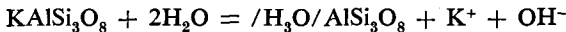


Fig. 1. The structural arrangement in monoclinic potassium feldspar, viewed normal to (001). Hydronium (encircled) now occupies the K-sites.

attachment of molecular water. Hydronium will presumably react: the loss of a proton will then degrade it to a water molecule.

The size of the water molecule is 1.38 Å and of potassium 1.33 Å, a fairly good agreement in size, offering a theoretical possibility for iso-structural exchange. It must be presumed, however, that the feldspar lattice is slightly "elastic". The lattice of the hydrolytically transformed feldspar will expand according to this model. This is even more the case when further expansion is to be expected if the proton reacts with environmental oxygens.

The exchange reaction in its simplest chemical formulation may accordingly be written:



Nor in this notation the OH-depression which TAMM and GARRELS and HOWARD observed in their experiments, can be explained. The explanation may be found in the nature of the proton reaction which follows the ion-exchange reaction.

A structurally based presentation is given in fig. 1. This shows the interspace in the "sheets" which are formed by crosslinkage of the Si-O-Al "chains", projected normal to (001) and now occupied by hydronium. The water molecules, with tetrahedral valence distribution are thus alternately linked: i.e. the tetrahedrons are pointing in opposite directions. The forces originally attracting the potassium ion are keeping the water molecule in ordered position; the "ionic" contribution acts herewith on the

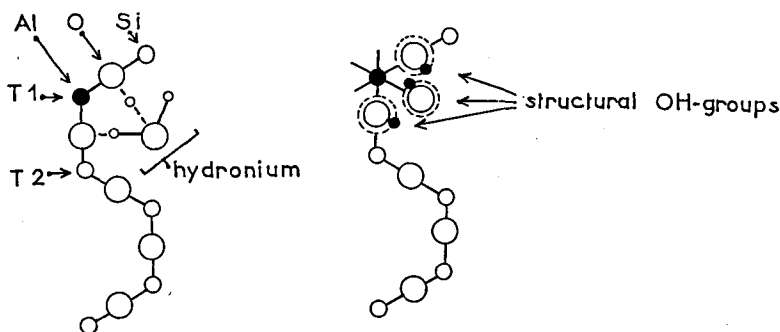


Fig. 2. The chain-like linkage in potassium feldspar parallel to [010].

- a) hydronium occupying the site of the potassium ion: the Al-atom on a T1-site is 4-coordinated.
- b) possible arrangement of structural OH-groups around the Al-atom, after desintegration of the hydronium molecule into its ionic components: simultaneous development of 6-coordination of aluminium seems required.

proton-configuration of the hydronium. The coordination is thus basically still the same after substitution.

A further weakening of the bonds, in this case also of the linkage in the water molecules, may break down the molecular water by incorporation of the ionic groups in the neogenetic structure, as shown in fig. 2.

This step may produce OH-groups which can be incorporated in the structure, especially around the Al-atoms which have a tendency to attain octahedral coordination, as the character of the bonds changes. It is supposed for this reason that proton-reaction simultaneously offers a possibility for incorporation of OH-groups, released by the ion-exchange reaction.

It may explain the OH-depression found by GARRELS and HOWARD. It is tentatively suggested that a certain number of released OH-groups will be attached to silica, forming monomeric $\text{Si}(\text{OH})_4$ which is slightly soluble in water.

In this way the continuous neogenetic transformation of the feldspar lattice is more or less selfsustaining, on the condition that the released cations and the released silica are continuously removed from the environment. The solvent must therefore steadily be renewed.

The proposed model shows two distinct features:

1. entering of ordered "molecular" water into the feldspar lattice: hydronium is suggested to balance the charges,
2. selfsustainment of the proton-reactions under weathering conditions, i.e. a constant flow of carrier solvent away from the environment.

