Journal of Thermal Analysis, Vol. 50 (1997) 473-486

THERMAL BEHAVIOUR OF FIBROUS ZEOLITES OF THE NATROLITE GROUP

A. Apte and A. V. Phadke

Department of Geology, University of Pune, Pune 411 007, India

(Received January 28, 1996; in revised form September 10, 1996)

Abstract

The western region of the Deccan Volcanic Province (DVP) is constituted of tholeiitic lava flows. They host numerous cavities, varying in size and shape, largely occupied by zeolites and a variety of secondary minerals, amongst which the fibrous zeolites (natrolite group), are particularly gorgeous and attractive. Scolecite and mesolite are the only two members commonly occurring in this region. Our data on their thermal behaviour significantly differs from that reported in previous literature. Scolecite, $Ca_8(Al_{16}Si_{24}O_{80})\cdot 24H_2O$ shows three distinct steps instead of two and water loss is observed even beyond 550°C. It is held that the first step corresponds to the expulsion of water from the site farthest away from Ca and the next two steps in succession correspond to the two sites nearer to Ca. Mesolite, $Na_{16}Ca_{16}(Al_{48}Si_{72}O_{240})\cdot 64H_2O$ has much more complex behaviour with four or five steps of water expulsion and a major loss around 248–270°C in a double reaction attributed here to the expulsion of water from scolecite type channels. It is further held that the natrolite type channels are emptied in further steps. Loss of water in steps even beyond 400°C is particularly noted and such reactions are well reflected in the TG and the DTG. Peak temperature dependence on sample amounts is also evident. Successive phase transformations above 700°C, up to 1000°C are reflected in the DTA curves.

Keywords: natrolite group, sequence escape of water molecules, zeolites

Introduction

The Deccan Volcanic Province (DVP) of the Cretaceous-Eocene age (65±5 Ma), essentially constituted of tholeiitic basalt lava flows, has been long known to host, attractive fibrous zeolites in cavities of varying size and shape. The most commonly noted members of the natrolite group in this region are natrolite, $Na_{16}(Al_{16}Si_{24}O_{80})\cdot 16H_2O$, mesolite, $Na_{16}Ca_{16}(Al_{48}Si_{72}O_{240})\cdot 64H_2O$ and scolecite, $Ca_8(Al_{16}Si_{24}O_{80})\cdot 24H_2O$.

On the basis of the frequency of occurrence of different zeolite species, three zones are marked in the western region of the DVP [1]. Scolecite is particularly well developed near Nasik, in the hills of Sinnar and Sangamner, 600 m above the mean sea level, and has its greatest thickness of almost 400 m towards south-

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

southwest between Panvel and Lonawala. The occurrence of mesolite, though not specified by its name for a particular zone, is profound in the region around Pune and further north above the altitude of 600 m, in the heulandite zone. Natrolite is, however, restricted to the coastal region near Bombay and is not found in its purest form, i.e. the chemistry reveals at least some replacement of Na by Ca. Mesolite and scolecite are usually distinguishable in hand specimens, on account of the slightly flattened nature of the scolecite needles as against those with squarish cross sections and pyramidal terminations of mesolite. In the present study the identity of the samples was done also from their optical characters and was confirmed from the X-ray powder diffraction patterns.

Thermal analysis

Pure, transparent crystalline needles of mesolite and scolecite from different stone quarries in Pune and Nasik districts; and natrolite from Malad near Bombay, Maharashtra, were subjected to thermal analysis involving DTA, TG and DTG. The samples were crushed to a fine powder in an agate mortar for two to three minutes and were loaded in Pt sample holders, keeping the thermocouples at the center of the sample. Heating rate of 10°C min^{-1} (approx.) was maintained in a continuous heating up to a little over 1000°C in air. Preheated alumina was used as reference inert. The conditions of the experimentation are summarised in Table 1. In these experiments T, DTA, TG and the DTG curves were simultaneously recorded on a photographic paper, using a Hungarian manufactured 'Derivatograph' OD Type 102 MOM. A pure sample of natrolite from Hammerunterwiesenthal, Germany (erstwhile GDR), was also subjected to similar conditions of experimentation for comparison. Separate experiments were conducted on mesolite and scolecite with sample amounts of 200, 400, 800 and 1000 mg, keeping the conditions identical for each. In case of natrolite from

