

Compositional and structural study of partially exchanged on Na⁺, K⁺, Mg²⁺ and Ca²⁺ natural heulandite

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Single crystals of natural heulandite (HEU) from Iskra deposit (Bulgaria) are the initial material for this study. Four parts of this material were selected and were subject to partial ion-exchange on Na⁺, K⁺, Mg²⁺ and Ca²⁺ ions. The chemical composition of the natural and the exchanged samples was obtained by EDS analysis and the derived crystal chemical formula for this HEU is Na_{1.05}K_{1.20}Ca_{1.90}Sr_{1.18})Al_{8.35}Si_{27.65}O₇₂·nH₂O. Weight losses associated with zeolitic H₂O in the channels were obtained by TG. The single crystal X-ray structural refinement revealed the topology of the framework and located the positions and site occupancies of the exchanging cations and water molecules in the channels A and B running along [010] and channel C along [001]. Initial heulandite crystals (natural HEU from Iskra deposit) contain predominantly Ca²⁺ as framework counter ion and some amounts of Na⁺, K⁺ and Sr²⁺. Sodium and strontium ions are positioned Sr and Na/Sr positions in channel A. It was found out that in this early stage of Ca-exchange that Ca²⁺ replaces Na⁺ from their mixed Na/Sr position. The K⁺-exchange leads to surplus of the positive charge, which removes indirectly Na⁺ without affecting Sr²⁺. In the Na⁺-exchanged form the sodium content increases in the mixed Na/Sr and Na position and small amount of Na⁺ is detected in the calcium position in channel B. The data obtained from EDS and structural refinement show that for the employed procedure Mg²⁺ ion exchange is not observed and its position at the center of the large channel A remains empty.

Key words: Heulandite, ion exchange, structure refinement, EDS.

INTRODUCTION

Natural zeolites are porous crystalline materials (aluminosilicates) obtained either by hydrothermal processes most commonly in cavities of basaltic lava flows, or through sedimentation and zeolitization of volcanic tuffs, etc. [1, 2]. The description of their crystal structure generally refers to two distinctive parts: a rigid negatively charged alumino-silicate framework producing two- and three-dimensional channels [3] and extraframework cations and water molecules residing in the channels. The latter are metal cations compensating the negative charge of the framework and H₂O molecules that may com-

plete the cation coordination, or can be trapped in the zeolites pores.

The capability of zeolites to exchange the extraframework cations with other cations (e.g. ion-exchange) is their most important feature for practical applications [4]. The exchange capacity and selectivity of zeolites are function of the Si/Al ratio and the types of framework pores. The HEU group includes heulandite and clinoptilolite (CPT). The crystal structures of the two zeolites are monoclinic, *C2/m*, with iso-structural spatial arrangement of the Si/Al framework. They differ between each other by Si/Al ratio, which is < 4 for HEU and > 4 for CPT. Because of this, both structures have different amount of charge balancing cations and water molecules located into the framework channels. The most common positions occupied by different extraframework cations have been described in several studies [5–8 and references within]. As heulandite

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very often contains Na and Ca charge balancing cations their positions are named C1 (channel A) and C2 (channel B) respectively [5]. Potassium is also frequently detected and its position is named by Khobaer et al., 2008 [7] as K3 (in channel C). The general positions (C1, C2, K3) may be occupied simultaneously by different cations and their location within the channels can vary (be shifted) depending on the type of cation (bigger, smaller etc.). As a prominent illustration in full exchanged strontium heulandite [8] Sr is distributed in positions close to the C1 and C2 [10].