The model, however, does not completely account for the structural change from a tectosilicate to a phyllosilicate structure, an aluminium-hydroxide- or aluminiumoxyhydroxide structure. At this point environmental conditions remain to be considered including a mechanism of dehydration of the reaction products.

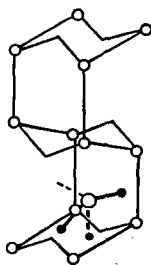


Fig. 3. The "double-chain" in potassium feldspar: tetrahedrally coordinated hydronium is incorporated in the structure.

Only (Si, Al)-sites are shown in the tecto-silicate network.

The self-sustainment of the suggested reactions makes the weathering process principally independable of the pH, as long as the condition for low alkali concentration and low silica content of the solvent is maintained.

It remains to account for the necessary expansion of the hydrolytically transformed feldspar lattice. The position of the molecular hydronium (or a water molecule) in the silicate network of feldspar may be visualized as shown in fig. 3. The model is viewed along a Si-O-Al "double chain", simplified by leaving the cross-linkage which forms a closed network out. The possibility for expansion of the feldspar structures lies in the different O-Si(Al)-O angles within the double chains (compare the structures of maximum microcline and of sanidine). If all the O-Si(Al)-O angles are at their maximum found, the length of, for example, the 001-spacing in monoclinic potassium feldspar will theoretically be 6,59 Å. In this respect the structural position of the Al-atoms may warrant a difference in the capacity for expansion for different potassium feldspars. However, a priori it does not seem to be a necessary condition for the model exchange reaction whether the Al-atom is found in the T_1 - or in the T_2 position in monoclinic feldspars.

A more elaborate view on the structure of monoclinic potassium feldspar discloses that the expansion may be expected to take place in two directions perpendicular to each other. The directions (001) and (010) are favoured, as these directions show a certain symmetry in linkage, which is also the weakest linkage in the feldspar structure, viz. cleavage.

Two features of the model may be experimentally verified:

1. a structural expansion, resulting in a shift of certain reflections in the XRD-diagrams towards extended spacing,
2. ordered water molecules in the structure, detectable in hydrolytically transformed samples by IR-spectroscopy.

EXPERIMENTAL DETAILS

Clear adularia from St. Gothard, Switzerland, was used in the experiments. The adularia was powdered to less than sieve mesh DIN 100 (0.6 mm).

Besides adularia, hydromica from a drill core taken near Åkirkeby, Bornholm (DGU, 247.115) was employed as check material, aiming to demonstrate that a weathered residu of potassium feldspar was not affected by the experimental conditions. This material was kindly placed at my disposal by the Geological Survey of Denmark, Charlottenlund.

Finally, blind runs were carried out to check possible influence on the pH from the polythene bottles and tubing used in the experiments. All runs were made at 22° C.

Five grams of the pulverised material was placed in a polythene bottle, the solvent was kept in circulation by peristaltic pumps. The solvent was renewed at intervals still keeping a controlled low cation-concentration.

The duration of the runs varied from 1 to 3 months.

The solvent was prepared by adding low concentrations of different cations and anions in order to study a possible influence on the hydrolytic process. The pH – though varying from run to run –, has been kept constant within certain limits.

Following runs were carried out:

1. pure water, pH-interval 6 – 6.5, using 0.1 m HCl for pH adjustment,
2. solvent of 0.05 m NaHCO₃ + 0.05 m KHCO₃, pH-interval 7 – 7.5, using 0.1 m oxalic acid for pH-adjustment, only 0.05 m KHCO₃-solvent was used for the experiment lasting over a month,
3. solvent of 0.01 m MgCl₂·6 H₂O + 0.01 m KCl, pH-interval 6 – 6.5, maintained by a slow CO₂ gasflow.

These three runs were done on both adularia and on hydromica. About 15 litres of solvent has been used in each experimental run. No quantitative determinations were made of the leached potassium, such data can be found in CORRENS (1962) and McNAMARA (1966), as the main object of the study was the detection of possible structural changes in the feldspar lattice, on hydrolysis.