Table 1 Sample preparatiion and conditions of heating experiments

Sample:	agate mortared, 200, 400, 800 and 1000 mg
Packing density:	loose packed, no pressing
Sample holder:	Pt. Crucibles
Reference inert:	preheated alumina
Furnace atmosphere:	air
Thermocouples:	Pt–Pt_{90}/Rh_{10}
Rate of heating:	10°C min^{-1}
DTA, DTG sensitivity:	1/10
TG sensitivity:	100, 200 and 500 as per sample amount
Apparatus:	'DERIVATOGRAPH' OD Type 102 MOM

Malad, only 200 and 400 mg samples were studied. The results are described below and are represented in Figs 1 to 3, and are summarised in Tables 2 and 3.

Natrolite

The DTA for natrolite from Germany, shows a single, sharp, somewhat asymmetrical endothermic peak at 380°C and there is a corresponding water loss amounting to 9.00% in a single step with a maximum reaction temperature at

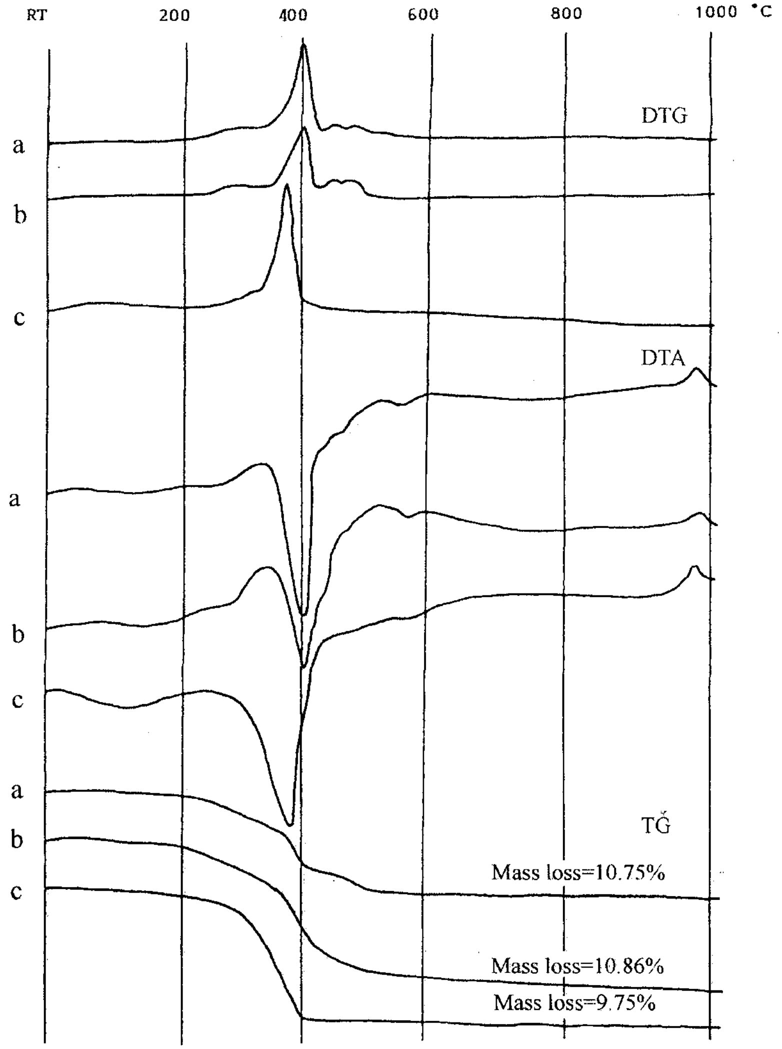

Fig. 1 Thermoanalytical curves of natrolite from Hammerunterwiesenthal, Germany (sample amount=200 mg) and from Malad, Bombay (sample amounts=200 and 400 mg)