The crystal structure of HEU [9] features three sets of intersecting channels. Two of the channels are parallel to the *c*-axis as follow: the larger A channels are formed by strongly compressed ten-membered tetrahedra rings (aperture 3.0 x 7.6 Å) and the smaller B channels are confined by eight-membered tetrahedra rings (aperture 3.3 x 4.6 Å). The C channels are parallel to the *a*-axis and are also formed by eight-membered tetrahedra rings (aperture 2.6 x 4.7 Å). Thus, the structure is a pseudo-layered with layers in *ac*-plane, parallel to (010) [10–13]. The ion-exchange properties of HEU have been studied theoretically [14, 15] and were experimentally confirmed [16–24]. However, most of the research work was focused on kinetic aspects. Our opinion is that there is an insufficient knowledge on the process of cation exchange and the structural features and chemical composition of exchanged forms of HEU and CPT minerals. In this study we purposely performed a partial exchange of natural HEU with four cations: Na, K, Ca and Mg in an attempt to investigate its initial stage and to assess the structural and compositional characteristics of the exchanged forms.

EXPERIMENTAL

Ion exchange

Heulandite crystals from Iskra deposit, Haskovo, Eastern Rhodopes, were exchanged with Na⁺, Ca²⁺, K⁺ and Mg²⁺ ions. The crystals with size around 1 mm³ were selected and gently crushed to sizes of approx. 100–500 μm. Four portions of the crystals (each one of ~100 mg) were placed in Teflon autoclaves and mixed with 20 ml 1M solution of relevant metal nitrates: Na-, K-, Ca- and Mg. The autoclaves were agitated four times per day with frequently refreshed solutions. The pH of the used solution (before refreshing) was > 4.7. The exchange procedure was carried out for seven days. The exchanged crystals were thoroughly washed with distilled water and dried at room temperature.

X-ray single crystal structural refinement

The data collection was carried out on an Agilent SupernovaDual diffractometer equipped with Atlas CCD detector using micro-focus Mo/Kα radiation ($\lambda = 0.71073$ Å) at 290 K. The determinations of the unit cell parameters, data collection and reduction were performed with CrysAlisPro software [25]. The structure was solved by direct methods ShelxS [26] and refined by the full-matrix least-squares method with the ShelxL-2013 programs [26]. All non-hydrogen atoms, including water molecules, were located successfully from Fourier maps and were refined anisotropically. Complete crystallographic data for the structure reported in this paper have been deposited in the CIF format with the FIZ Karlsruhe as supplementary publication No. CSD: 428990 (natural-HEU) for natural heulandite, 428991(Na-HEU) for Na⁺ exchanged heulandite, 428992(K-HEU) for K⁺-exchanged and 428993(Ca-HEU)* for Ca²⁺ exchanged.

Scanning and transmission electron microscopy (SEM)

SEM analyses were performed on a JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with ultrahigh resolution scanning system (ASID-3D) in regimes of secondary electron image (SEI) and back scattered electrons (BEC) mode. All samples were cleaned and completely dried before attempting SEM characterization. The samples were Carbon coated with time of coating ~20 sec. The accelerating voltage was 20 kV, I ~65 μA. The pressure was of the order of 10⁻⁴ Pa.

Differential scanning calorimetry (DSC) and thermo-gravimetric (TG) analyses

The thermal effects and mass losses were obtained by DSC/TGA analyses in a temperature range of the 20–420 °C. Small amount (10 ±0.2 mg) of the crystals from each sample were placed in alumina crucibles and the data were collected at constant heating rate of 10° min⁻¹ in an air flow of ~35 ml/min on a SETARAM, LABSYS EVO.

* Further details on the investigated cation-exchanged HEU-structures can be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de; http://www.fiz-karlsruhe.de/request_for_deposited_data.html).

RESULTS AND DISCUSSION

The DSC-TGA curves of the samples (Fig. 1) disclose the typical thermal behavior of HEU with expected release of the extra-framework water at relatively wide temperature range (70–170 °C). The amounts of released water vary slightly around 8.1 wt.% (natural-HEU), 7.1 wt.% (Na-HEU), 5.7 wt.% (K-HEU) and 8.5 wt.% (Ca-HEU). The destruction of the Si/A framework occurs at about 350 °C and is not associated with weight losses as the related high-temperature Al-Si-O compounds are stable at this temperature.

