3630	3640	3640	3640
			3680	
3690		3680		3690
3760	3760	3710		
5060				

The transformation into metascolecite I, up to 350° C, changes the infrared spectrum of the unheated material: besides the 3000 to 3800 cm⁻¹ range with 5 or 6 sharp absorption bands, there turn up now 3 absorption bands also in the 1600 cm⁻¹ range. These decrease in both number and intensity on heating to 350° C. (To 4 in the 3000 to 3800 cm⁻¹ range, and to 1 in the 1600 cm⁻¹ range.) Also in the absorption ranges typical of the silicate structure, the formation of the crypto-crystalline structure indicated by the DTA graph is reflected by substantial changes. The one molecule of water escaping on the scolecite — metascolecite I transformation is, in our opinion, bound like crystal water, because:

a) Its escape is accompanied by the disappearance of several sharp bands of absorption.

b) The unheated sample exhibits in the 4000 to 6000 cm⁻¹ absorption range a sharp absorption band at 5060 cm⁻¹, which suggests the presence of crystal-water (Table 3).

The infrared spectrum of scolecite heated at 400° C already exhibits a more substantial change. The absorption bands suggesting the presence of some water have disappeared and there have remained in the silicate structure some almost indefinable areas of absorption. However, the transition metascolecite I—II lies about 100° C higher, at 500° C, because the second water molecule is expelled in two stages and the size of the second endothermic peak is incremented by a contribution from the process of formation of metascolecite II. This transition could not take place at a temperature higher than 500° C, either, because X-ray diffractometry has revealed the substance heated at 500° C to be amorphous roentgenographically. The endothermic peak at 540° C is due to the escape of the OH radicals bound to the tetrahedra. The regeneration graph proves that the crystal-water-like water of metascolecite I can be regenerated by rehydration, whereas the water of metascolecite II cannot, since the structure has become crypto-crystalline. The water imprisoned on lattice collapse — less than one molecule — escapes at a higher temperature, in two steps without any sharp endothermic reaction. (For figures see É. PÉCSI-DONÁTH [1965, 1966].)

c) As regards thomsonite, it was M. H. HEY [1952] who stated that this mineral reversibly passes into metathomsonite at 270 to 300° C or slightly above: the temperature of transition is a function of water content (thomsonite higher in water transforms at a lower temperature). In the course of her investigations, the present author has found the following DTA peaks, as compared with those of KOIZUMI [1953] (Fig. 1).

X-ray diffractometry gave for thomsonite from three localities temperatures of structural transitions as seen in Table 5.

The dehydration graph (Fig. 2) shows the release of 5 molecules of water up

Table 4

KOIZUMI [1953]	É. PÉCSI-DONÁTH [1962]	É. PÉCSI-DONÁTH [1966]
75° C endo.	100° C endo.	250° C endo.
358 endo.	350—360 endo.	—
428 endo.	420—430 endo.	420 endo.
523 endo.	460—520 endo.	460 endo.
	930—960 exo.	510 endo.
		560 endo.
		1010 exo.

Table 5

Origin	Base	300—325° C	425° C	460° C	500° C	525° C	560—580° C	600—800° C	1000° C
Theiss, Tirol	all thomsonite lines as in literature	thomsonite with 1—2 lines of changed intensity (stronger or weaker)	1—2 very weak peaks resembling faroelite plus an amorphous phase intensity weakened but still sharp peaks, amorphous phase subordinate	—	amorphous phase only	—	amorphous phase only	amorphous phase only	very strong lines of anorthite and nepheline
Dunbarton, Scotland			a few lines all very weak, amorphous phase abundant	amorphous phase only	—	amorphous phase only	amorphous phase only		
Farøer Is. Iceland				—	—	—	a few very weak lines plus an amorphous phase		

to 400° C. The escape of water in connection with the endothermic peak at 360° C indicates at the same time also the transformation into metathomsonite. The infrared spectrum of the unheated sample (Fig. 3) presents within the wide absorption range of water from 3800 to 2900 cm⁻¹ a few narrow bands, at 3280 and 3400 cm⁻¹ and also at 1680 and 1610 cm⁻¹. Heating to 350° C makes these disappear, so that only the wide band remains and even that with a much reduced intensity. Simultaneously, the absorption bands of the silicate structure also disappear (Table 6). The regeneration experiments have also shown that the mineral is capable of regeneration up to 250° C, whereas at higher temperatures rehydration takes place only immediately before the formation of the new phase (Fig. 4).