360°C as seen on the DTG curve. A moderately strong exothermic peak at 980°C is marked on the DTA curve. The endothermic peak at 380°C is at a much higher temperature than that recorded for sample from Tierno, Trento, Italy [2]. Still higher peak temperatures for this peak are also known [3–4]. The sample of natrolite from Malad (Fig. 1b, c) shows a very strong endothermic peak at 400°C with two small inflections on either side at 360 and 440°C respectively. There is also a small endotherm at 560°C and a moderately strong exotherm at 980°C on the DTA curve. Similar to that for the sample from Germany, (Fig. 1a) the endothermic peak at 400°C in this sample is also much higher than that for the sample from Italy [2]. Corresponding to the endothermic reaction with a peak at 400°C there is quite a sharp step of mass loss seen on the TG in the narrow temperature

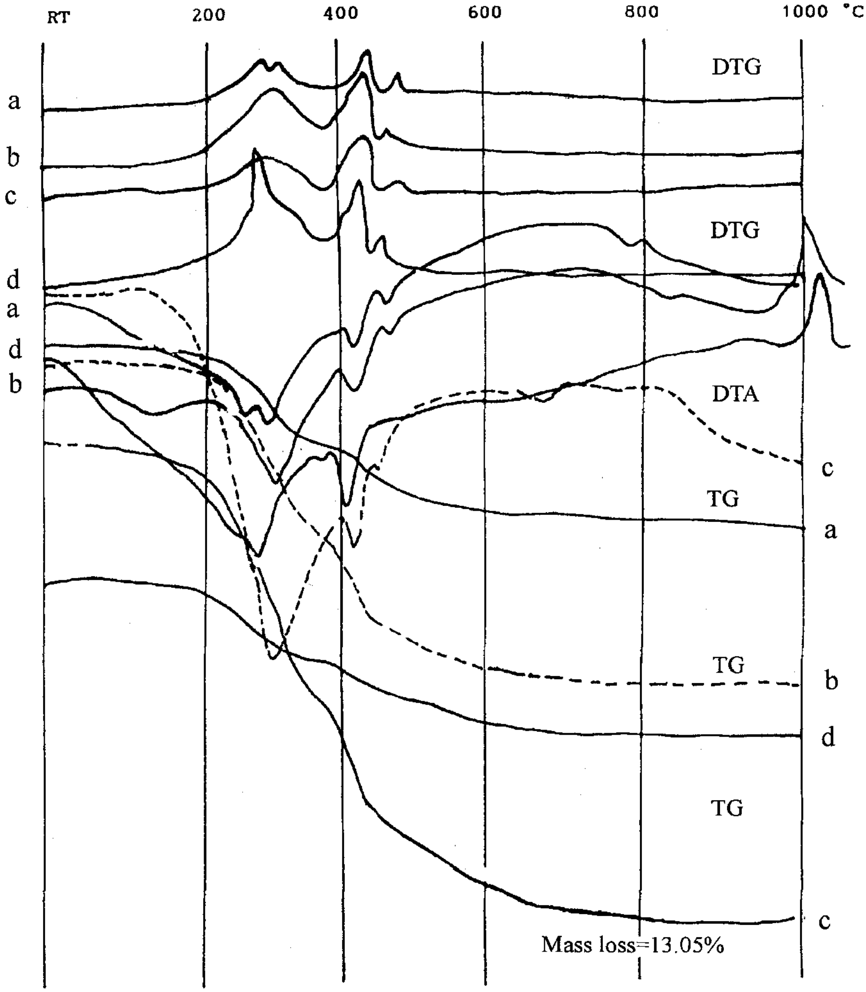

Fig. 2 Thermoanalytical curves of scolecite from Sinnar, Nashik district, Maharashtra, India. (a, b, c, and d respectively represent 200, 400, 800 and 1000 mg samples)

range from 360 to 440°C, amounting to a mass loss of 6.79%. However, there is also an earlier step of mass loss from 220 to 360°C amounting to 2.01%. Another very small mass loss of 1.0% in a step-like manner has taken place between 460 to 500°C at which the dehydration is yet not complete. The DTG shows a single, strong and sharp peak at 400°C but is accompanied by two small upwards on either side of it, each with a maximum at 280 and 480°C.

