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Influence of content of pressure-transmitting medium on structural evolution of heulandite: Single-crystal X-ray diffraction study

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ABSTRACT

The structural evolution of natural heulandite $Ca_{2.90}Na_{2.07}Sr_{0.25}K_{0.16}Ba_{0.06}(H_2O)_n[Al_{8.65}Si_{27.35}O_{72}]$ was studied upon compression in penetrating (water-containing) and non-penetrating (paraffin) media using single-crystal X-ray diffraction data in a diamond-anvil cell. Compression in a water-containing medium results in an additional hydration of heulandite from 23 molecules per unit cell at ambient conditions to ≈27 at 3.27 GPa. Water molecules enter both initially vacant and partly occupied positions. Additional hydration stabilizes the crystal structure decreasing its compressibility.

1. Introduction

Zeolite heulandite, belonging to the heulandite-clinoptilolite series [1], is a common mineral in post-volcanic environments. Heulandite-clinoptilolite rocks are used in ion-exchange processes, in the first place as a potential repository for high-level radioactive wastes [2]. While the ion-exchanging and catalytic abilities as well as the thermal stability of this type of minerals have been investigated extensively, our knowledge of their structural behaviour under pressure is insufficient.

In the last decade, the number of structural studies of zeolites at high pressures has increased drastically [3]. Among them, several studies have shown that composition of pressure-transmitting medium can significantly affect the structural evolution of zeolites under high pressure [4]. Zeolite structures are characterized by "open" system of interconnected channels and cavities, responsible for their reversible dehydration [1]. Additional H_2O molecules can enter the channels on compression in water-containing medium; this process is reversible also [4]. For some zeolites [5,6], such overhydration was observed upon compression in the so-called "nominally penetrating medium" – methanol:ethanol:water mixture with volume ratio of 16:3:1. In contrast, no overhydation was observed upon compression of phillipsite [7] and thomsonite [8] in "nominally penetrating medium", whereas thomsonite, being compressed in the ethanol:water 1:3 mixture, transformed at 2 GPa into a new phase with high water content [9]. This example shows that the relative content of water in the hydrostatic medium is of particular importance.

Heulandite was one of the first zeolites structurally studied at high pressures [10]. Later its compression has been studied repeatedly, but again in a non-penetrating medium [11]. Structural changes of heulandites at high pressure in the presence of water were not studied. The aim of the present contribution is to compare the structural evolution of heulandite under compression in water-containing and anhydrous fluids.

2. Experimental

The sample of heulandite (Nidym river, East Siberia, Russia) was provided by Igor A. Belitsky. The chemical composition was determined using wavelength-dispersive spectroscopy on Cameca Camebax Micro electron microprobe at 20 nA and 20 kV with a

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Table 1
Lattice parameters and volumes of heulandite at high pressure.

P, GPa	*a*, Å	*b*,Å	*c*, Å	*β*, °	*V*, Å
0.0001	17.7003(4)	17.9244(3)	7.42363(16)	116.453(3)	2108.69(7)
Compression in water:ethanol 1:1					
0.28	17.6644(6)	17.907(4)	7.4104(3)	116.486(4)	2098.0(5)
0.51	17.6290(6)	17.890(4)	7.3982(3)	116.521(5)	2087.7(5)
0.65	17.6083(5)	17.853(3)	7.3917(3)	116.539(4)	2078.8(3)
0.75	17.5918(5)	17.851(3)	7.3878(3)	116.569(4)	2075.0(4)
0.97	17.5527(8)	17.821(3)	7.3743(4)	116.628(6)	2062.1(4)
1.20	17.5271(13)	17.764(6)	7.3669(5)	116.700(9)	2049.2(7)
1.60	17.4599(8)	17.751(4)	7.3468(3)	116.773(6)	2032.9(5)
1.86	17.4423(15)	17.732(10)	7.3363(6)	116.981(10)	2022.1(10)
2.10	17.3995(7)	17.687(5)	7.3264(3)	116.874(5)	2011.1(6)
2.44	17.3548(6)	17.661(5)	7.3087(3)	116.941(5)	1997.1(5)
2.96	17.2892(8)	17.610(6)	7.2817(3)	117.058(6)	1974.4(7)
3.27	17.2707(7)	17.640(5)	7.27223)	117.176(5)	1970.9(6)
0.06[a]	17.6998(6)	17.918(4)	7.4233(2)	116.479(4)	2107.3(4)
Compression in paraffin					
0.17	17.6688(6)	17.908(5)	7.4144(2)	116.491(4)	2099.7(6)
0.73	17.5614(6)	17.833(6)	7.3790(3)	116.588(4)	2066.5(7)
1.68	17.3862(6)	17.670(5)	7.3212(3)	116.711(4)	2009.1(6)
2.68	17.2701(6)	17.480(6)	7.2826(9)	116.787(5)	1962.6(6)
3.66	17.1886(10)	17.329(7)	7.2586(4)	116.894(7)	1928.2(8)