McNAMARA (1966) gets the following results, after shaking microcline powder in water in polythene bottles for several days:

	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	H ₂ O+	H ₂ O-	total
K-feldspar untreated	66.3	18.3	0.3	4.4	10.2	0.5	0.2	100.2
K-feldspar disintergrated	64.8	18.8	0.2	3.8	9.1	1.3	1.8	99.8

anal. V. GRUNDULIS.

He states that there is a decrease in alkali content upon hydrolysis accompanied by an increase in alumina and water. When the analyses are recalculated on an anhydrous basis, an increase in silica is also apparent.

Other quantitative data concerning the reaction between potassium feldspar and water are mentioned by TAMM (1929), who also noted that the finest fraction of feldspar crushed in water for several days (2–23), having an average particle size of 0.47 μ contained 3.7 per cent water, which only could be expelled at temperatures above 110° C. This is obviously structurally incorporated water. Similar results were produced in plagioclase. The

hydromica was apparently not affected by the present experimental procedure. No structural change could be detected by means of XRD, nor did the solvent contain resolved silica.

STRUCTURAL CHANGES IN ADULARIA

As might be expected from the model proposed, the three runs gave similar results. The model reaction-scheme predicts that given the conditions, i.e. a buffered solvent, the only expectable change is a superficial exchange of potassium by hydronium, moderated by the cations in solution. The object of the experiments was mainly to demonstrate that this step in the reaction was basically independent of the cation content of the solvent, being a reaction between water and potassium feldspar. That this reaction took place could be detected by the gradual rise of the pH of the solvent when not adjusted by adding acids.

After eight to twelve days the finest fraction of the pulverised material gets slimy. Very fine particles, less than 1μ , may then be caught by the circulating solvent. At this stage X-ray diffraction reveals the development of a shoulder on the 3.25 \AA reflection of adularia, positioned around 3.30 \AA , which gradually develops into a separate peak at 3.31 \AA in oriented airdried powder samples, sedimented on glass. During the experiment the position of this newly developed peak does not change. Fig. 4 shows the XRD-diagrams of hydrolytically transformed adularia with an interval of two months. It shows the structural changes in the first experimental run, from the moment at which the 3.31 \AA peak became clearly visible, 22 days after start, until the moment at which the experiment was stopped, nearly two months later. The other two runs followed exactly the same pattern.

The simultaneous relative decrease of the adularia reflections at 6.46 \AA and 3.25 \AA shows that the structural changes occur on the cleavage planes. The "monoclinic" diffraction pattern of adularia, according to these XRD-diagrams, makes it impossible to distinguish between the $00l$ and $0k0$ reflections. The 2θ -equivalent of the Ångström spacing makes it moreover virtually impossible to detect the structural change on the first order reflection. On the basis of X-ray diffraction alone, there seems to be little doubt that the structural change must be interpreted as lattice expansion, since the development of the 3.31 \AA reflection occurs simultaneously with the diminishing of the 3.25 \AA reflection in the second order of the 001 spacing.

The infrared spectrum in the region 3000 to 4000 cm^{-1} of hydrolytically transformed adularia is given in fig. 5. The sample is the same as the one which has been used for X-ray diffraction, as shown in fig. 4.

H-adularia shows infrared absorption bands at 3380 , 3400 , 3450 , 3532 and 3628 cm^{-1} .