Scolecite

As seen from Fig. 2, the DTA curves for this mineral shows at least four endotherms in the temperature range of 200 to 575°C. The peak temperatures show higher values with increasing sample amounts. The first peak is much stronger and almost equaling the other two in respect of peak areas. The double reaction peak in the range 400 to 500°C is well resolved for the 200 mg and the 400 mg samples, whereas a shoulder each is seen before the peak maximum for the 800 mg and the 1000 mg samples. The third endotherm is quite sharp, highly symmetrical and has correspondingly lower peak temperatures for smaller sample amounts. Three major steps of mass loss, obviously due to expulsion of

Table 2 DTA and DTG peak temperatures in °C for natrolite from Germany and natrolite, scolecite and mesolite from India

Sample amount	DTA		DTG
	endo	exo	
Natrolite			
(Germany)			
200 mg	380	970	360
(India)			
200 mg	285, 410, 440, 560	990	300, 405, 455, 470
400 mg	285, 415, 470, 570	995	310, 410, 460, 470
Scolecite			
200 mg	245, 400, 420, 505		230, 405, 445, 535
400 mg	245, 400, 430, 510		255, 440, 525
800 mg	305, 460, 500, 575, 910		400, 445, 490, 580
1000 mg	290, 435, 490, 550		300, 490, 545
Mesolite			
200 mg	240, 280, 415, 465, 820		260, 290, 425, 480
400 mg	280, 405, 470, 860, 945	1000	240, 270, 420
800 mg	215, 255, 360, 390, 960	1020	255, 410, 450
1000 mg	340, 490, 520, 740, 860		325, 470, 515, 740

Table 3a Data on mass loss in natrolite from Germany and from India

Sample amount	Temperature range/°C	Mass loss/%
Germany		
200 mg	40–240	0.50
	240–440	9.00
	440 onwards	0.25
	Total	9.75
India		
200 mg	40–200	0.95
	200–340	2.23
	340–440	4.79
	440–500	1.91
	500 onwards	0.98
	Total	10.86
400 mg	40–200	0.86
	200–340	2.38
	340–440	4.56
	440–500	1.98
	500 onwards	0.92
	Total	10.70

water molecules in steps, are marked from the TG and the DTG curves (Fig. 2, Tables 2 and 3b). The first major step almost equals the next two. The double reaction at the second stage, well resolved in the DTA for the sample amounts of 200 and 400 mg, is weakly resolved in the DTG. There is also a distinct third stage of water loss in a step like manner beyond 500°C. To the best of our knowledge the three or even more stages of water loss are recorded here for the first time for the mineral scolecite.

Mesolite

The thermal curves for mesolite (Fig. 3), even in the present studies, are very complicated in accordance with earlier workers [5–6]. The DTA curves show numerous endotherms with a major reaction occurring in the range of 200 to 400°C. For a sample amount of 1000 mg the peak temperature for this reaction occurs at 340°C, whereas for the sample amount of 400 mg, it is lowered to

Table 3b Data on mass loss in scolecite from India

Sample amount	Temperature range/°C	Mass loss/%
200 mg	RT– 80	0.00
	80–140	0.60
	140–270	4.10
	270–380	1.11
	380–455	3.00
	455–540	1.11
	540–660	1.85
	660–820	0.60
	820 onwards	0.75
	Total	13.12
400 mg	RT–160	0.00
	160–280	3.85
	280–365	0.85
	365–450	2.60
	450–510	1.35
	510–540	1.35
	540–600	1.25
	600–710	1.25
	710 onwards	0.85
	Total	13.35
800 mg	RT–140	0.00
	140–330	4.70
	330–430	0.75
	430–460	0.75
	460–510	1.80
	510–560	0.85
	560–600	1.70
	600–860	2.90
	860 onwards	0.22
	Total	13.67

Table 3b Continued

Sample amount	Temperature range/°C	Mass loss/%
1000 mg	RT–140	0.20
	140–305	4.00
	305–405	0.80
	405–455	1.30
	455–470	1.70
	470–525	0.70
	525–560	1.40
	560–600	1.00
	600–810	1.90
	810 onwards	0.25
	Total	13.25

280°C, and for the 200 mg sample it is around 270°C. For 400 mg sample, this reaction shows a shoulder at 260°C, whereas it is well resolved in the 200 mg sample with peaks at 240 and 270°C. The next two endothermic reactions around 400 and 460°C also correspond with the steps of mass loss marked on the TG and the DTG. The minor endothermic deflections in the higher temperature range up to 960°C are feeble and a gradual mass loss beyond 500°C is seen from the smooth and continuous TG curve without any corresponding DTG deflections, though the different steps of mass loss in the lower temperature range are clearly seen with the first major step corresponding to a double reaction recorded in the DTA, being well resolved in the DTG. It is fairly clear from the thermal curves of this mineral, that the water expulsion is not complete around 400°C but continues to take place much above this. Higher temperatures of this reaction are observed for the larger sample amounts.

