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THERMAL DECOMPOSITION OF ULEXITE

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The thermal decomposition of ulexite, $NaCa[B_5O_6(OH)_6]\cdot 5H_2O$, monocrystals was investigated by thermal, X-ray, IR and optical microscopy methods at normal and elevated temperatures.

It was found that the thermal decomposition has an intraframework character and proceeds in a few separate stages: 1) release of part of the molecular water coordinating the Ca and Na cations; this leads to a rearrangement of the ulexite structure; 2) release of the remaining molecular water and some part the OH groups, which causes breakdown of the ulexite structure, with the simultaneous crystallization of $CaO\cdot B_2O_3$ and $2CaO\cdot B_2O_3$; 3) the slow release of the remaining OH groups up to 600°C, which causes decomposition of the borate rings and the crystallization of NaB_3O_5 and $NaCaBO_3$.

The special type of solid-state reaction called an "intraframework reaction" [1-3] is influenced by small structural changes. Investigations of the thermal reactions of borates, i.e. compounds with different internal structures, but with similar chemical compositions, can contribute to an understanding of intraframework reactions. Earlier investigations of the thermal decomposition of hydrated calcium borates, i.e. colemanite with a chain structure and pandermite with a layer structure, confirmed that the decompositions proceed in accordance with the mechanism of intraframework reactions [4-6].

Hydrated calcium-sodium borate ulexite, $NaCa[B_5O_6(OH)_6]\cdot 5H_2O$, belongs in the group of pentaborates containing isolated polyanions. The anion $[B_5O_6(OH)_6]^{3-}$ is formed by two six-membered boron-oxygen rings, each of which contains a central BO_4 tetrahedron, a $BO_2(OH)_2$ tetrahedron and a $BO_2(OH)$ triangle sharing corners. The structure also contains Ca coordination polyhedra and Na coordination octahedra. The Ca and Na polyhedra form chains, bonding the anions $[B_5O_6(OH)_6]^{3-}$ into a three-dimensional framework. The Na and Ca atoms are coordinated by water molecules and by OH groups [7]. The thermal decomposition of ulexite has been investigated by many authors (Table 1). Various thermoanalytical

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methods have been used, but the conclusions concerning the course of the thermal decomposition of ulexite differ.

Table 1 Thermal effects of ulexite

Endothermic effects						Exothermic effects	Reference
t, °C	Moles of H_2O	t, °C	Moles of H_2O	t, °C	Moles of H_2O	t, °C	
80	2	100-140	3	140-600	3	615-770	[8]
115-231		752-758		805		576-630	[9]
115-250	8	770		806			[10]
103-145	2	145-180	4	270-500	2	595-625	[11]
100-200	3	200-600	5			650	[12]

Experimental

Material

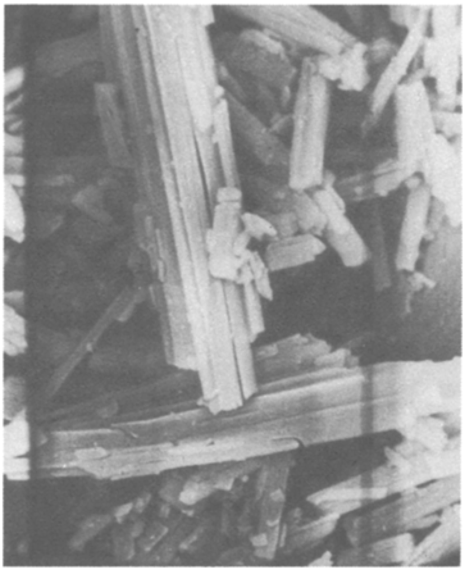
The examined ulexite from Iquique in Peru was obtained from the collection of the Mineralogical Museum at Wroclaw University. Ulexite crystallizes in a triclinic system, forming needle-like crystals, arranged in parallel (Picture 1).

X-ray and IR spectroscopic examinations and also optical microscopic observations on thin sections confirmed the monomineral character of the sample.

Methods

Conventional TG, DTG, DTA and Q-TG, Q-DTG and Q-DTA measurements were carried out with a microcomputer-controlled derivatograph C (Hungarian Optical Works). Simultaneous TG, DTG and DTA examinations were performed with a sample of 40 mg, a platinum crucible, in air atmosphere, at a heating rate of 10 deg/min^{-1} or 2.5 deg/min^{-1}. In the Q measurements, a labyrinth crucible and a sample of 40 mg were used. A constant decomposition rate of 0.15 mg min^{-1} was maintained.