Since the bands around 3400 cm^{-1} correspond to stretch vibrational frequencies of water molecules, it seems likely that absorbed water is the main cause of the bands at 3380 , 3400 and 3450 cm^{-1} . DEKEYSER, WOLLAST and DELAET (1963) studying the dehydration of Zettlitz (=Sedlec) kaolin came to the conclusion that the broad absorption band at 3440 cm^{-1}

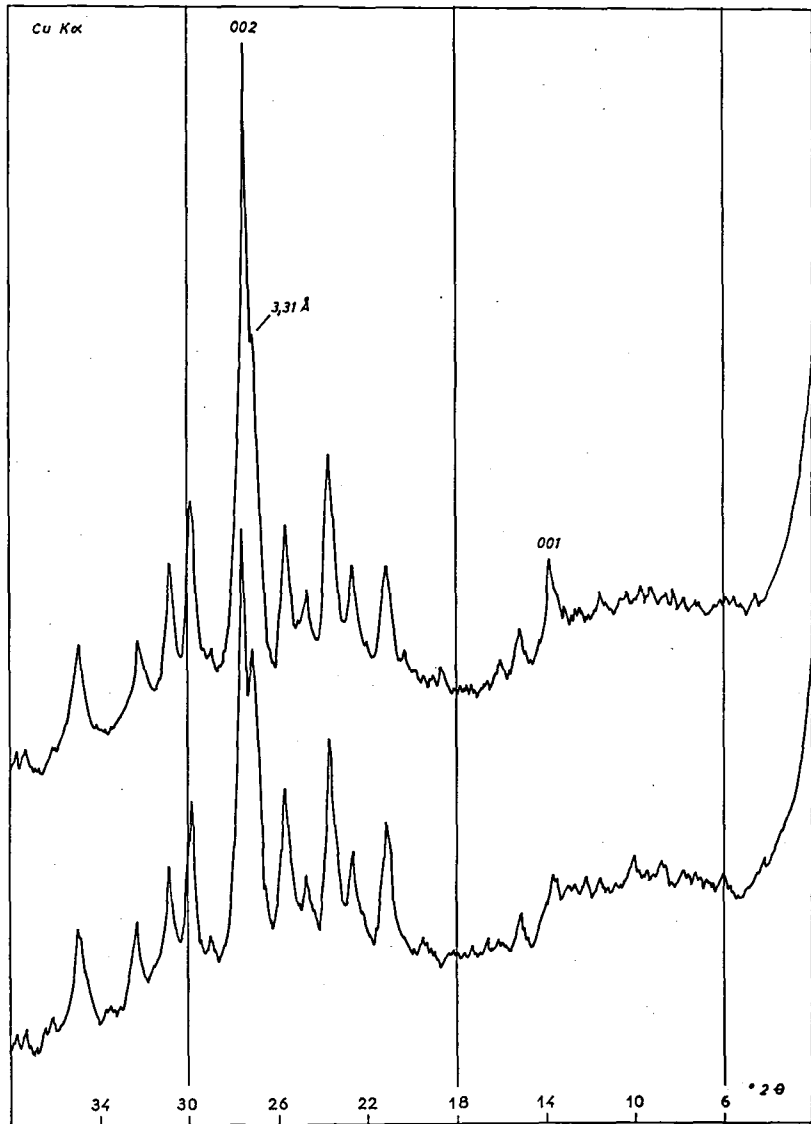


Fig. 4. X-ray diffraction diagrams of hydrolytically transformed adularia, showing the development of the 3.31 Å-spacing (expanding lattice) as discussed in the text.

should be attributed to "OH groups situated in structural defect where they undergo strong interactions" (op.cit. p. 77), since the band, though diminishing upon heating, was still visible in the IR-spectrum after heating at 400° C , where the kaolin had lost 87 % of its "water" content. However,