Discussion

On the basis of topology and tetrahedral frameworks observed in natural silicates, the natural zeolites have been classified into six groups [6], including natrolite, mesolite, and scolecite comprising the 'fibrous zeolites'. The structure of the members of this group, often called as natrolite group, is also fairly known [6–9] and is schematically represented in Fig. 3. The thermal behaviour of this group of minerals is investigated by many workers [2–5, 11–16]. The summarised account and the available thermal curves [6] show that the behaviour of natrolite is relatively simple and there is only one single water loss at 330°C in a complete dehydration followed by structural transformation to metanatrolite. Literature also shows [3–4, 10] higher peak temperatures in the range 350–430°C. Temperatures for this peak recorded in the present investigations

Table 3c Data on mass loss in mesolite from India

Sample amount	Temperature range/°C	Mass loss/%
200 mg	RT–160	0.85
	160–300	4.35
	300–405	2.60
	405–440	1.35
	440–470	1.25
	470 onwards	2.65
	Total	13.05
400 mg	RT–120	0.28
	120–180	0.65
	180–260	2.80
	260–300	1.42
	300–400	1.42
	400–410	0.38
	410–420	2.60
	420–490	1.42
	490–620	1.42
	620 onwards	0.65
	Total	13.04
800 mg	RT–160	0.75
	160–255	3.35
	255–300	1.96
	300–370	1.45
	370–410	1.86
	410–440	1.35
	440–550	0.94
	550–630	0.84
	630 onwards	0.70
	Total	13.20

Table 3c Continued

Sample amount	Temperature range/°C	Mass loss/%
1000 mg	RT–160	0.20
	160–320	3.25
	320–360	1.30
	360–400	1.50
	400–440	1.10
	440–490	1.90
	490–540	0.70
	540–760	2.50
	760 onwards	0.60
	Total	13.05

(380°C for the sample from Germany and at 400°C for the sample from Malad) are thus fairly consistent with those given by the earlier workers [3–4]. A shallow endothermic trough in the range 40 to 200°C accompanied by a gradual mass loss is also recorded for the samples from Malad. The X-ray crystal structure studies [17], in this range of temperature, however, do not suggest any relevant variations in the lattice. A low endothermic deflection at 530°C for the sample from Germany and 560°C is, however, consistent with structural transformation to one of the metanatrolite phases without causing any dehydration step. This result is comparable with that noted from literature [5, 15, 18]. Mass loss beyond 400°C, and even after the transformation to metanatrolite phases, continues to take place till the end of the experiment up to 1000°C. After 900°C a reorganization of the structure, indicated by the exothermic peak at 980°C, to a-carnegieite and further to nepheline takes place as also shown by Peng [11]. The difference in the thermal behaviour of the sample from Malad and the samples from Italy [2] is attributed here to partial replacement of Na by Ca, similar to that shown by Hey [19] and Foster [20], giving rise to scolecitic type channels [6] in the structure allowing accommodation of additional water as observed from the small mass loss at a slower rate in the temperature range 22–360°C. This is further supported from the presence of crystal-type water as well as zeolitic water (freely movable) in the samples from Malad as seen from by the continued mass loss beyond 400°C even after the transformation to metanatrolite phase.