To study the changes in the ulexite structure during heating, X-ray investigations were carried out. Samples of ulexite heated at 140°, 260°, 400°, 550° and 700° were examined. X-ray powder patterns were obtained with a Dron-3 (USSR) diffractometer, using CuK_α radiation.



Picture 1 Scanning electron microscope picture of ulexite crystals

To establish the temperatures of OH group loss and molecular water loss, IR spectroscopic examinations were performed. Natural ulexite and ulexite heated at the above temperatures were examined. A Zeiss UR-10 spectrometer was used and the samples were prepared as KBr discs. IR spectra were recorded in the wavenumber range 4000-3000 cm^{-1} at a speed of 50 cm^{-1}.

Changes in the shape of a ulexite sample during heating were observed in a heating Leitz microscope and in a scanning electron microscope (Tesla).

Results and discussion

Measurements under conventional and under quasi-isothermal-isobaric conditions showed that the decomposition of ulexite proceeds in a few separate stages.

DTA curves of ulexite samples examined under conventional conditions (Fig. 1) exhibit three endothermic peaks. The first, at 118°, is connected with the loss of 1.5 moles of H_2O, and those at 152° and 181° with the loss of

4.5 moles of H_2O. The remaining 2 moles of H_2O are released very slowly in a continuous way up to about 600°.

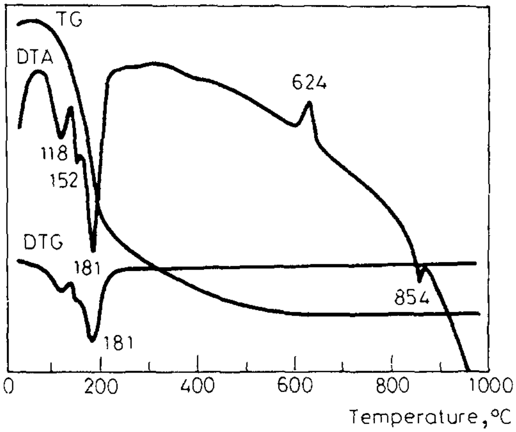


Fig. 1 TG, DTG and DTA curves of the thermal decomposition of ulexite

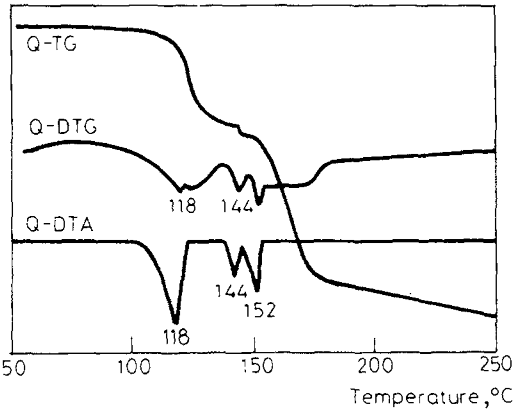


Fig. 2 Q-TG, Q-DTG and Q-DTA curves of the thermal decomposition of ulexite

At 624°, there is an exothermic peak not accompanied by any change in the weight of the sample, preceded by a weak endothermic peak. Its shape indicates that it is caused by crystallization.

At 854°, the endothermic effect of ulexite melting is recorded.

The Q-TG, Q-DTG and Q-DTA curves of ulexite obtained under quasi-isothermal and quasi-isobaric conditions are shown in Fig. 2. These results indicate that water is removed from ulexite at various rates.

When heated up to 118°, ulexite loses about 1.5 wt.% of H_2O. This is adsorption water and probably water filling the inclusions in the ulexite crystals. The removal of water from ulexite proper begins at 118° and proceeds at a constant rate. The amount of the removed water equals 6.3 wt.%, which correspond to 1.5 moles of H_2O.