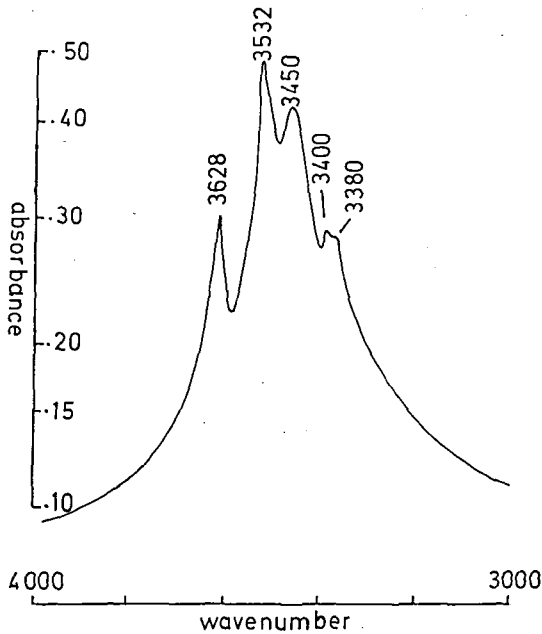


Fig. 5. Infrared absorption in the 3000–4000 cm^{-1} wavenumber range of hydrolytically affected adularia.

according to GLEMSER and RIECK (1958) and others this band represents “undisturbed” OH groups.

As the symmetry of the system particle-water is not ideal, liquid water adsorption could be assigned to the 3380 and 3400 cm^{-1} bands, indicating a very weak bonding (= adhesion) to the particle surface, judged from the frequency shift. The interpretation of the 3450 cm^{-1} band is likely to be in accordance with the position of liquid water in “structural defects”, more specifically caused by the interaction between edge valencies of the particles and OH-vibrations of adheared water molecules.

Of the remaining hydroxyl bands, at 3532 and 3628 cm^{-1} , only the latter points to a layer-like structural arrangement of OH groups in combination with metal ions, primarily to a hydrosilicate structure (RYSKIN et al., 1960).

Whether the absorption band at 3532 cm^{-1} can be interpreted as caused by structurally incorporated water molecules must be left open at present, though it seems to be an acceptable interpretation. The rise in frequency is of the order of 100 to 120 cm^{-1} , pointing to a stronger bonding of liquid water. This is, the circumstances given, only possible when the water molecule has entered the feldspar lattice. The bonding energy is accordingly of the order of 3 kcal/mole.

The occurrence of two rather weak absorption bands, at 2949 and 2865 cm^{-1} seems to be of little interest. These bands occur in the region of C–H stretch vibrations and are therefore in general interpreted as being

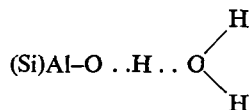
caused by organic impurities in the reaction materials. On this ground they are usually neglected. RYSKIN et al. (1960) however attributed the doublet around 2900 cm^{-1} to "water of crystallization" in synthetic torbermorite. The infrared spectrum of the same mineral, as published by KALOUSEK and ROY (1957) does not reveal these absorptions.

The infrared spectra of a minus $2\ \mu$ fluorphlogopite film, on which water was "gained" by wet-grinding, as described by ROUXHET and BRINDLEY (1966) showed doublets (2936 and 2869 cm^{-1}) at various temperatures (op.cit. fig. 6.). The authors have interpreted these absorption bands as caused by CH-stretching, attributed to organic impurities on the natural micas.

GLEMSER and RIECK (1958) again have attributed the band at $3.45\ \mu$ (2900 cm^{-1}) to $-\text{OH} \dots \text{O}$ stretching. The doublet must then be considered as stretch vibrations with respect to the special position of the proton in its hydrated form, or due to metal ion interaction.

Theoretically the formation of hydrogen bonds in acid-salt crystals with which the hydrogen equivalent of potassium feldspar can be compared, is in fact quite possible.

Accepting the ionic character of the O-H bond, offers following bonding situation,