TAYLOR's [1933] rigorous examination of the structure revealed that thomsonite contains three types of water. These were called Aq1, Aq2 and Aq3 by TAYLOR. In his opinion, Aq1 and Aq2 are bound more strongly than Aq3 which is of the type found in natrolites.

Comparing this statement with our own findings we can state concerning the transition thomsonite → metathomsonite and the nature of the water involved that thomsonite loses half its water content (3 molecules, Aq3) up to 300° C, whereas on heating to 400° C it loses another two molecules in crystal-water-type bond (Aq1 and Aq2) while it passes into metathomsonite. The removal of these latter gives rise to a sharp peak in the DTA graph and to the

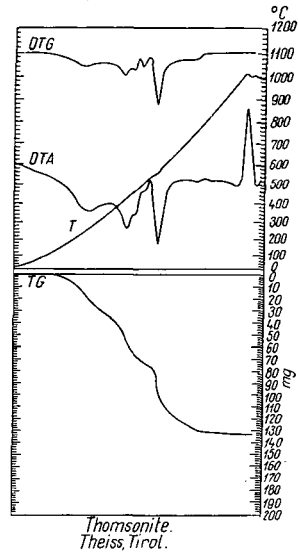


Fig. 1. Derivatogram of thomsonite (Fassa Valley, Tirol)

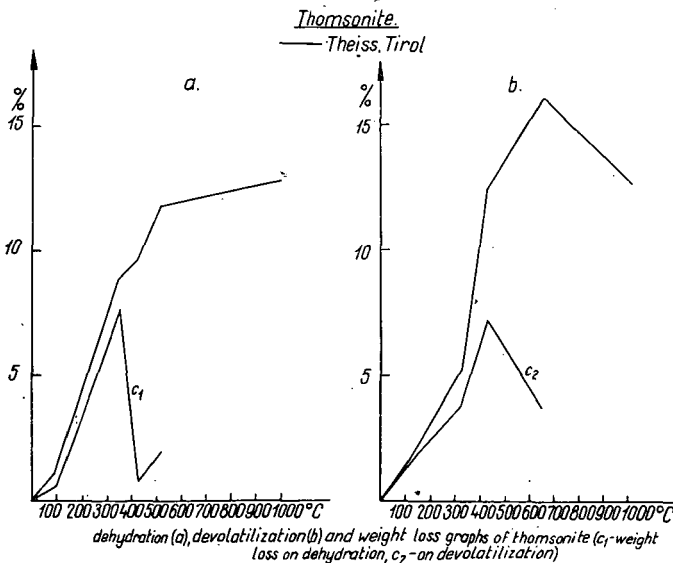


Fig. 2. Dehydration and devolatilization graphs of thomsonite

disappearance of the narrow bands of absorption in the wide range from 3850 cm^{-1} to 2800 cm^{-1} in the infrared spectrum. Dehydration is accompanied by loss of structure up to 430°C . The one molecule of water left in the structure then escapes up to 700°C .

