

# ON THE RELATIONSHIPS BETWEEN LATTICE STRUCTURE AND „ZEOLITE WATER” IN GMELINITE, HEULANDITE AND SCOLECITE

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Research into relationships between the lattice and the “zeolite water” content of some zeolites [PÉCSI—DONÁTH, 1965, in print] has suggested that “zeolite water” might occur in various types of bond. This could indeed be proved for e. g. natrolite and desmite, whereas the water content of chabasite turned out to consist in the main of typical “zeolite water”. In therefore seemed indicated to carry out a manysided, detailed study of zeolite minerals of the same lattice type as the above-named, in order to enquire into the nature of the bond in which their water content occurs and into the relationship of that bond to the lattice. The substances studied were:

Gmelinite	Nova Scotia	Canada
Heulandite	Fassa Valley	Switzerland
Scolecite	Attlitz Valley	Switzerland
	and	Boulands Tundra
		Iceland

Investigation started with the recording of the derivatograms of these zeolites, and with the study of the DTA graphs forming part of those derivatograms. Parts of the samples were heated for some time at the peak temperatures indicated by the DTA graphs. Both the original substance and the heated samples were subsequently submitted to X-ray diffractometry and infra-red spectroscopy. The above examinations were completed by full chemical analyses and regeneration tests.

Gmelinite is closely related to chabasite both structurally and chemically. Its silicate lattice has, according to H. STRUNZ [1956], L. S. DENT and J. V. SMITH [1958], R. M. BARRER [1944], BARRER and KERR [1959], the following structure: There is a cage parallel to the *c* axis, consisting of rings of 12 SiO<sub>4</sub> tetrahedra. This cage have on both ends hexagonal double rings of six SiO<sub>4</sub> tetrahedra each, the cavities of which are likewise parallel to the *c* axis, and narrower than the foregoing ones: indeed, the minimum diameter of the cage is about 6,4 Å that of the hexagonal ring, about 3,4 Å. In principle, the cage should be more adsorptive, but most of the water actually absorbed in the rings, because, according to R. M. BARRER [1944], most of the Na ions occupy the cation positions of the larger cavities.

The dehydration process of gmelinite may be traced on the DTA and DTG graphs (Fig. 1). There are two sizable endothermic peaks at 240 and 340 degrees centigrade, respectively, and a weak one at 380 degrees.

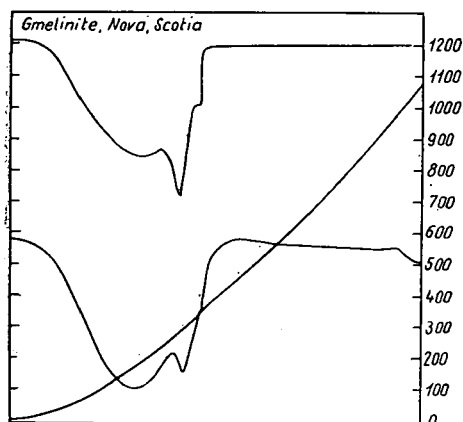


Fig. 1. Gmelinite, Nova Scotia, Canada. DTA and DTG graphs.

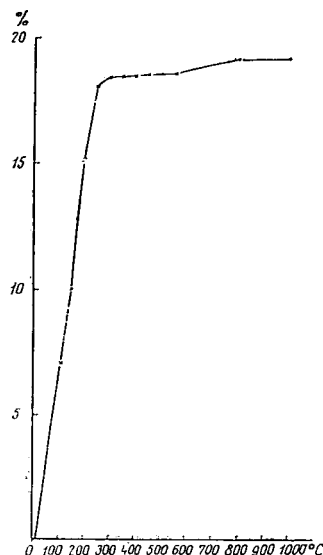


Fig. 2. Dehydration graph of gmelinite

The weight loss during the heating indicates that 18,40 per cent of the total water content of 19,20 per cent escapes up to 300 degrees centigrade, a few further tenths of one per cent leave up to 400 degrees; the rest escapes slowly, gradually up to 1000 degrees (Fig. 2).

The first peak indicates the escape of most of the water content, the second one the escape of a few tenths of a per cent of water and some change in the lattice. This is presumably the cause also of the small endothermic peak at 380 degrees, which also entails some weight loss (see DTG graphs).

Weight loss in a current of air, as established by the devolatilization method of SZÁDECZKY—KARDOSS E.—SIMÓ, B. [1962], is given in the Table 1.