The chemical composition for all samples was calculated based on 72 framework oxygen. The results are given in Table 1. The composition of natural HEU shows that it is dominantly Ca-form containing some Na⁺, K⁺ and Sr²⁺ as well.

The chemical composition of the natural and partially exchanged HEU obtained from single crystal structures refinement (for the exchanging cations)

Table 1. Chemical composition of natural and exchanged heulandite (EDS)

Sample	Crystal-chemical formulae
natural HEU	(Na _{1.05} K _{1.2} Ca _{1.9} Sr _{1.18})Al _{8.35} Si _{27.65} O ₇₂
Na-HEU	(Na _{2.1} K _{0.32} Ca _{1.8} Sr _{1.08})Al _{8.4} Si _{27.60} O ₇₂
K-HEU	(Na _{0.35} K _{2.05} Ca _{1.75} Sr _{1.18})Al _{8.28} Si _{27.72} O ₇₂
Ca-HEU	(K _{1.0} Ca _{2.55} Sr _{1.1})Al _{8.46} Si _{27.54} O ₇₂

and by EDS (for Si and Al) are given in Table 2. It is worth to note that the cations amounts evaluated by EDS are lower than the ones assessed from single crystal structural data. Given the intrinsic limitations of EDS analysis due to its local sample probing and shallow surface penetration (1–2 μm), we choose to use the cations contents and their site occupancies derived from single crystal structural refinement.

The chemistry of the other three ion-exchanged samples shows different degree of partial ion exchange for Na⁺, K⁺ and Ca²⁺, which will be discussed below.

The purpose of the single crystal structure refinement was to review and compare the structural features of ion-exchanged HEU samples to these of the natural one. The crystal structures of all 4 samples with located positions of the cations and H₂O molecules are displayed on Fig. 3, while Table 3 show the evaluated site occupancies for all participating exchanging cations.

In the natural HEU, which is dominantly a calcium form, almost all amount of Ca²⁺ cations is located in the split Ca-position Ca2 (C2 according to Alberti, 1973 [5]) in the smaller channel B. Potassium is located in its usual position K (K3 according to Khobaer et al., 2008 [7]) at the intersection of channels A and C (Fig. 3 and Table 3).

It is interesting that the regular Na-position (C1 according to Alberti, 1973 [5]) in channel A in the structure of the natural-HEU is transformed to one mixed Na/Sr and one – Sr. In fact, they are located so close to each other that could be considered as a single crystallographic site with a complex cation occupancy. A clear separation of the two sub-sites is visible on Fig. 3 due to the difference in their ionic radii and scattering power. This complex cation site accommodates the initial amounts of Sr²⁺ and Na⁺ and even some extra Ca²⁺.

The detected water molecules are distributed amongst five positions. Three of the positions are located in channel A: Ow1, Ow2 and Ow3 [6, 7]. Water molecules are in positions (Ow1, Ow2) sitting on the mirror plane coordinating Na and Sr