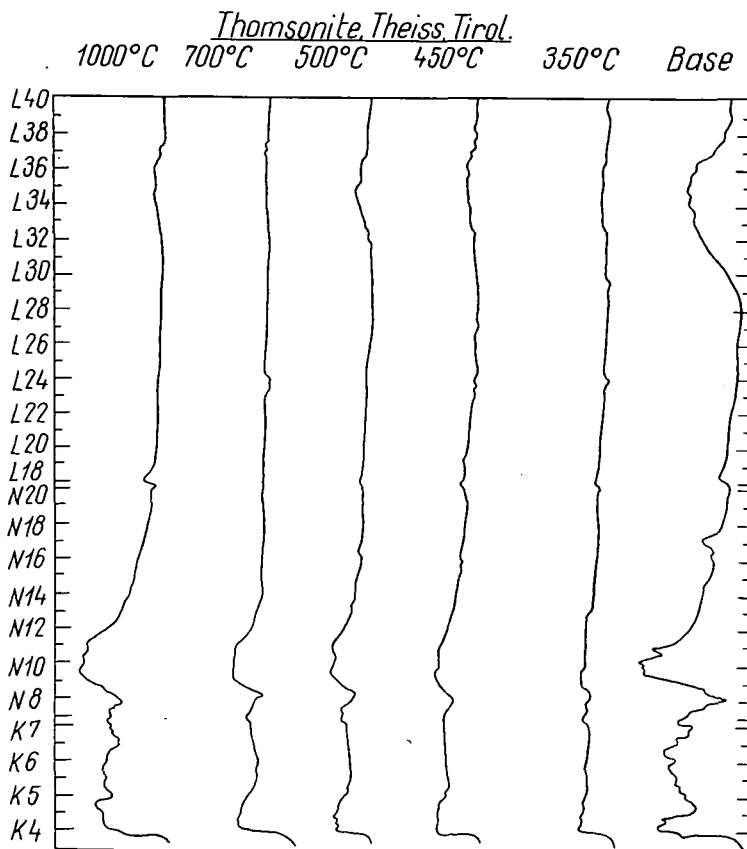


Fig. 3. Infrared spectra of thomsonite; unheated, and after heating to 350 and 1000 °C, respectively; with KBr pills

2. As regards water in the various sorts of zeolite, it has been pointed out in the papers already cited of KOIZUMI, PENG, ROSHKOVA, AVERBUCH, SMITH etc. that „zeolite water” is a complicated notion. An evaluation of the complex experiments performed by the present author on some of the zeolite species has made it possible to establish the nature of the water bond, and moreover to find out whether the water is typical zeolite water or not. Water in natrolite is largely crystal-water and so is water in scolecite, mesolite, thomsonite and laumontite. The presence of crystal-water in crystal-water-type bond is proved *a*) by repeated weight loss at given temperatures on the TG graph, *b*) by sharp endothermic peaks on the DTA graph, *c*) by narrow bands of absorption in the infrared spectrum, *d*) by characteristic bands in the long-wave infrared (4000 to 6000 cm^{-1}), *e*) fine structure investigations published in literature (natrolite: MEIER et al. [1960], laumontite: COOMBS [1952]

Table 6
Infrared absorption bands of thomsonite (Theiss, Tirol)

Unheated sample	Sample heated at				
	350° C	450° C	500° C	700° C	1000° C
	wave number (cm ⁻¹)				
410	405	410	410		
435	425	440	440	440	450
455		475			
505			500		
540		520	520		535
585	585				570
630		610			
660	680	670	690		
710		710	710	710	675
910		920			720
940	940		950	960	930
1000			1030		1030
1070	1070	1050			1090
1230	1270	1170			1370
1430					
1480	1480		1480		1460
1530	1530				
1610		1610	1640		1630
1680	1690				
	2080				
		2400			
3850					
2800	3500	3700	3750		3720
	2940	3100	3180		3100
3400	3400				
3580		3550	3460		3460
3630		3670	3630	3680	3620
		3690		3690	
		3740	3740	3740	3700

etc.) have proved that the water molecules occur in definite positions, annexed to definite cations by hydrogen bridge bonds.