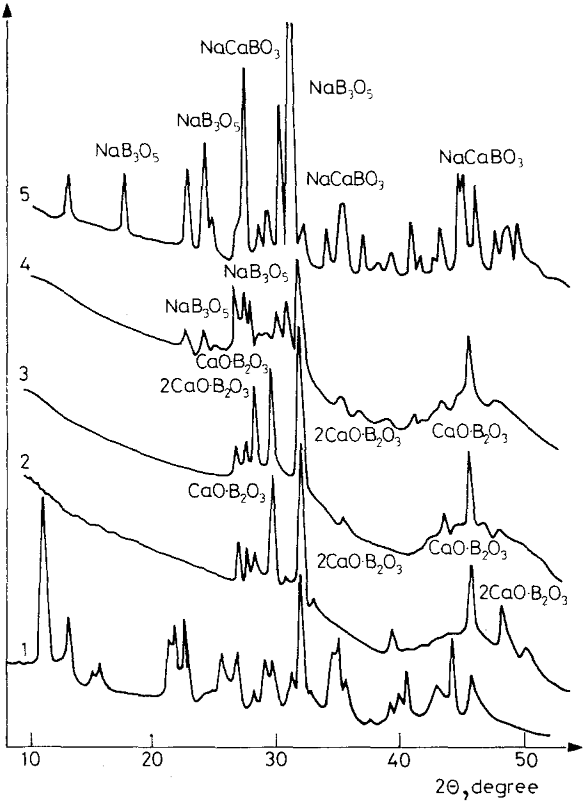


Fig. 3 X-ray diffractograms of ulexite heated at: 1 - 140°C, 2 - 260°C, 3 - 400°C, 4 - 550°C, 5 - 700°C

For the further removal of water at the given rate of 0.15 mg/min, a temperature increase is necessary. At 144°, a sudden removal of water (about 1.2 wt.%) occurs. This is indicated by a step in the Q-TG curve with a Q-DTG and Q-DTA peak (Fig. 2).

For the further removal of water at the same decomposition rate, a temperature of 152° is necessary. Then, under isothermal conditions, further removal of water occurs. The amount of the removed water equals 11.4 wt.%, which corresponds to 3 moles of H_2O (together with the loss at 144°). With the increase of temperature, the remaining 3.5 moles of H_2O is released in a continuous way, up to about 600°.

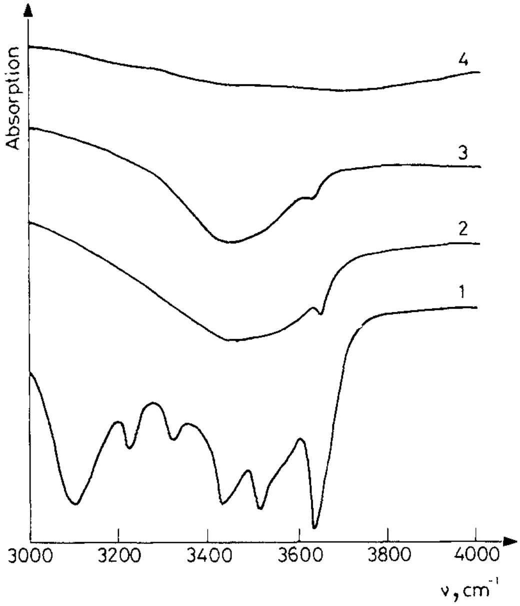


Fig. 4 Hydroxyl and H_2O stretching bands of ulexite heated at: 1 - room temperature, 2 - 260°C, 3 - 500°C, 4 - 700°C,

Water release during the first stage of dehydration produces changes in the structure of ulexite. In the X-ray pattern of a sample heated up to 140° (Fig. 3), the lines of ulexite, the strongest one with d = 12.2 Å [13], are already invisible. The new set of lines appearing most probably correspond to a less hydrated borate formed as a consequence of the release of part of the water coordinating the Ca and Na cations. At 260°, these lines have disappeared completely, and lines appear that indicate crystallization of the anhydrous borates $CaO\cdot B_2O_3$ and $2CaO\cdot B_2O_3$. At 400°, the X-ray pattern is unchanged. At 550°, the intensity of the calcium borate lines is distinctly diminished, while there appear new, weaker ones, indicating the presence of the sodium borate NaB_3O_5. A ulexite sample preheated up to 700° shows the existence of well-crystallized borates: NaB_3O_5 and $NaCaBO_3$.