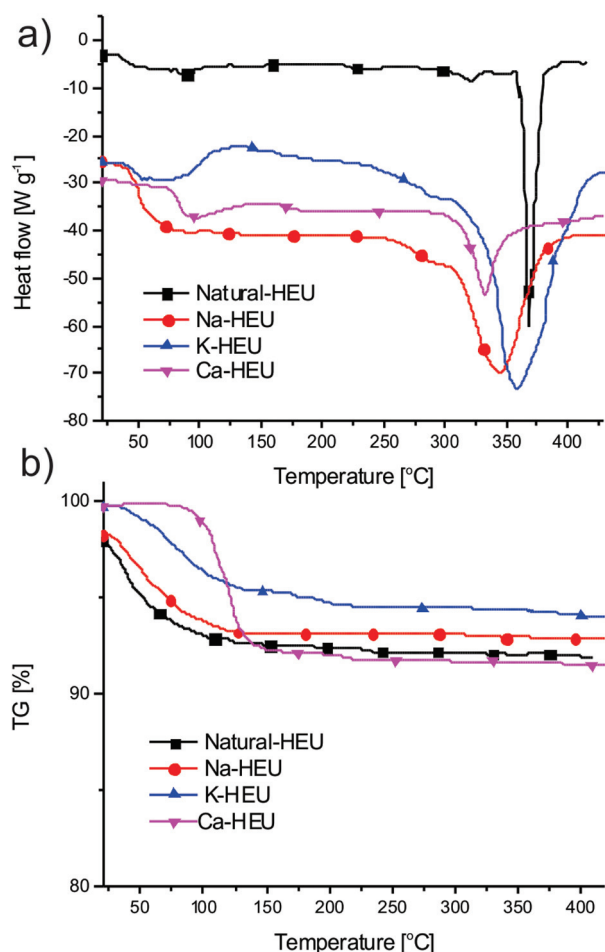


Fig. 1. DSC and TG curves of natural heulandite and exchanged forms

Table 2. Compositional and structural data obtained from single crystal structure refinement of native and cation exchanged forms of heulandite

Compound reference	Natural-HEU	Na-HEU	K-HEU	Ca-HEU
Chemical formula	(Na _{1.18} K _{1.44} Ca _{1.89} Sr _{1.43})* Al _{8.35} Si _{27.65} O ₇₂ H ₂ O _{20.99}	(Na _{2.54} K _{0.40} Ca _{1.80} Sr _{1.28})* Al _{8.35} Si _{27.65} O ₇₂ H ₂ O _{22.48}	(Na _{0.37} K _{2.18} Ca _{1.81} Sr _{1.43})* Al _{8.3} Si _{27.7} O ₇₂ H ₂ O _{20.77}	(K _{1.30} Ca _{2.60} Sr _{1.28})* Al _{8.46} Si _{27.54} O ₇₂ H ₂ O _{20.45}
a/Å	17.7671(9)	17.7207(11)	17.7378(11)	17.7176(7)
b/Å	17.8308(7)	17.8236(8)	17.8568(8)	17.9418(6)
c/Å	7.4340(4)	7.4352(4)	7.4247(5)	7.4277(3)
α/°	90	90	90	90
β/°	116.458(6)	116.484(8)	116.560(8)	116.490(5)
γ/°	90	90	90	90
Unit cell volume/Å ³	2108.4(2)	2101.9(2)	2103.5(2)	2113.27(16)
Temperature/K	290(2)	290(2)	290(2)	290(2)
Space group	C2/m	C2/m	C2/m	C2/m
No. of formula units per unit cell, Z	1	1	1	1
Radiation type	MoKα	MoKα	MoKα	MoKα
Absorption coefficient, μ/mm ⁻¹	1.73	1.59	1.76	1.66
No. of reflections measured	7510	9420	9729	9697
No. of independent reflections	3053	3406	3415	3441
No. of reflections with I > 2σ(I)	2587	2917	2980	3062
θ _{max} /θ _{min} , °	30.7/3.4	31.7/3.0	32.1/3.0	32.0/3.0
Parameters	182	198	179	183
Refinement/Least-squares matrix	F ² /full	F ² /full	F ² /full	F ² /full
R _{int}	0.0328	0.0333	0.0395	0.0322
Final R ₁ values (I > 2σ(I))	0.0577	0.0441	0.054	0.0589
Final wR(F ²) values (I > 2σ(I))	0.1336	0.1504	0.1347	0.1466
Final R ₁ values (all data)	0.0685	0.0531	0.0626	0.0659
Final wR(F ²) values (all data)	0.1386	0.1599	0.1393	0.1501
Goodness of fit on F ²	1.181	1.155	1.195	1.233

* The amount of the cations is calculated based on their site occupancies from structure refinement, while Al and Si contents are obtained from EDS analysis.