In the present studies a major deviation from the results of the thermal analysis of scolecite by earlier workers (op.cit.), particularly in respect of the escape of water molecules is notable. They are generally in agreement that the loss of water takes place in two major steps, first around 240°C and the second around 420°C. However, the presently studied samples clearly show more steps (Fig. 2,

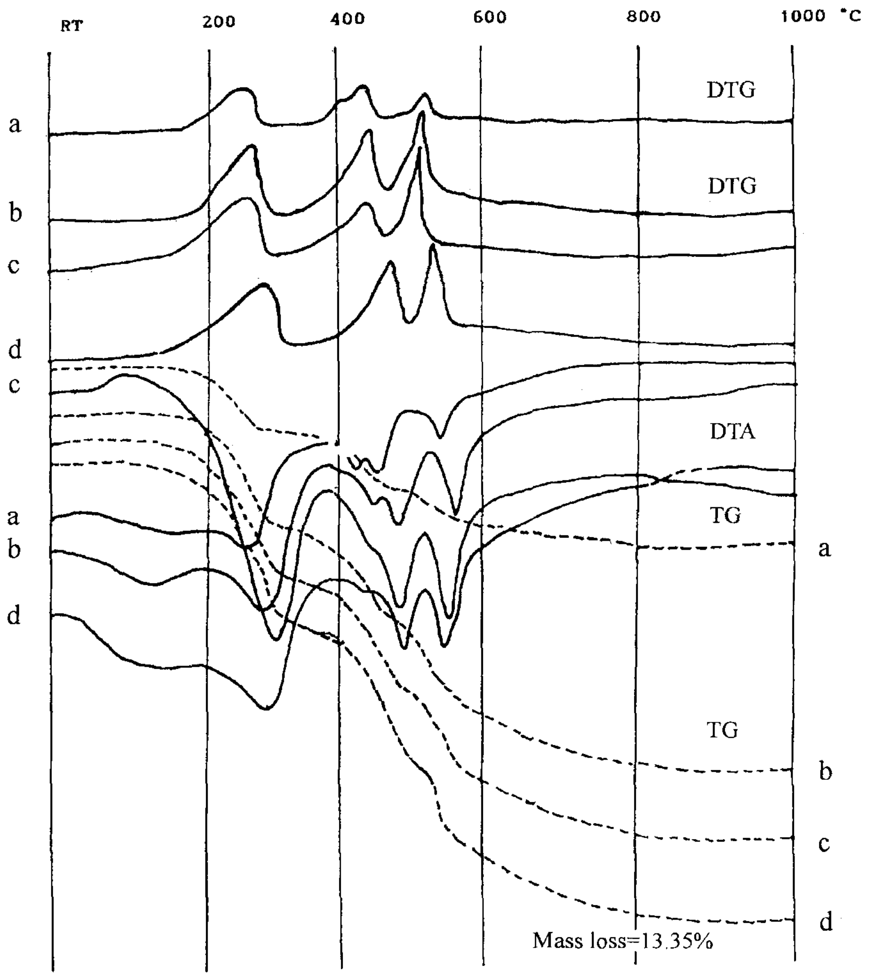

Fig. 3 Thermoanalytical curves of Mesolite from Pashan, Pune district, Maharashtra, India. (a, b, c, and d respectively represent 200, 400, 800 and 1000 mg samples)

Table 2) and also that water continues to escape gradually beyond 560°C till the end of the experiment. The endothermic DTA peak at 560°C, observed by Reeuwijk [5], is also recorded in the present investigations and corresponds to a step of water loss which is well reflected not only in the TG but also in the DTG. This step like expulsion of water at this temperature, is reported here for the first time. This reaction is a result of structural disintegration [e.g. 4, 5, 11]. The peak temperatures, however, for different amounts of samples vary in the reasonable range. Varadarajan and Desh Mittra [16] have not given the DTA and the DTG curves for sample from Nasik, India, studied by them. It may be seen that a double reaction of the second dehydration peak is well resolved also in the DTA and the corresponding DTG during the present investigations. The structure of scolecite heated at 300°C [9] shows that the H_2O molecules which occupied the site corresponding to the Na-site of natrolite (Fig. 3) is missing. Pauling [7] gives the arrangement of water molecules in the scolecite structure with one Ca–H_2O=3.5 Å and two molecules at 2.5 Å. However, these values are different than those given by Taylor *et al.* [8]. The structure of scolecite becomes weak on account of the introduction of water molecule to occupy one of the Na-sites of the natrolite structure, reducing the stability of the scolecite structure [11]. It is therefore logical to attribute the first endothermic reaction to the expulsion of water molecules occupying the Na-sites of natrolite structure, and the two sites nearer to Ca, having been emptied in succession in (i) the double reaction in the second stage, and (ii) the third step beyond 500°C with a maximum around 560°C. This is perhaps the consequence of the attainment of increasing rigidity in the structure on loosing water molecules in succession. The double reaction peaks in all probability may be due to the difference in the distances of the two