The IR absorption spectrum of natural ulexite [14] shows bands in the region 400-1700 cm^{-1}, derived from the valency vibrations of the bonds B-O and B-OB and characteristic of borates. The short-wave part of the spectrum exhibits absorption bands at 3140, 3230, 3320, 3435 and 3540 cm^{-1}, connected with the vibration of water particles, and a band, ab 3620 cm^{-1}, assigned to the OH groups. At 260° (Fig. 4), the bands of molecular water disappear, and one broad band (3500 cm^{-1}) is observed, which indicates the breaking-off of the molecular water coordinated to the Ca and Na atoms. The intensity of the band at 3620 cm^{-1} is rapidly reduced and the residual band is shifted to 3630 cm^{-1}, which is an indication of the simultaneous breaking-away of the OH groups. A similar pattern of the absorption bands persists up to 500°. This fact confirms the very slow breaking-off of the OH groups. At 700°, the OH group band disappears completely, which means

Picture 2 Scanning electron microscope picture of ulexite heated at 260°C

that the water the OH groups has been completely removed from the ulexite structure.

The decomposition of ulexite begins with dehydration, resulting in the loss of first 1.5 moles of H_2O and then 3.0 moles of H_2O.

This dehydration proceeds without any major changes in the external form of the ulexite crystals. Only the cracking of the prismatic crystals of this mineral along the cleavage planes induced by the pressure of the water vapour can be observed. Some of them become separated into thin strips (Picture 2). The removal of water is also responsible for the rather small shrinkage of the sample observed in a high-temperature microscope.

The first stage of dehydration causes the rearrangement of the ulexite structure. The second stage of dehydration causes the decomposition of the structure of this mineral, with simultaneous crystallization of the calcium borates $CaO \cdot B_2O_3$ and $2CaO \cdot B_2O_3$. They are probably formed in the X-ray amorphous matrix enriched with sodium cations. The borate rings with the OH groups are preserved. The OH groups are gradually removed up to about 600°. It seems that the existence of the OH groups stabilizes the amor-

Picture 3 Scanning electron microscope picture of ulexite heated at 400°C

phous state of the matrix. When these groups are removed, sodium and sodium-calcium borates recrystallize to the accompaniment of a strong exothermic effect.

During dehydroxylation, lenticular-shaped pores were formed within the ulexite crystals, most probably where water vapour form the released OH groups accumulated (Picture 3).

The decomposition of ulexite, similarly to that of other calcium borates examined earlier (colemanite and pandermite), has an intraframework character. Internal or intraframework chemical reactions are reactions which are localized inside the structure of a solid body and proceed within the bulk of the solid grain. The solid product of this process is formed inside the structural framework of the parent substance (precursor), usually remaining in a topotactic relation with respect to the primary structure. However, the decomposition of ulexite proceeds in a different way. The essential difference is the slow release of the OH groups, which starts after the removal of the molecular water. This continues up to about 600°. The borate rings are retained up to higher temperatures than in the case of borates containing only the calcium cation, and amorphous phase rich in sodium is formed after the dehydroxylation. This is a compact mass with relatively low softening point and hinders the release of water particles to the outside. This is responsible for the high temperature of OH group release. The crystallization of sodium and sodium-calcium borates is possible, due to the release of the OH groups and the decomposition of the complex borate anions.

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Zusammenfassung — Mittels thermischer, röntgenographischer, IR- und optisch mikroskopischer Verfahren wurde bei Normal- und bei hohen Temperaturen die thermische Zersetzung von Ulexiteinkristallen $NaCa[B_5O_6(OH)_6]\cdot 5H_2O$ untersucht.

Die Untersuchungen zeigten, daß die thermische Zersetzung von Ulexit einen Innergittercharakter trägt und in einigen separaten Schritten verläuft: 1) Freisetzung desjenigen molekularen Wassers, welches Ca und Na Kationen koordiniert; hierdurch geschieht eine Wiederherstellung der Ulexit-struktur, 2) Freisetzung des verbleibenden Kristallwassers und einem Teil der OH-Gruppen, wodurch eine Zersetzung der Ulexit-struktur unter gleichzeitiger Kristallisation von $CaO\cdot B_2O_3$ und $2CaO\cdot B_2O_3$ erfolgt, 3) langsame Freisetzung der verbleibenden OH-Gruppen bis 600°C, was eine Spaltung der Boratringe und die Kristallisation von NaB_3O_5 und $NaCaBO_3$ zur Folge hat.