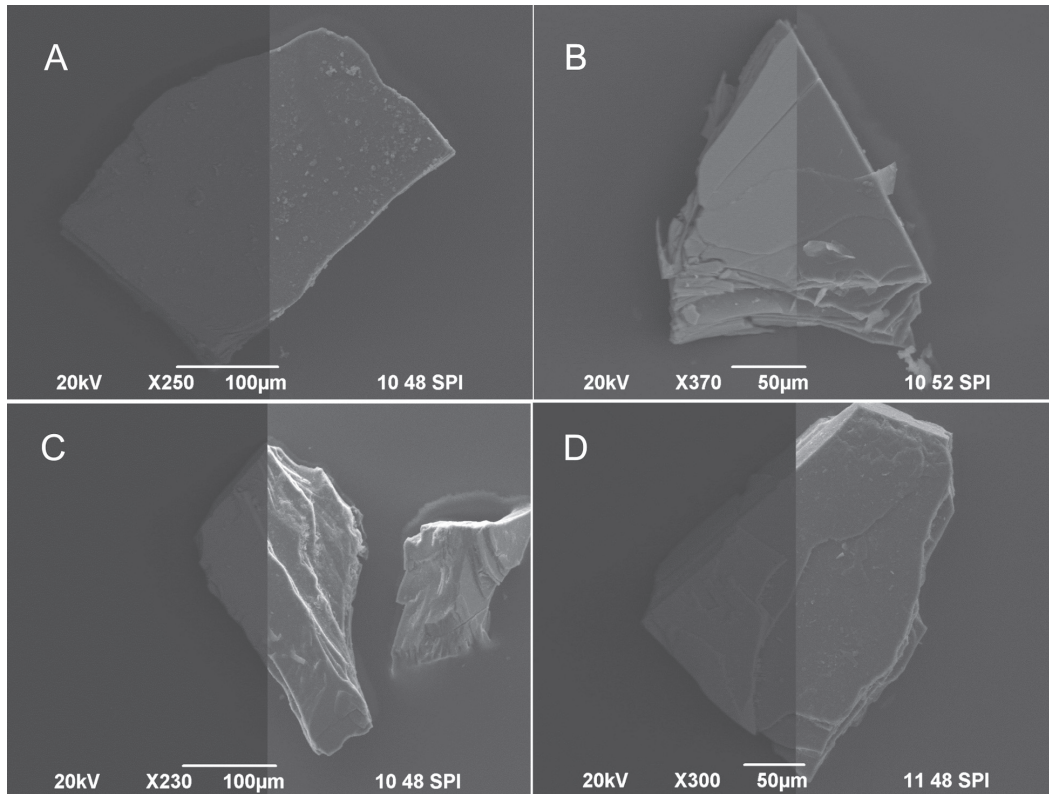


Fig. 2. SEM morphology of A) natural HEU, B) Ca-HEU, C) K-HEU and D) Na-HEU

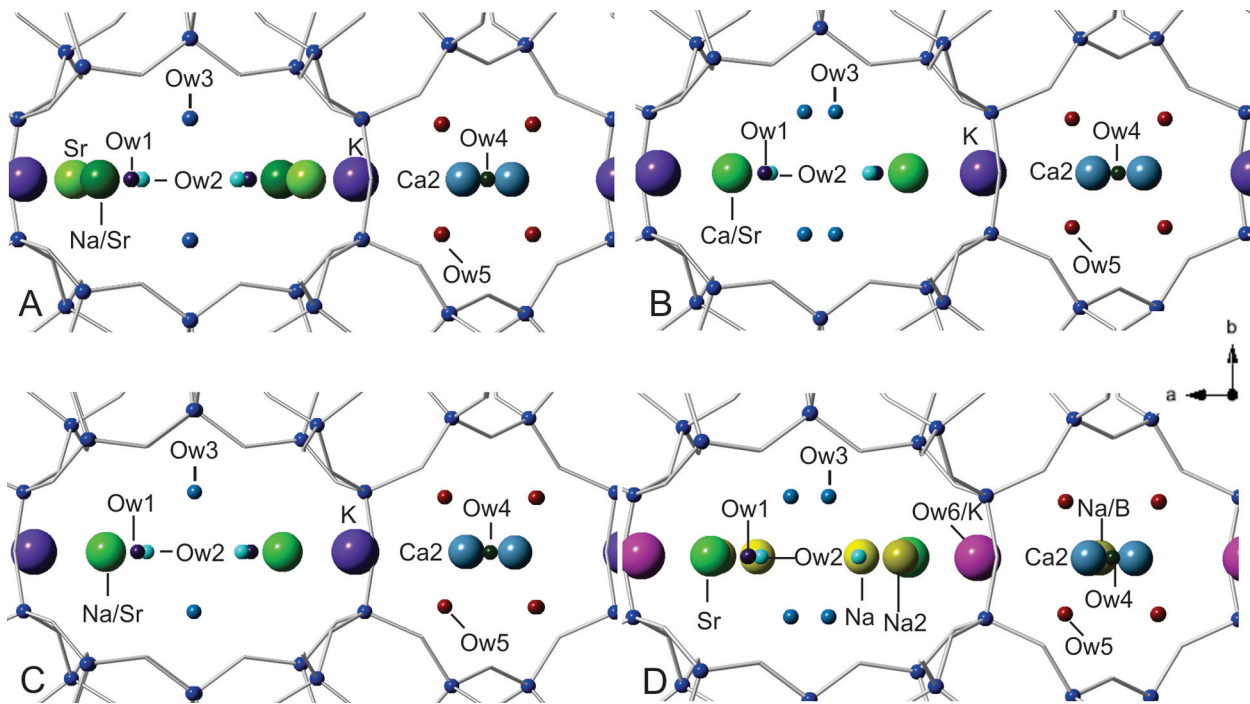


Fig. 3. Cation and H₂O positions in natural heulandite end exchanged forms. A) natural-HEU, B) Ca-HEU, C) K-HEU and D) Na-HEU

Table 3. Occupancy of the cation positions as displayed on Fig. 3

Channel	Cation positions (references)	Cation positions (Fig. 3)	Occupancy of the cation positions			
			nat-HEU	Ca-HEU	Na-HEU	K-HEU
A	C1[5]	Na/SrCa/SrNa	0.29/0.3	0.18/0.32	0.4	0.09/0.36
A	C1[5]	Na			0.18	
A	C1[5]	Sr	0.05		0.32	
B	C2[5]	Ca ²⁺	0.47	0.47	0.45	0.45
B	C2[5]	Na			0.06	
C	K3[7]	K	0.36	0.32	0.1	0.54

cations. Water molecule Ow3 is positioned on two folder axis and coordinate Na/Sr position. Waters molecules Ow4 and Ow5 [6, 7] are located in channel B participating in Ca coordination (position C2).

It was found out that at this early stage of cation exchange, Ca-HEU (Fig. 3-B) does not provide significant changes in the structure. As expected, the Ca content increases twice and because the occupancies of the Ca-sites in channel B are almost full (0.47), the excess of Ca²⁺ completely replaces Na in the mixed Na/Sr position as it is transformed to a Ca/Sr one. The located in the channels water molecules (positions Ow1, Ow2, Ow4 and Ow5) remain at the same positions as in the natural HEU, while Ow3 is split in two causing a decrease of occupancy from ~1 to 0.5 apu. Probably the split is due to the presence of two bivalent cations in the mixed Ca/Sr position.

The partial exchange on K in the K-HEU (Fig. 3-C) increases the K⁺ content in the unit cell from 1.3–1.4 to 2.18 apu. While the contents of Ca²⁺ in Ca2 position and Sr²⁺ in the mixed Na/Sr position are not quite affected, the extra K⁺ ions are filling up to the limit the position in channel C (K3 according to Khobaer 2008 [7]). Due to the requirement that the sum of K, Sr and Na should not exceed 1, this leads to indirect displacement of Na⁺ from its Na/Sr position decreasing 3 times of its content in the unit cell. The five water positions (Ow1-5) remain unchanged.