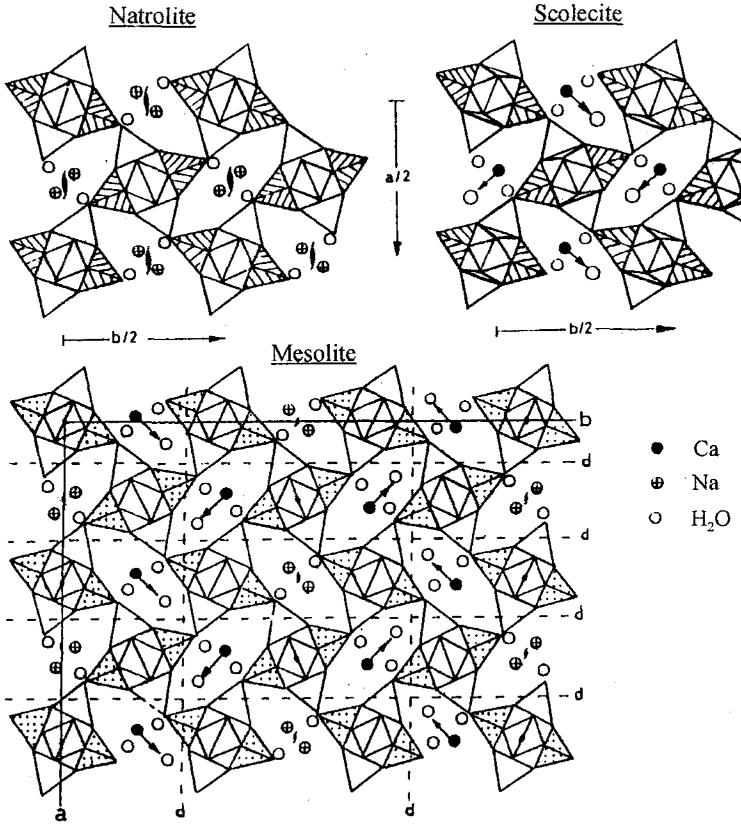

Fig. 4 Schematic representation of structure of natrolite, mesolite and scolecite, projected along c. (after Gottardi and Galli, 1985)

H_2O molecules from Ca and not equaling to 2.5 Å [7] for both the molecules. Phase transformations in the higher temperature range are noticed only in larger sample amounts in a weak endotherm with a maximum at 910°C, representing a possible transformation to anorthite, similar to that for samples from Attlitz valley, Switzerland [13].

The thermoanalytical curves for mesolite (Fig. 3) are the most complex in comparison with those for natrolite and scolecite. Obviously this is due to the structural complexity of mesolite in which natrolite and scolecite structures prevail (Fig. 4). The first endothermic reaction observed in the DTA curve is well resolved for the 200 mg sample having peaks at 240 and 270°C. This resolution is also seen in the DTG curve. Koizumi [3], and Pecsi-Donath [4], have recorded this reaction in a single peak around 260°C while Peng [11], and Reeuwijk [5] have marked this double reaction, though with a slight variation in the peak temperatures, suggesting a structural transformation to metamesolite [5]. The second step of mass loss around 400°C is also a double reaction resolved in the 400 mg sample. This stage of water loss is marked on the DTG curve. The thermal curves given by Alberti *et al.* [in 6] also represent this step prominently, but in a single reaction, and there are no further steps of dehydration in their records. The endothermic reactions in the higher temperature range, beyond 500°C observed in the present investigations, particularly those in the thermal curves for the 1000 mg sample (Fig. 2), may be attributed to successive phase transformations finally leading to anorthite rich plagioclase ($An_{\sim 80}$), and nepheline.