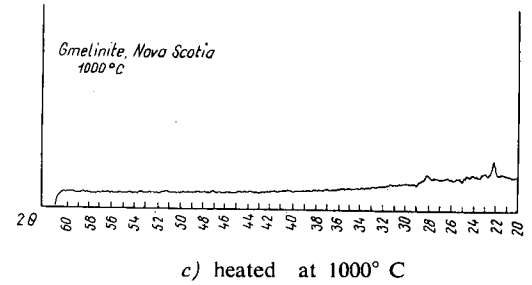
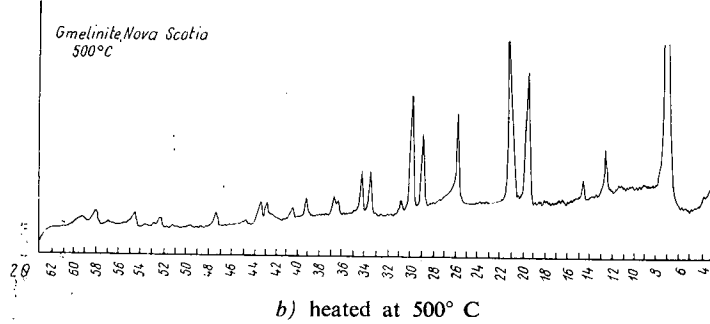
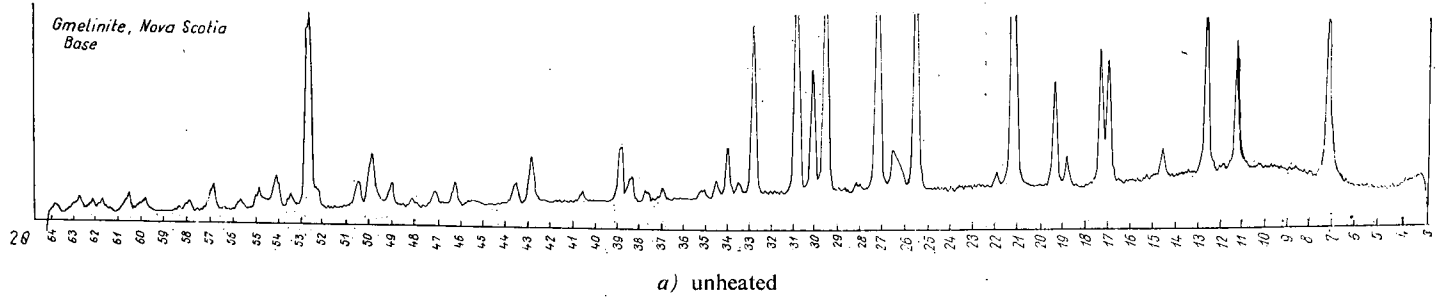
TABLE 1

Weight loss as determined by devolatilization in per cent, for two hours

Temperature degrees C	Gmelinite, Nova Scotia, Canada
280	18,22 %
280 to 340	0,42
340 to 370	0,09
370 to 430	0,05

Escape of water proceeds in essentially the same manner, except that the air-current withdraws the majority of water (18,3 per cent) below 280 degrees.

Fig. 3. X-ray diffractometry patterns of gmelinite



X-ray diffractometry (Fig. 3/a) has been applied to trace the structural modifications taking place under heating. The lines of gmelinite were present on all heated samples, with at most some decrease in intensity. Above 350 degrees centigrade, some amorphous substance is also formed and a slight shift of the  $d/hkl$  values suggests a certain measure of lattice deformation (Fig. 3/b).

Oligoclase and quartz could be identified in the sample of gmelinite heated at 1000 degrees (Fig. 3/c). There was however, quartz also in the original sample; as the lines of quartz were weaker in the heated sample, quartz cannot be declared with certainty a product of transformation.

Infra-red spectroscopy has been performed on both the original sample and on the heated samples subjected to X-ray diffractometry (Fig. 4). Peaks occurring between  $3460$  and  $3700\text{ cm}^{-1}$  in the one hand and between  $3000$  and  $3460\text{ cm}^{-1}$

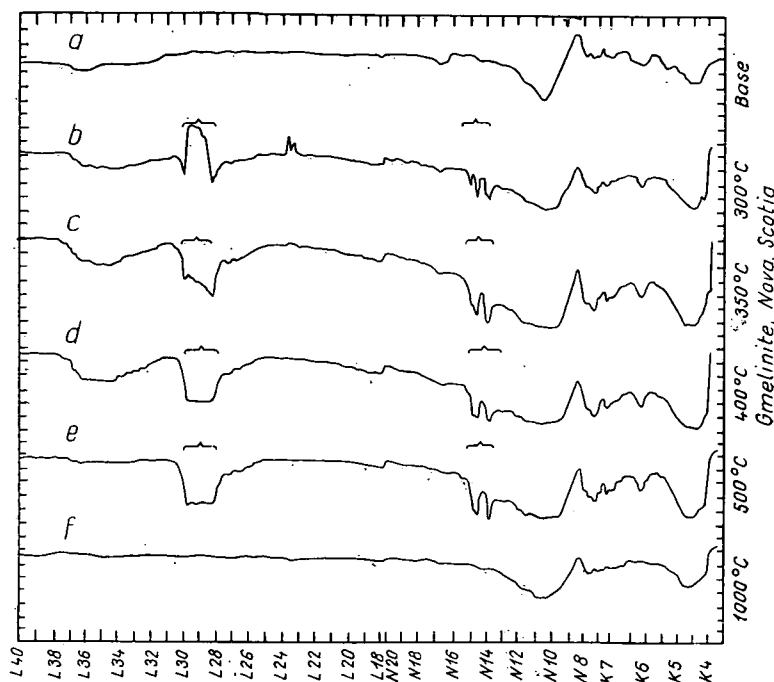


Fig. 4. Infra-red spectrograms of gmelinite

- a) unheated
- b) heated at 300°C
- c) heated at 350°C
- d) heated at 400°C
- e) heated at 500°C
- f) heated at 1000°C

on the other indicate two types of water. The absorption band between  $1620$  and  $1720\text{ cm}^{-1}$  is typical of the  $\text{OH}^-$  radical, that between  $400$  and  $1200\text{ cm}^{-1}$  of the silicate lattice.

In this latter band, the  $\text{OH—Al}$  bond could be detected at  $920\text{ cm}^{-1}$  and the  $\text{Si—O—Al}$  bond at  $750\text{ cm}^{-1}$ . All the above-said substantially holds also for the

samples heated at 300, 350, 400 and 500 degrees, respectively, with the modification that in the latter the absorption band at  $550\text{ cm}^{-1}$  typical of the Si—O—Al[VI] bond is also present. The sample heated at 1000 degrees contained no water at all and its silicate lattice could be identified with that of feldspar.