The electron cloud liberated by hydrogen bond formation should in consequence of the above arrangement be located on an oxygen-oxygen axis. The presence of "squeezed" octahedral directions on a slightly distorted $\text{Al}^{\text{IV}}\text{O}_4$ -tetrahedron, as it is found in potassium feldspar, makes a bonding configuration which is comparable to π -bonding, possible by sharing the electron cloud of the H-atom with that of the oxygen on the Al-O axis. This position will strengthen the covalency of this bond by an increase of multiplicity, comparatively weakening the ionic contribution of the existing bonds and presumably resulting in a more pronounced distortion of the existing AlO_4 -tetrahedron. It is, in other words, looked at as if the Al-atom in the position $\text{Al}-\text{O} \dots \text{H}$ is no longer 4-coordinated in the substitutional sense. The picture of electrons sharing in the above mentioned system is not unequivocal though, as the tetrahedrally coordinated water molecule may as well act as partner in a similar bond formation by incorporation of one of its hydrogen atoms in a configuration, as pictured above. In that case the water molecule may no longer rotate freely. PETCH et al. (1956) discuss the possible structural arrangement both of SiO_3OH groups and of "water of crystallization" in afwillite. They come to the conclusion that the predicted infrared spectrum of the $\text{OH} \dots \text{O}$ bonds does not change if the hydrogen atom is shifted from one oxygen to another, as long as not only water is involved.

The frequencies of the absorption bands in the region of Si,Al-O stretching vibrations, between 400 and 1200 cm^{-1} , are given in table I. for

α -quartz, adularia, hydrolytically affected adularia and its dehydrated residuum.

Table I. Wavenumbers of the infrared absorption bands in the region 400–1200 cm^{-1} of quartz, adularia, hydrolytically affected adularia and its dehydrated residuum, ignited at 400° C.

quartz	460	520	—	695	—	—	780/798	—	1082
adularia	432	542	586	648	730	755	775	—	1030
H-adularia	453	520	557	670	—	742	800	965	1018
dehydrated									
H-adularia	440	542	587	650	735	—	770	—	ab. 1100

The shift of the frequencies 452, 520, 557, 670 and 800 cm^{-1} in H-adularia, compared to adularia proper, shows a remarkable uniformity, either to lower or to higher frequencies. The frequencies at 520, 670 and 800 cm^{-1} correspond to a quartz-like Si–O network. It may be interpreted in terms of free silica in the hydrolytically affected reaction product, but since the 650 and 770 cm^{-1} bands are restored on ignition, it must be assumed that the change in frequency, amounting to about 20 cm^{-1} is caused by a looser bonding of the Si–O modes, due to replacement of K^+ by a differently bonded water molecule. However, the modes mentioned above are also in correspondance with those for gibbsite, especially if the bending mode at 965 cm^{-1} , involving a hydroxyl group and an octahedral cation, is taken into account. This mode appears as a shoulder in H-adularia but is not present in the IR-spectrum of adularia proper. It is not likely though that gibbsite itself is present, judged from the X-ray diffraction pattern.

It may also be significant that there does not occur an absorption band at 730 cm^{-1} in H-adularia: it reappears on ignition. No explanation is as yet available for this phenomenon.

Although some silica and possibly some gibbsite may be formed, the general infrared spectrum of dehydrated H-adularia does leave little doubt that a feldspar-like structure still exists in the hydrolytically affected adularia, as also revealed by X-ray diffraction. The relative intensities of the absorption modes in both adularia proper and in H-adularia correspond largely.

Further details concerning the modes of vibration are still to be worked out by comparison with similar water containing silicate structures. However, as pointed out above, a looser bonding seems to occur within the feldspar structure upon ion-exchange of K^+ by H^+ . Together with the X-ray diffraction data, the interpretation of the infrared spectra makes it a reasonable assumption to take water penetration into the void left by dissolved potassium into account.

The dehydration curve of a sample of hydrolytically transformed adularia, the same of which X-ray and infrared data have been discussed already, is reproduced in fig. 6. The heating-rate of the instrument has been 2.5° C/min.