In the Na-HEU, Na⁺ increased its content in the unit cell twice. Na and Sr cations are distributed in three disordered positions close to the Na one (C1 according to Alberti, 1973 [5]). These positions are indicated as Na, Na2 and Sr on Fig. 3 and their combined occupancies are close to 1 (full occupancy). This causes an indirect displacement of K⁺ in its position in channel C, which content dropped down more than 3 times – from 1.44 to 0.4 apu. Ow3 water position is splitting by two

creating 4 crystallographic sites positioned closer to the two Na-enriched positions in channel A. Potassium shared its position with H₂O molecule named Ow6. (Table 3-D and Fig. 3). Small amount of Na⁺ is detected in Ca position in channel B. Small amount of Na⁺ is detected in Ca position in channel B.

Finally, both EDS and structural refinement of Mg-HEU, could not register the presence of Mg²⁺. The refinement of the so called Mg-HEU samples (two single crystal experiments on different crystals were performed) established that the assumed Mg position M4 [13] located in the center of the A channel is empty. This finding correlates with the results from EDS analysis and ultimately proves that the Mg²⁺ ions do not participate in the exchange under the applied exchanging conditions.

CONCLUSIONS

The performed DSC/TGA analyses, chemical analyses (EDS) and single crystal structure refinements presented in this study aimed to bring some light on the effect of partial cation exchange with K⁺, Na⁺, Ca²⁺ and Mg²⁺ of natural heulandite from Iskra deposit. The natural HEU is Ca-HEU form although some amounts of Na, K and Sr cations are also detected in its structure. It was found out that for the employed conditions no Mg ion-exchange is observed. The single crystal structural refinement of the Na- K- and Ca-exchanged HEU-forms shows that at the early stage of ion-exchange (up to seven (7) days) only cations located in the large channel A are affected except the Sr²⁺ one. The amounts of Ca²⁺ in channel B remain almost unchanged.

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СЪСТАВ И СТРУКТУРА НА ЧАСТИЧНО ОБМЕНЕН НА Na⁺, K⁺, Mg²⁺ И Ca²⁺ ПРИРОДЕН ХЕЙЛАНДИТ

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(Резюме)

Използваният материал е монокристален природен хейландит от находище Искра (България). Изходните монокристали са разделени на четири части и е осъществен йонообмен на Na⁺, K⁺, Mg²⁺ и Ca²⁺. Химичният състав на изходния природен и йонообменените хейландитни форми е направен чрез енергийно дисперсионна рентгенова спектроскопия като получената кристалохимична формула за природния хейландит е (Na_{1.05}K_{1.20}Ca_{1.90}Sr_{1.18})Al_{8.35}Si_{27.65}O₇₂·nH₂O. Тегловните загуби, свързани със зеолитната вода в каналите, са получени чрез термо-гравиметричен анализ. Монокристалният рентгеноструктурен анализ разкрива топологията на зеолитния скелет, позициите и заетостта на намиращите се в каналите катиони, водни молекули на природната и обменени форми. Кристалите на природния хейландит (от находище Искра) съдържат предимно Ca²⁺ и по-малки количества от Na⁺, K⁺ и Sr²⁺ катиони, които компенсират негативния заряд на Al/Si скелет. Натриевите и стронциевите йони са позиционирани в канал А. Частичният Ca-обмен показва, че в първоначално Ca²⁺ измества Na⁺ от общата Na/Sr позиция в канал А. Калиевият йонообмен води до излишък на положителния заряд, като това води до индиректно изместване на Na⁺, без да се засяга количеството на Sr²⁺. При натриевия йонообмен се увеличава съдържанието на натрий в общата Na/Sr позиция като Na⁺ се позиционира и в канал В, допълвайки Ca²⁺. Данните, получени от енергийно дисперсионната рентгенова спектроскопия и от структурната разшифровка на магнезиево обменен природен монокристал от находище Искра, показват, че йонообменът с Mg²⁺ не се наблюдава, като позицията в центъра на „големия А канал“ остава празна.