In some other zeolites (chabasite, levyne, gonnardite, harmotome, stilbite) the above-mentioned measurements have also proved the presence of crystal-water, even if in a less striking form. In the course of the dehydration of chabasite, the weight loss measurable up to and above 500° C, the narrow absorption band at 3400 cm⁻¹ and the drawn-out one between 3000 and 3700 cm⁻¹ even at 560° C indicate that water is still present in chabasite at this temperature although not in the form of crystal-water. Thus water stays in the structure up to fairly high temperatures (to 800° C) and forms on the DTG graph a well-defined peak corresponding to the OH radicals bound to the (Si,Al)O₄ tetrahedra. Hence, this water is present in hydroxyl form. According to several authors it is largely bound to the Al substituting the Si in the (Si, Al)O₄ tetrahedra of the silicate lattice.

A small group of zeolites (gmelinite, edingtonite, gismondite, brewsterite, clinoptylolite, heulandite, mordenite) largely contains „zeolite water” in the classical sense: this water moves freely about in the structure, without being bound to any well-defined position or cation. Its distribution is random. One of its types is water around the cations, in coordination with it, which represents a special type among

zeolites. It is not bound by a strong OH bond to the cation: on the contrary, it forms a hydrate shell about it without the development of any strong cation-OH bond.

The weak binding of these H₂O molecules is proved:

a) by the endothermic trough without a well-defined peak, indicative of gradual water escape, on the DTA graph,

b) by the gradual weight loss indicated by the TG graph,

c) by the broad, elongate absorption band about the 3000 cm⁻¹ wave number, characteristic of water, and the complete absence of any absorption in the higher wave number range (4000 to 6000 cm⁻¹),

d) by a largely constant ability of almost total rehydration, in spite of heating up to 1000° C, or, more precisely speaking, up to the temperature of transformation of the structure.

Most of the zeolites contain besides the much-examined and easily distinguished types of water enumerated above one or two molecules of water which gradually escape on heating at higher temperatures. This water escapes in most cases in a temperature range where diffractometry already reveals a roentgenographically amorphous substance. Considering that e.g. in the case of scolecite a cryptocrystalline structure could be surmised in spite of this, the water in question is in our opinion a water bound to the disintegrating tectosilicate lattice, imprisoned by the collapsing structure up to quite high temperatures.

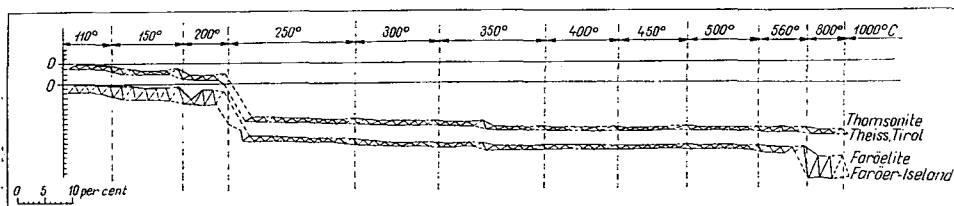


Fig. 4. Regeneration graphs of thomsonite and faroelite

It is recorded in literature that silica gels are capable of storing water and gradually letting it escape up to quite high temperatures. The escape of this type of water is not accompanied by a sharp endothermic reaction. Water loss is indicated partly by weight loss (dehydration measurements), and partly by the prolonged descent of the TG graph also at high temperatures. We are of the opinion that this type of water is lattice-bound and we have found it invariably in zeolites which carry water bound to the lattice in the form of OH radicals (e.g. in natrolite).