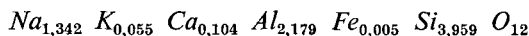
Its *chemical composition* is given by the *Table 2*.

TABLE 2

Anal.: dr. Simó B.  
Gmelinit, Nova Scotia, Canada

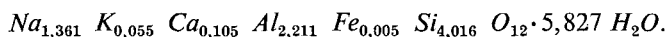
SiO <sub>2</sub>	59,44 %
TiO <sub>2</sub>	0,00
Al <sub>2</sub> O <sub>3</sub>	17,21
Total iron	0,43
MnO	0,00
MgO	0,02
CaO	0,92
Na <sub>2</sub> O	6,45
K <sub>2</sub> O	0,40
Total water	16,04
P <sub>2</sub> O <sub>5</sub>	0,00
CO <sub>2</sub>	0,00
	<hr/> 100,91 %

This chemical composition results in the following structural formula:



(The quartz content furnished by X-ray diffractometry has been subtracted from the SiO<sub>2</sub> data.)

Taking into account also the water content, we get



*Studies into the regeneration* of gmelinite have shown that upon heating at 100 degrees centigrade and exposition to an atmosphere saturated with water vapour the mineral resorbs its full original water content, and even about 1 percent more than that. Heating at 150 and 200 degrees yields the same result. This is remarkable in as much as water loss increases with temperature:

a maximum of 7 percent at 100 degrees centigrade

10	150
15	200

whereas water content after saturation in vapour always attains the maximum, about 18,50 percent. That is, regeneration tends to improve with increasing temperature. However, resorption after heating at 250 and 350 degrees does not exceed an average 9 to 10 percent (*Fig. 5*).

These *results* largely support the resemblance between gmelinite and chabasite, while pointing out also some differences in their properties.

Besides the similarity of the lattices, it is the similarity of the process of regeneration that should be emphasized in the first place. The infra-red absorption bands

of the silicate lattice, occurring in the 400 to 1000  $\text{cm}^{-1}$  range, also resemble those of chabasite and confirm the above statement. Gmelinite, like chabasite, loses most of its water content below 200 degrees centigrade and only a small part (less than chabasite) above.

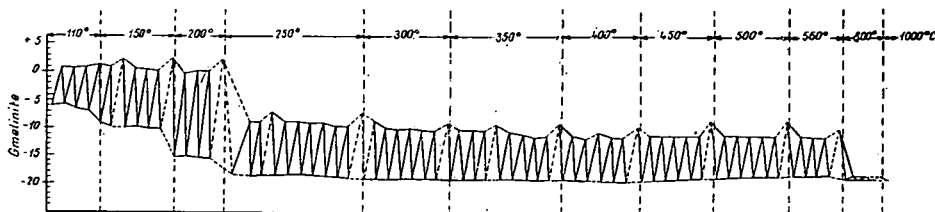


Fig. 5. Regeneration graph of gmelinite

The DTA graph of gmelinite, however, is widely different from that of chabasite. Also, the absorption band of water in the 3000 to 3700  $\text{cm}^{-1}$  range of the infrared spectrum is different. Comparison of the dehydration and devolatilization processes also suggests that the difference resides in the nature of the water bond. In the author's opinion the majority of the water content is typical "zeolite water" also in gmelinite the rest being water bound to the cation. This latter, however, seems to be bound much stronger than in chabasite [PÉCSI-DONÁTH É., 1965] and its removal takes more energy, as witness the sharp endothermic peak of the DTA graph. As stated above, structural research has pointed out the presence of two kinds of cavities in the lattice, and water may be present in both the wider and the narrower cavities. It seems likely that lack of space beside Na and other cations substituting it in the wider cage as suggested by R. M. BARRER [1944] forbids the entry of any considerable amount of water, and any water entering into those cavities is immediately bound to the cations. Most of the water content occupies the small cavities in a weaker type of bond. This type water escapes gradually up to 300 degrees centigrade, whereas the type bound to the cations leaves under the formation of a sharp endothermic peak and a certain change in lattice dimensions. Complete collapse of the lattice takes place at 800 degrees, whereas a new phase (feldspar) is not formed until 1000 degrees.

From a practical standpoint, gmelinite heated to any temperature below 800 degrees performs as a fairly high-grade adsorbent and regenerates almost completely. Best adsorption is attained by heating at 250 degrees. This is presumably the optimum temperature for dislocating the lattice to such a degree as permits the substitution of almost all the escaping water by the substance to be adsorbed.

Study of the heulandite lattice [M. H. HEY, 1935, M. H. HEY, and F. A. BANNISTER, 1934, W. H. TAYLOR, 1934, U. VENTRIGLIA, 1955, J. WYART, 1933] has revealed that the  $(\text{Si}, \text{Al})\text{O}_4$  tetrahedra constitute six-unit rings which in their turn form a honeycomb-type structure parallel to [100]. Parallel to [001], on the other hand, there are minute channels bounded by five- and eight-unit rings respectively. The cations occupy all these cavities. Just like the water molecules, they are free to move about rather than having a fixed position.