[a] Data collected under decompression.

Table 3
Parameters of data collection and structure refinement for heulandite compressed in paraffin.

Pressure (GPa)	0.17	1.68	3.66
a (Å)	17.6688(5)	17.3862(6)	17.1886(10)
b (Å)	17.908(5)	17.670(5)	17.329(7)
c (Å)	7.4144(2)	7.3212(3)	7.2586(4)
β (°)	116.491(4)	116.711(4)	116.894(7)
V (Å^3)	2099.7(6)	2009.2(6)	1928.2(8)
Space group	*C*2/*m*		
d (g/cm^3)	2.191	2.289	2.385
Scan width (°/frame)	0.5	0.5	0.5
Exposure (s/frame)	30	30	30
2*θ* Range (°)	5.16–63.50	5.24–63.60	5.32–63.32
μ (MoKα) (mm^{-1})	1.029	1.075	1.121
Number of I_{hkl} measured	9661	9269	7434
Number of unique F^2_{hkl}	1188	1145	1105
R_{int}	0.0637	0.0631	0.0748
Reflections with $I > 2\sigma(I)$	936	880	740
Number of variables	187	178	187
*R*1, *wR*2 for observed reflections [$I > 2\sigma(I)$]	0.0477, 0.1139	0.0516, 0.1306	0.577, 0.1393
*R*1, *wR*2 for all data	0.0645, 0.1174	0.0714, 0.1368	0.0947, 0.1499
GooG	1.247	1.063	1.081
Residual electron density (*e*/Å^3)	0.538, −0.399	0.581, −0.302	0.957, −0.434

defocused beam of 20 μm and counting time of 20 s. Water content was measured by thermogravimetric analysis, using Mettler TA3000 equipment (temperature range 20–750 °C, heating rate 10 °C/min). The obtained sample composition was $Ca_{2.90}Na_{2.07}Sr_{0.25}K_{0.16}Ba_{0.06}(H_2O)_{23.1}[Al_{8.65}Si_{27.35}O_{72}]$.

Several fragments of a large crystal were first inspected under a polarizing microscope to avoid twinning. As a result, 0.17 × 0.15 × 0.06 mm tabular crystal was selected for the X-ray diffraction study.

Diffraction data were firstly collected under room conditions (crystal in air) on an Oxford Diffraction Xcalibur Gemini diffractometer (MoKα radiation, 0.5 mm collimator, graphite monochromator, *ω* scan, scan step 1°, 15.9 s per frame). Data reduction, including a background correction and Lorentz and polarization corrections, was performed with the *CrysAlis Pro* 171.36.32 program package. A semi-empirical absorption correction was applied using the multi-scan technique. The structure was solved and refined with SHELX-97 program package [12]. The Si/(Al + Si) ratio for each tetrahedral site was estimated using the method described in Ref. [13]. All non-H atoms were refined with anisotropic displacement parameters. The O–H distances of water molecules were restrained to 1.00(2) Å during the refinement. The notations for the atomic positions are used as in Ref. [13]. Na^+ cations were distributed between M1 and M2 positions in 2:1 ratio; the occupancies of Ca^{2+} were refined.