3. The rehydration properties of zeolites are partly structure dependent and partly determined by the nature of the water content.

a) It is a general experience that zeolites heated to constant weight at a given temperature can always be rehydrated, provided the structure was not destroyed to a roentgenographically amorphous state.

b) Natrolite, scolecite, etc., that is, the zeolite species largely containing crystal-water lose very little water if any, up to a temperature characteristic of the mineral species, and hence they do not rehydrate, either (Fig. 5). Heated at a given temperature, these minerals lose most of their water content, but on rehydration they take in one or two per cent more than they have lost (they are strongly „activated“). This feature is preserved over a temperature interval of 100 to 150° C. On heating to higher temperatures these minerals lose their capacity of rehydration,

and take in but small quantities of water, presumably by adsorption on the surface. The amount of the water thus attached remains below 0,5 per cent. The zeolites containing crystal water and water in hydroxyl bond, as well as the minerals largely containing zeolite water (chabasite, harmotome, clinoptylolite, mordenite etc. which become reontgenographically amorphous only at high temperatures) rehydrate almost completely (Fig. 6). A drop in rehydration takes place after the loss of crystal-water, but rehydration is still significant up to the complete collapse of the structure.

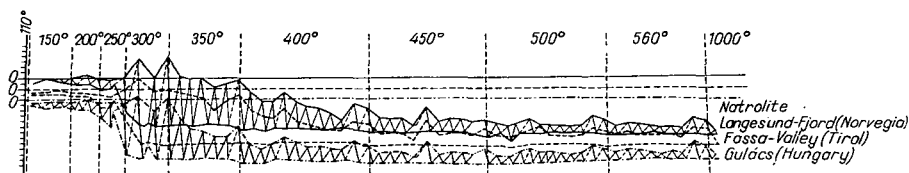


Fig. 5. Regeneration graph of natrolite

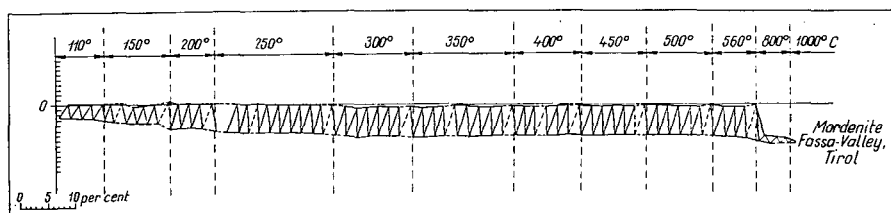


Fig. 6. Regeneration graph of mordenite

A peculiar group as regards the capacity of rehydration is that of thomsonite, which, when heated to higher temperatures, exhibits a second rehydration at the beginning of the formation of the new crystalline phase. It was proved by X-ray analysis that at the given temperature the new lattice was not as yet fully developed whereas the old one was considerably disintegrated. The capacity of rehydration disappeared with the full development of the new crystalline phase.

C) On the basis of their manifold and typical water contents, zeolites can be classified, according to a new system, as follows:

1. Zeolites with water mainly in crystal-water form:
natrolite, scolecite, mesolite, etc.
2. Zeolites containing water in the crystal-water form but also in the form of OH radicals bound to the lattice:
chabasite, desmine, etc.
3. Zeolites with typical zeolite water, in which some of the water forms hydrate shells about the cations:
mordenite, clinoptylolite, etc.

All three groups contain, however, besides the above-mentioned types of water also the so called lattice-bound water.

SUMMARY

For the 20 or so species of zeolite studied, transformation temperatures have been established. The transformation into wairakite, of some zeolites and to heulandite or clinoptilolite of others, have been observed. As a new technique, imbibition with siliconoil has been introduced in the X-ray diffractometry of certain zeolite structures.

Concerning the nature of the water content of the several „meta” varieties coming to exist on heating and of the water in unheated zeolites it is possible to state that

1. natrolite, scolecite and thomsonite contain water in a crystal-water-type bond, and the meta variety is formed about 100° C above the escape of this water,

2. the lattice that became roentgenographically amorphous by heating still imprisons about one molecule of water until much higher temperatures;

3. Zeolites contain

a) water in crystal-water-like bond,

b) the above type of water plus water bound to the lattice by OH bonds,

c) typical zeolite water.

It is characteristic of all three types that some small amounts of water are preserved strongly bonded to the tetrahedra of the disintegrating lattice.

4. On the basis of rehydration properties, the above groups containing various types of water are easily distinguished, and this may serve as a basis for a new classification.

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