It may be recalled that the first major endotherm in scolecite corresponding to a major water expulsion occurs in the range 210 to 310°C (peak temperatures varying with sample amount). In the mesolite structure, there are alternating planes with one $Na_2(H_2O)$ and two $Ca(H_2O)$ in c-channels. Since mesolite contains both the 'natrolite type' and the 'scolecite type' channels [6], it is considered here more likely that the water sites associated with the scolecite type channels are emptied first and the natrolite type channels in later stages. This is also obvious as natrolite itself needs a much higher temperature for its only step of water loss (Fig. 1). Peng [11] has assumed two types of water molecules in the mesolite structure having different volatility, without assigning specific positions to the water molecules. The complexity in thermal curves at higher temperatures is evidently a result of the structural complexity of this mineral and the higher temperature requirements beyond 400°C for the expulsion of water bonded with the cations being the result of added rigidity to the structure due to the expulsion of successive water molecules.

The results of the present study provide a clue to clarify the succession of expulsion of the water molecules from different sites in the structure of the fibrous zeolites, and also demonstrates water expulsion in a step like manner beyond 400 and 450°C for mesolite and scolecite respectively. This suggests that the water molecules still remain bonded with the cations beyond these temperatures till a complete structural collapse takes place. It may also be seen that the peak temperatures for different reactions show a more or less consistent variation towards higher values with increasing amounts of sample subjected to the heating experiments. On the basis of the work of Alberti *et al.* [in 6] it is noted that different patterns of thermal curves are possible for samples from different localities. Present study further shows that there is also a variation in the thermal curves for different sample amounts from the same location.

* * *

The authors gratefully record their sincere thanks to Shri. K. L. Gadre, of Pune for a handsome donation to support the work on zeolites. Dr. A. Y. Bhale, and Shri. M. B. Makki, of Pune have very generously provided help in sample collection. The authors are thankful to the Head, Geology Department, University of Pune, for providing facilities for this work. We are highly indebted to Janos Kalmár of Hungarian Geological Survey, and Dr. Vivek S. Kale and Dr. Himanshu Kulkarni for their valuable help in preparing illustrations and critically reading the manuscript. The first author (AA) acknowledges with thanks the grants provided by the CSIR, New Delhi, through Research Fellowship (SRF), and partial Travel Grant for attending the IMA'94 at Pisa, Italy.

References

1 R. N. Sukheswala, R. K. Avasia and M. Gangopadhyay, Min. Mag., 39 (1974) 658.
2 A. Alberti, D. Pongiluppi and G. Vezzalini, Neues Jahrb. Miner. Abhandlungen, 143 (1982) 231.
3 M. Koizumi, Miner. J., 1 (1953) 36.
4 E. Pecsi-Donath, Acta Geol. VI Fasc., 3–4 (1962) 429.
5 L. P. Van Reeuwijk, Am. Mineral., 57 (1972) 499.
6 G. Gottardi and E. Galli, Natural Zeolites, Springer Verlag, (1985) 409.
7 L. Pauling, Proc. Nat. Acad. Sci. USA, 16 (1930) 453.
8 W. H. Taylor, C. A. Meek and W. W. Jackson, Z. Kristallogr., 84 (1933) 373.
9 G. Adiwidjaja, Diss. Univ. Hamburg, 1972. (In: G. Gottardi and E. Galli) Natural Zeolites, Springer-Verlag, 1985.
10 V. N. Sveshnikov and V. G. Kusnetzov, Izvest. Akad. Nauk, USSR. Otdel. Khim. Nauk., (1946) 25.
11 C. Y. Peng, Am. Mineral., 40 (1955) 834.
12 E. Pecsi-Donath, Acta Geol. IX (1965) 235.
13 E. Pecsi-Donath, Acta Miner. Petr. XVII Fasc., 2 (1966) 143.
14 E. Pecsi-Donath, Acta Miner. Petr. XVIII Fasc., 2 (1968) 127.
15 L. P. Van Reeuwijk, Meded. Landbouwhoogesch. Wageningen., 74 (1974) 1–88.
16 S. Varadarajan and Desh Mittra, Ind. Mineralogist, 24 (1984) 244.
17 D. R. Peacor, Am. Mineral., 58 (1973) 676.
18 A. Alberti and G. Vezzalini (in: G. Gottardi and E. Galli, 1985), Natural Zeolites, Springer Verlag, 1983, p. 409.
19 M. H. Hey, Min. Mag., 23 (1932) 243.
20 M. D. Foster, US Geol. Surv. Prof. Pap. 504-D (1965) E:D1-E10.