The same heulandite crystal was used for high-pressure measurements in a Boehler–Almax diamond-anvil cell (DAC) [14] (0.200 mm stainless steel gasket pre-indented to 0.120 mm, hole diameter 0.3 mm). In all experiments, pressure was estimated from the shift of the ruby R1 band (±0.05 GPa) [15]. An ethanol–water (1:1) mixture was used as the pressure-transmitting fluid in the first series of high-pressure experiment. Single-crystal X-ray

Table 2
Parameters of data collection and structure refinement for heulandite compressed in penetrating medium.

Pressure (GPa)	0.0001	0.28	0.75	1.20	1.60	2.10	2.44	3.27	0.06[a]
a (Å)	17.7001(4)	17.6644(6)	17.5918(5)	17.5271(13)	17.4599(8)	17.3995(7)	17.3548(6)	17.2707(7)	17.6998(6)
b (Å)	17.9240(3)	17.907(4)	17.851(3)	17.764(6)	17.751(4)	17.687(5)	17.661(5)	17.640(5)	17.918(4)
c (Å)	7.42352(16)	7.4104(3)	7.3878(3)	7.3669(5)	7.3468(3)	7.3264(3)	7.3087(3)	7.2722(3)	7.4233(2)
β (°)	116.453(3)	116.486(4)	116.569(4)	116.700(9)	116.773(6)	116.874(5)	116.941(5)	117.176(5)	116.479(4)
V (Å^3)	2108.58(7)	2098.0(5)	2075.0(4)	2049.2(7)	2032.9(5)	2011.2(6)	1997.1(5)	1970.9(6)	2107.3(5)
Space group	*C*2/*m*								
d (g/cm^3)	2.181	2.192	2.217	2.245	2.263	2.287	2.303	2.334	2.183
Scan width (°/frame)	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Exposure (s/frame)	15.89	30	30	30	30	30	30	30	30
2*θ* Range (°)	3.43–63.72	5.16–33.62	3.46–63.84	3.46–63.46	3.48–63.62	3.50–63.80	3.50–63.48	3.52–63.78	3.44–63.76
μ (MoKα) (mm^{-1})	1.025	1.030	1.041	1.054	1.063	1.074	1.082	1.096	1.025
Number of I_{hkl} measured	21,299	9634	9508	6253	4980	9132	9186	8828	8541
Number of unique F^2_{hkl}	3616	1411	1530	1468	1429	1266	1253	1230	1414
R_{int}	0.0456	0.0584	0.0669	0.0912	0.0600	0.0770	0.0767	0.0791	0.0688
Reflections with $I > 2\sigma(I)$	3106	1115	1194	1042	1022	948	911	874	1086
Number of variables	212	203	208	212	211	209	194	195	210
*R*1, *wR*2 for observed reflections [$I > 2\sigma(I)$]	0.0501, 0.1226	0.0470, 0.1207	0.0494, 0.1254	0.0497, 0.1218	0.0491, 0.1242	0.0451, 0.1146	0.0558, 0.1455	0.0612, 0.1571	0.0433, 0.1064
*R*1, *wR*2 for all data	0.0603, 0.1286	0.0619, 0.1254	0.0657, 0.1295	0.0725, 0.1306	0.0707, 0.1328	0.0641, 0.1205	0.0760, 0.1522	0.0855, 0.1643	0.0603, 0.1112
GooG	1.114	1.005	0.976	0.909	0.956	1.031	1.167	1.331	1.005
Residual electron density (*e*/Å^3)	1.902, −1.056	1.160, −0.363	1.414, −0.485	1.445, −0.476	1.164, −0.535	0.989, −0.481	1.016, −0.520	0.757, −0.504	0.911, −0.478

[a] Data collected under decompression.