*Derivatograms* reveal that heulandite loses its water content in three steps (Fig. 6), with peaks at 220, 420 and 520 degrees centigrade on the DTA graph. The weight loss values observed at the end of these endothermic processes were

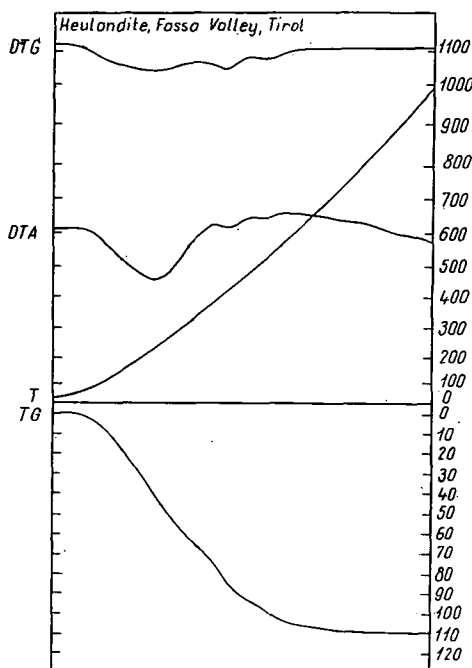


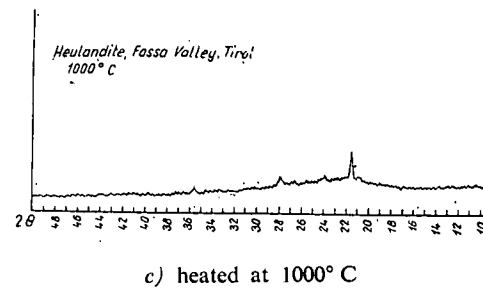
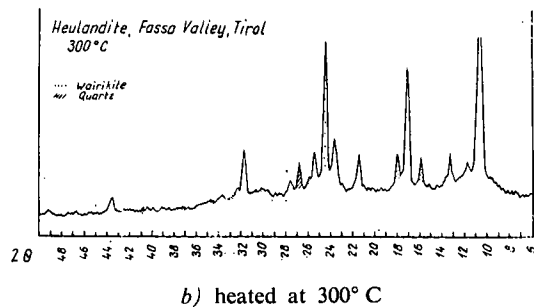
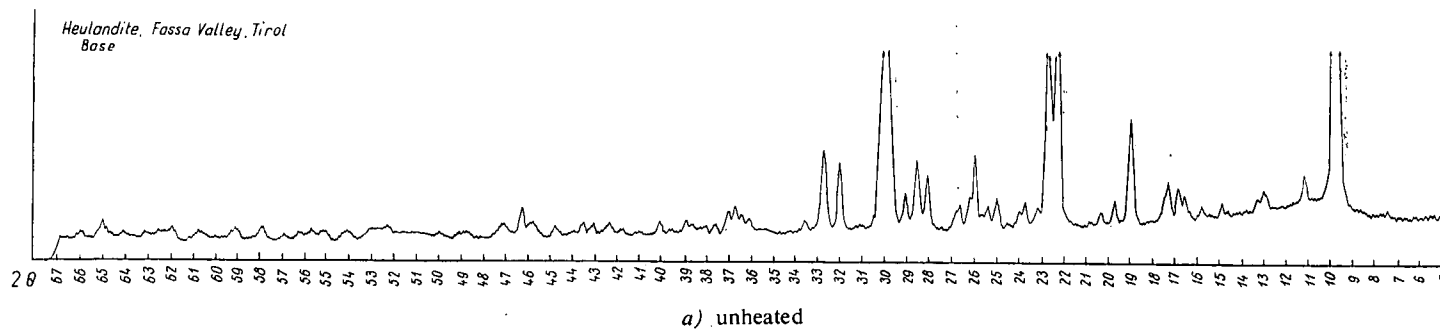
Fig. 6. Derivatogram of heulandite with DTG, DTA, T and TG graphs

1,83	percent at 110 degrees centigrade,
8,57	360
3,00	490
2,17	780
<hr/>	
15,57	percent.

X-ray diffractometry has been performed on both the unheated sample (Fig. 7/a) and on the samples heated at 300, 400, 600, 800 and 1000 degrees, [M. KOIZUMI and R. ROY, 1960] state heulandite to have been decomposed into wairikite and  $\text{SiO}_2$  at 320 degrees. In our sample heated at 300 degrees, we could demonstrate the presence of these substances, although the d/hkl values of heulandite could still be identified (Fig. 7/b). The sample heated at 400 degrees included a substantial amorphous phase, indicating that the mineral had essentially been decomposed up to that temperature, but some of the d/hkl values of heulandite were still present, although with considerable angle shifts. Heulandite heated at 600 to 800 degrees centigrade becomes completely amorphous and turns at 1000 degrees into a feldspar of about bytownitic composition. (Fig. 7/c).

The infra-red spectrum of heulandite includes bands of absorption between 3000 and 3700  $\text{cm}^{-1}$  and a peak at 1640  $\text{cm}^{-1}$ , indicating the presence of water, and bands occurring between 400 and 1500  $\text{cm}^{-1}$ , characteristic of the silicate lattice and agreeing well with data found in literature [R. G. MILKEY, 1960, H. MOENKE, 1961]. As there are two weak peaks at 3620  $\text{cm}^{-1}$  and in the 3400 to 3490  $\text{cm}^{-1}$

Fig. 7. X-ray diffractometry patterns of heulandite





range, respectively, one may think of an incomplete agreement of the water contents. (Infra-red spectrograms of the heated samples have been prepared with nu-jole.) The absorption band due to water in heulandite heated at 300 degrees centigrade is characterized by a peak at about  $3600\text{ cm}^{-1}$ , that of the sample heated at 400 degrees, by a broad band in the same range. The absorption band at about  $1600\text{ cm}^{-1}$  vanishes from the diagram of this latter sample. The absorption band between 400 and  $1200\text{ cm}^{-1}$ , due to the silicate structure, does not change up to 400 degrees centigrade, but there it becomes very broad and vague. The sample heated at 1000 degrees turned out entirely waterless; its silicate lattice is that of a feldspar (Fig. 8).