The air-dried sample contained 4.50 % H_2O , of which 1.90 % is humidity water, released in the temperature interval between 105° and

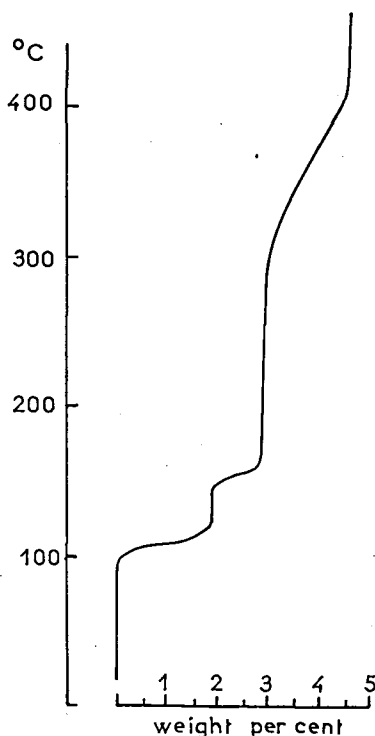


Fig. 6. Dehydration curve of hydrolytically transformed adularia from the first experimental run, in weight per cent. Temperature range from 22° C to 445° C. Heating rate: 2.5° C / min.

115° C. Between 148° C and 158° C another dehydration step has been observed, presumably representing "ordered" water near or at the surface of the adularia particles, amounting to 0.85 % of the water content. The more gradual dehydration between 306° C and 410° C must be interpreted as loss of structurally incorporated water molecules and OH-groups already formed within the feldspar lattice. It represents 1.75 % water content.

The DTA-curve of the same sample, reproduced in fig. 7, shows largely the same features as the TGA-curve. The maxima of dehydration are 102°, 142° and 385° C respectively, giving a slight deviation from the figures found by TGA.

The dehydration pattern resembles the one which can be deduced from the infrared data given by ROUXHET and BRINDLEY (1966, fig. 6). In their experiments the 3400 cm^{-1} band had virtually disappeared at 235° C (humidity water and near-surface water). Using the expression $E = 3/2 kT$ for the dehydration energy involved in the temperature interval between 306° C and 410° C, it is found that it will be of the order of 2 kcal/mole for each grade of freedom. As postulated the hydrogen bond in the system $\text{Al-O} \dots \text{H} \dots \text{OH}_2$ is mainly colinear with the axis of the covalent bond.

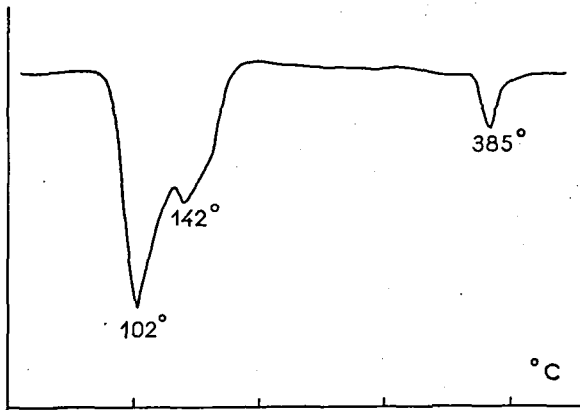


Fig. 7. DTA-curve of hydrolytically transformed adularia.

This means that the H-bond energy cannot be much different from the above figure. It has been pointed out by BADGER and BAUER (1937) that the decrease in IR-absorption frequency on the formation of a hydrogen bond is approximately proportional to the energy of the hydrogen bond, being the fundamental about 35 cm^{-1} . From the observed shift in the infrared absorption of water, it can be deduced that the bond energy most probably will be about 3 Kcal/mole.

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A Norelco diffractometer was used in these studies: Cu $K\alpha$ radiation at 36 kV and 20mA, samples were sedimented on glass. For measurements of the infrared absorption, a Beckmann IR-9 was employed, using pressed disc samples (0.5 %) mixed with KBr as dispersing agent.

The experimental work was mainly done at the laboratories of A/S Hasle Klinker- og Chamottestensfabrik, Rønne and at the Mineralogical Institute, DTH, Lyngby. I thank prof. dr. J. J. FRIPIAT and prof. dr. I. ROSENQVIST for inspiring discussions, suggestions and help.

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