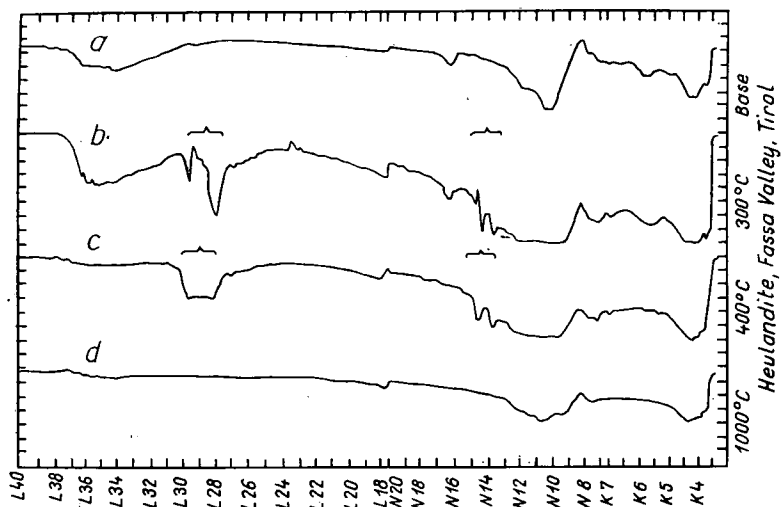


Fig. 8. Infra-red spectrograms of heulandite

- a) unheated
- b) heated at  $300^{\circ}\text{C}$
- c) heated at  $400^{\circ}\text{C}$
- d) heated at  $1000^{\circ}\text{C}$

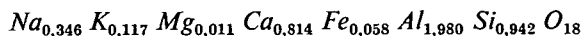
TABLE 3

Anal: dr. Simó, B.

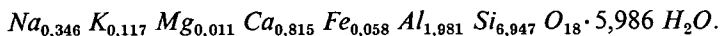
Heulandite, Fassa Valley, Tirol

SiO <sub>2</sub>	59,62 %
TiO <sub>2</sub>	0,00
Al <sub>2</sub> O <sub>3</sub>	14,44
Total iron	0,68
MnO	0,00
MgO	0,06
CaO	6,52
Na <sub>2</sub> O	1,52
K <sub>2</sub> O	0,80
Total water	15,39
P <sub>2</sub> O <sub>5</sub>	0,00
CO <sub>2</sub>	0,00
	<hr/> 99,03 %

On the basis of the above *chemical composition* (Table 3) referred to the waterless substance and to 18 O<sub>2</sub>, one obtains the formula



and taking into account the water content, too



A diagram composed of the data on regeneration (Fig. 9) shows that the mineral is consistently able to resorb up to 200 degrees centigrade more water than it loses on heating, although it loses more water at higher temperatures (that is, its regenerative ability increases with rising temperature). Heating at 250 degrees and above may bring about a lattice change which precludes any further intake of water. Nevertheless, further heating causes some weight loss, indicating that the mineral still contains some water. Above 400 degrees it turns, however, into a substance that is hardly capable even of superficial adsorption.

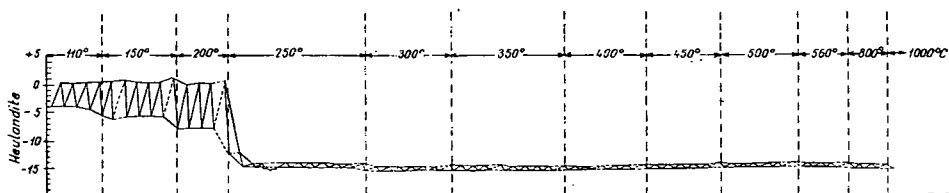


Fig. 9. Regeneration graph of heulandite

On the basis of the above-described *results* one may state concerning the relationship between lattice structure and water content in heulandite that part of the water content is fixed whereas the rest may move relatively freely in the cavities of the lattice. It is this latter part which escapes freely and is as freely substituted; in some instances water intake may exceed the preceding water loss.

Heating above 250 degrees centigrade destroys the regenerative ability of heulandite. According to J. WYART, [1933], the escape of water above 210 degrees entails a substantial change in structure. The dimensions of the unit cell also change. According to ROSKOWA [1962], water occurs in layers and is in some way bound to the cations. She also thinks that the removal of these water molecules is most likely above 200 degrees.

The *d/hkl* values of heulandite heated above 300 degrees are shifted partly to lower, partly to higher angles, thus confirming the above statement.

In the present author's opinion, water escaping at 250 degrees plays some part also in the layered structure of heulandite, perhaps even in bonding together the layers, as its removal brings about a change in the lattice, a ceasing of the regenerative ability. It is at 300 degrees that the transformation into wairikite and SiO<sub>2</sub> begins. Hence, the peak reaching up to 360 degrees on the DTA graph reflects both the lattice change and the loss of almost 9 percent of water. As to water still present at 500 to 600 degrees centigrade, the author thinks that it may be in a bond, resembling that of water in gels, in the considerable amorphous phase evinced by X-ray diffractometry. Near collapse of the lattice at those temperatures precludes any regeneration.

Up to 300 degrees, heulandite is a fairly high-grade adsorbent, and its regeneration even improves up to 250 degrees centigrade.

Scolecite. Two scolecite specimens from two different localities exhibited a highly similar behaviour under the investigative procedures employed.

*Tracing the water loss process* of scolecite by means of the derivatograph, one obtains a TG graph indicating measurable water losses as high up to 900 degrees centigrade. Both the DTA and DTG graphs bear four sharp and two flat endothermic peaks. The sharp peaks occur between 200 and 220, at 470, between 490 and 520, and between 540 and 560 degrees centigrade, respectively; the flat peaks reach their maxima at 690 and 840 degrees respectively. The weight losses corresponding to the terminal ends of the peaks are as follows:

Scolecite			
Attlitztal, Switzerland		Boulands Tundra, Iceland	
360 °C	4,57—4,37 %	374 °C	4,70—4,70 %
455 °C	6,34—1,77	480 °C	6,4 —1,70
520 °C	9,19—2,85	540 °C	9,3 —2,9
571 °C	9,83—0,64	580 °C	10,25—0,95
765 °C	11,86—2,03	765 °C	12,47—2,22
950 °C	13,39—1,53	970 °C	13,60—1,13
13,39 %		13,60 %	

*X-ray diffractometry* has been applied besides the original sample to samples heated at 350, 400, 500, 800 and 1000 degrees centigrade. The results of these as well as of the other examinations (chemical analysis, infra-red spectroscopy, deriva-

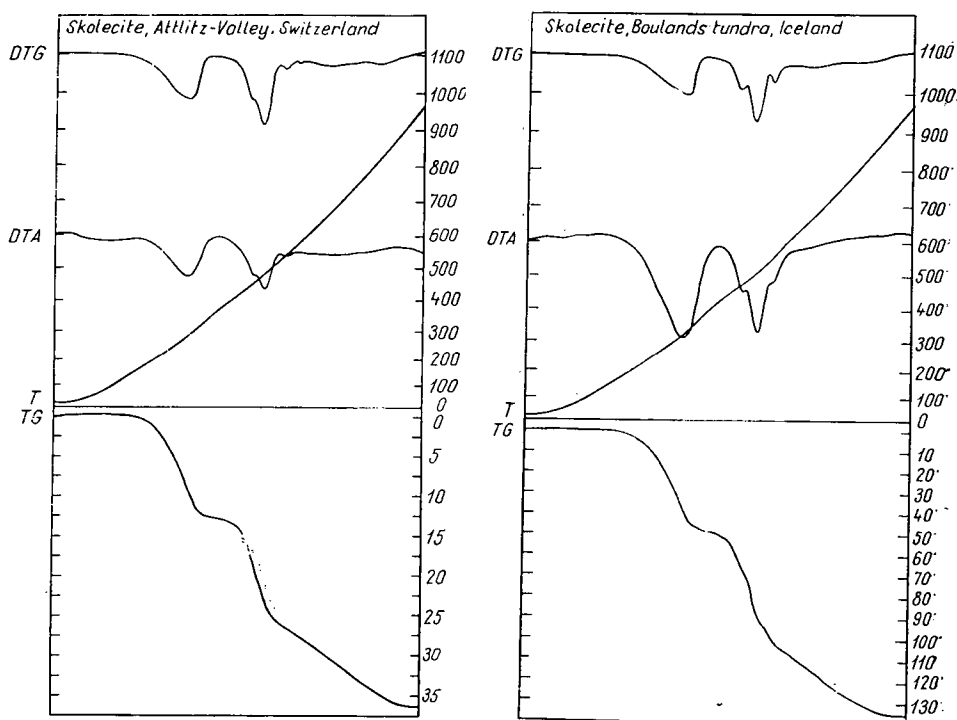
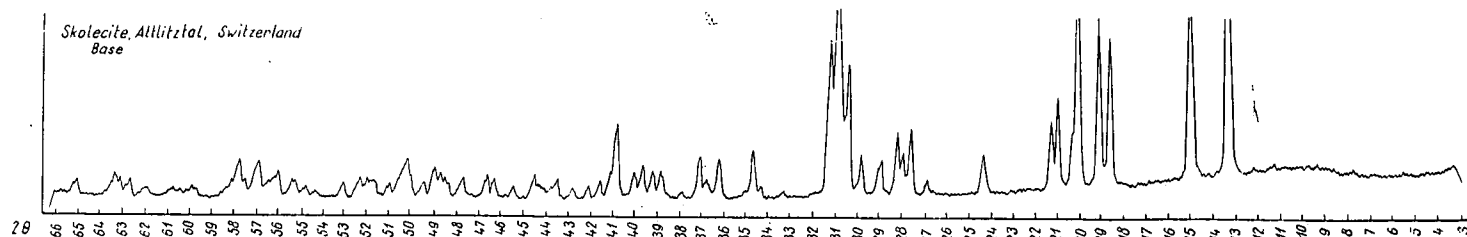
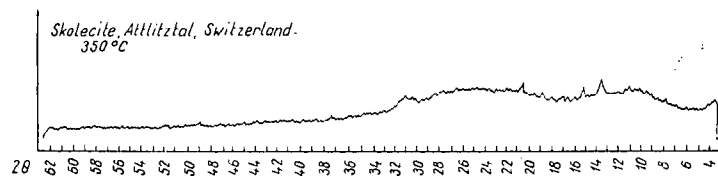


Fig. 10. Derivatogram of scolecite with DTG, DTA, T and TG graphs

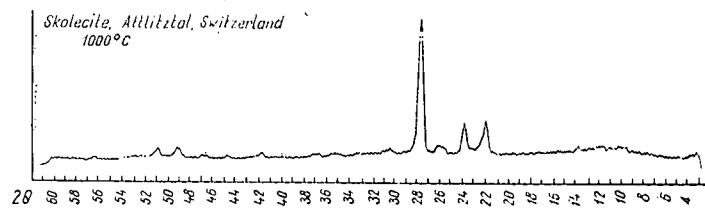
Fig. 11. X-ray diffractometry patterns of scolecite



a) unheated



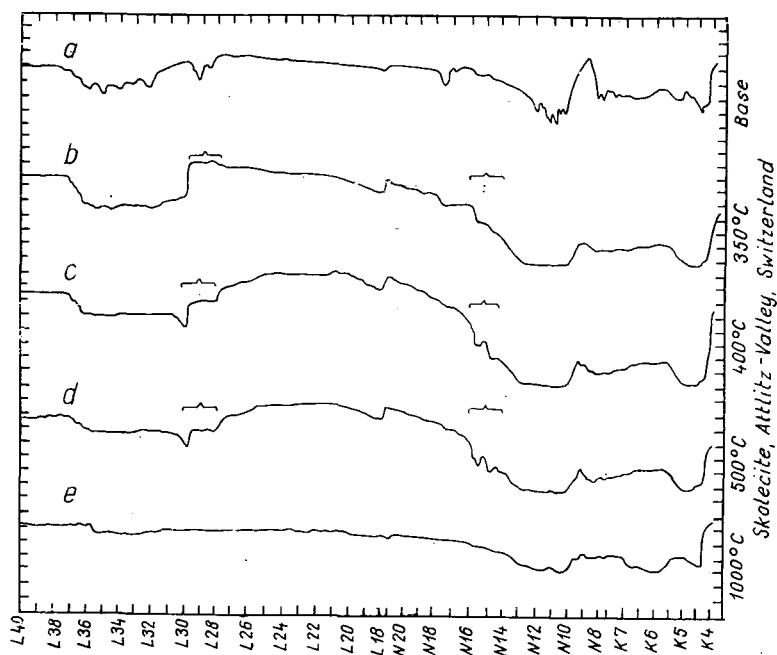
b) heated at 350°C



c) heated at 1000°C

tograms) all show a fairly good agreement between the two specimens and with data encountered in literature (*Fig. 11/a*) and have called the attention to certain specific properties, unobserved so far, of scolecite. In samples heated at 350 degrees (*Fig. 11/b*), one or two principal  $d/hkl$  values of scolecite could still be identified besides a substantial amount of amorphous substance. The samples heated at 400, 500 and 800 degrees were completely amorphous, and the mineral turned into anorthite at 1000 degrees (*Fig. 11/c*).

*Infra-red spectrograms* have been prepared on the unheated samples and on the samples heated at 350, 400, 500 and 1000 degrees, respectively of both specimens. The unheated spectrogram (*Fig. 12*) is in full agreement with those found in literature [R. G. MILKEY, 1960] concerning both absorption bands, that of 3100 to 3700  $\text{cm}^{-1}$  as well as that of 400 to 1200  $\text{cm}^{-1}$  (this latter being characteristic of the silicate lattice). The first band clearly indicates by six narrow bands of absorption the discrete bond energy levels of water in scolecite as opposed to heulandite and gmelinite. In the silicate lattice, both  $\text{OH}-\text{Al}^{3+}$  930  $\text{cm}^{-1}$  and 910  $\text{cm}^{-1}$  are clearly defined. After heating at 350 degrees, the above-mentioned water peaks are still distinct and there is also the common water band at 1620 to 1640  $\text{cm}^{-1}$ . In the sample heated at 400 degrees, the intensity of the peak at 1640  $\text{cm}^{-1}$  is substantially decreased. The peaks between 3100 and 3700  $\text{cm}^{-1}$  broaden into bands but there are still four distinct peaks indicating the presence of water in a fairly



*Fig. 12.* Infra-red spectrograms of scolecite from Attilitz-Valley, Switzerland

- a) unheated
- b) heated at 350° C
- c) heated at 400° C
- d) heated at 500° C
- e) heated at 1000° C

strong bond. At 500 degrees, the peak at  $1640\text{ cm}^{-1}$  disappears, but the one at  $3600\text{ cm}^{-1}$  is still weakly visible. At 1000 degrees, a diagram representative of anorthite turns up.

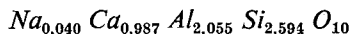
The results of the *chemical analyses* are given below (Table 4).

TABLE 4

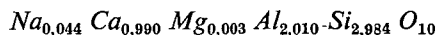
Anal.: dr. Simó, B.

	Scolecite	
	Boulands Tundra Iceland	Attltitz Valley Switzerland
SiO <sub>2</sub>	46,23 %	46,00 %
TiO <sub>2</sub>	0,00	0,00
Al <sub>2</sub> O <sub>3</sub>	26,40	27,12
Total iron	0,00	0,00
MnO	0,00	0,00
MgO	0,03	0,01
CaO	14,32	14,30
Na <sub>2</sub> O	0,35	0,32
K <sub>2</sub> O	0,00	0,00
Total water	13,59	13,35
P <sub>2</sub> O <sub>5</sub>	0,00	0,00
CO <sub>2</sub>	0,00	0,00
	100,92 %	101,10 %

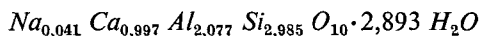
These results yield the following structural formula, referred to 10 O<sub>2</sub> and the waterless substance: Attltitz Valley, Switzerland:



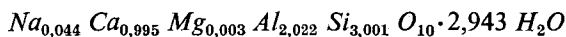
Boulands Tundra, Iceland:



Taking into account the water content, too, this modifies to Attltitz Valley, Switzerland:



Boulands Tundra, Iceland:



*Data of regeneration.* As distinct from heulandite and gmelinite, scolecite does not lose any of its water content up to 200 degrees centigrade and is incapable of absorbing more water than it has lost on dehydration. At 200 degrees there is a weight loss of about 4 per cent; at 250 degrees, weight loss amounts to 11 per cent occurs, but whereas the water lost at 200 degrees may be resorbed, that lost at 250 degrees may not. At higher temperatures the substance gradually loses water up to 1000 degrees. This water loss is incapable of regeneration (Fig. 13).

The above *results* concerning the behaviour of scolecite permit to draw the following conclusions as to the relationship between its lattice and water content:

The water content of scolecite is, as that of the rest of the natrolite group, in a "crystal-water-type" bond which is reflected by several bands of absorption in the infra-red spectrum. DTA, DTG and infra-red spectroscopy all reveal that water escapes in six steps. Differences in water bond force are reflected in a non-

uniform rate of water escape. Most of water (about 6 percent) leaves up to 350 degrees, which temperature is also the upper limit of the thermal stability of the lattice.

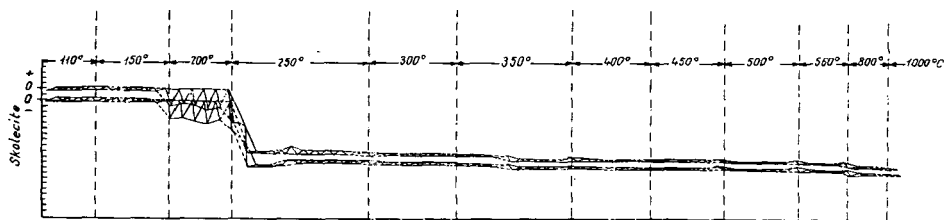


Fig. 13. Regeneration graphs of scolecites

KOIZUMI and ROY [1960] state scolecite to decompose into anorthite, wairikite and  $H_2O$  at 300 degrees centigrade. In the experience of the present author, this decomposition reaches a fully amorphous stage at 350 degrees. Hence, water escaping up to that temperature is an essential element of the lattice, as its removal entails the collapse of the structure. X-ray diffractometry evinces a completely amorphous substance above 350 degrees, and the infra-red spectra also indicate the collapse of the silicate lattice. However, since the presence of further amounts of water is proved by further peaks on the DTA and DTG graph, respectively and well-defined bands of absorption on the infra-red spectrogram, it is to be supposed that lattice collapse is not complete after all and that there remains a fine-grained crystalline phase capable of binding water at various energy levels. This water gives three sharp endothermic peaks at 455, 480 and 540 degrees centigrade, that is, at fairly well-defined bond energy levels, whereas the remaining water, about 3 per cent up to 900 degrees, may occur in a bond resembling that of water in a silica gel. In the course of further research the author deems it of particular importance to investigate this amorphous phase, in order to clear up the positions and eventually also the bond type of this high-temperature residual water content.

#### ABSTRACT

The author has applied the derivatograph, the X-ray diffractometer, and the infra-red spectrograph to the study of three zeolites representing three different lattice types, gmelinite, heulandite and scolecite. She has studied their regeneration and chemical composition as well. Besides the natural minerals, some of the above-named experiments have been performed also on samples heated at various temperatures.

The silicate lattice of gmelinite does not change up to 800 degrees centigrade. At 1000 degrees it turns into an oligoclase feldspar. Most of its water content occupies the smaller cavities of the lattice, being bound neither to the cations, nor to any specific lattice points. Some of it is held in the larger cavities, most of which are occupied by the cations, and is bound to these latter. The mineral is highly absorptive up to the complete collapse of the lattice at 800 degrees centigrade: its optimum adsorption is attained after heating at 250 degrees.

The silicate lattice of heulandite is stable up to 200 degrees centigrade. Upon heating at 300 degrees, one observes a lattice deformation that has taken place at a slightly lower temperature and the presence of some wairikite and quartz. At 400 degrees it is the amorphous phase that dominates the picture, with one or two of the  $d/hkl$  values of heulandite still present. At a higher temperature the substance grows roentgenographically amorphous and at 1000 degrees it is transformed into a bytownitic feldspar. A large part of its water content constitutes an essential element of the lattice, presumably intercalated between the layers and playing a role in holding them to-

gether. The loss of this type water at 250 degrees means the simultaneous loss of the regenerative ability. About 5 percent of the original water content stays behind and only leaves at 400 degrees; it is presumably bound to the amorphous phase like the water bound by gels.

The silicate lattice of scolecite can still be identified at about 400 degrees centigrade. Above that, this mineral also turns roentgenographically amorphous. Its transformation into metascolecite and the loss of one mole of its water content takes place by the end of the first endothermic peak on the DTA graph, that is, up to 400 degrees. If heated at 200 degrees, the mineral preserves its ability to regenerate: it is presumably at this temperature that its transformation into metascolecite takes place. At 1000 degrees centigrade it turns into anorthite. Its water molecules are bound to well-defined points of the lattice. Up to 570 degrees a second mole of water escapes, giving rise to a further sharp endothermic peak. X-ray patterns suggest that this water is bound to a crystalline phase of a grain so fine as to go undetected on the diffraction patterns. The third mole of water leaves above 600 degrees from a completely amorphous (gel) phase.

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