Crystal Structure of a Natural and a Partially Silver-exchanged Heulandite

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The crystal structure of a natural calcium heulandite (Ca)heu and a partially silver-exchanged heulandite (Ag,Ca)heu is reported. The monoclinic crystals, space group $C2/m$, have cell parameters $a = 17.672(6)$, $b = 17.930(6)$, $c = 7.443(4)$ Å, $\beta = 116.5(1)°$, $Z = 1$, and formula $Ca_{3.1}Na_{1.1}K_{0.1}Al_{7.6}Si_{28.5}O_{72}\cdot 24H_2O$ (from electron microprobe analysis) for (Ca)heu. For (Ag,Ca)heu $a = 17.741(6)$, $b = 17.974(6)$, $c = 7.408(4)$ Å, $\beta = 116.4(1)°$, $Z = 1$, and the formula is $Ca_{3.1}Na_{0.1}Ag_{1.3}Al_{7.8}Si_{28.2}O_{72}\cdot 25H_2O$ (from electron microprobe analysis). The final R index is 0.041 for (Ca)heu and 0.051 for (Ag,Ca)heu using 1 863 and 1 414 independent reflections respectively in the least-squares refinement. Chemical analysis and X-ray results show that Ag^+ ions have exchanged only univalent cations which are all located in one of the two occupied cationic sites, the other being populated by only Ca^{2+} ions. These results may be interpreted on the basis of the chemical and structural features of heulandite.

THE properties of zeolites depend upon the anionic framework, the size, charge, kind, and location of exchange ions.[1,2] Location of cations may be determined, in principle, by X-ray diffraction analysis, when suitable single crystals are available. On the other hand, low occupancy and distribution of different cations on the same crystal site make uncertain their location even with this technique. However, a controlled exchange of cations with other heavy ions and the use of X-ray diffraction analysis before and after the ion exchange may be successful in establishing the approximate distribution of cations over the same site.

As the first step towards a systematic study of the structural features of transition-metal ion-exchanged zeolites, we report the crystal structure of a natural [(Ca)heu] and a partially silver-exchanged heulandite [(Ag, Ca)heu].

TABLE 1

Chemical analysis (%)* and crystal data

Species present	(Ca)heu	(Ag,Ca)heu
SiO_2	62.25	59.1
Al_2O_3	14.1	13.95
CaO	6.30	6.00
Na_2O	1.20	0.15
K_2O	0.20	
Ag_2O		5.05
H_2O	(15.7)	(15.75)
E	2.96	4.39
Formula per unit cell	$Ca_{3.1}Na_{1.1}K_{0.1}Al_{7.6}$-$Si_{28.5}O_{72}\cdot 24H_2O$	$Ca_{3.1}Na_{0.1}Ag_{1.3}Al_{7.8}$-$Si_{28.2}O_{72}\cdot 25H_2O$
a/Å	17.672(6)	17.741(6)
b/Å	17.930(6)	17.974(6)
c/Å	7.443(4)	7.408(4)
β/°	116.5(1)	116.4(1)
Z	1	1
R	0.041	0.051
Space group	$C2/m$	$C2/m$
Crystal dimensions/mm	0.2 × 0.05 × 0.4	0.15 × 0.05 × 0.3

* Values in parentheses were obtained by difference. The balance error is calculated from $E = 10^2(Al - Al_{calc.})/Al_{calc.}$ where $Al_{calc.} = Na + K + Ag + 2Ca$.

EXPERIMENTAL

Preparation and Analysis of Samples.—The natural heulandite was from N. E. Azerbaijan, Iran[3] and was assigned on the basis of chemical analysis and heat behaviour, to type 1 in the classification of Alietti *et al.*[4]

A small quantity of single crystals, sieved between 128 and 254 µm, was ion-exchanged in 1 mol dm^{-3} aqueous $Ag[NO_3]$ solutions for 6 weeks at 55 °C.

Wavelength-dispersive microprobe analysis was carried out on six and four single crystals of (Ca)heu and (Ca, Ag)-heu respectively, using a fully automated ARL SEMQ instrument. The mean chemical analysis and atomic ratios are given in Table 1.

TABLE 2

Crystallographic and chemical analyses in (Ca)heu and (Ag, Ca)heu

(*a*)

	Mean Si–O (Å) (isotropic refinement)	% Al	Mean Si–O (Å) (anisotropic refinement)
Si(1)	1.627(6)	25	1.624(3)
Si(2)	1.655(6)	40	1.658(3)
Si(3)	1.630(6)	25	1.630(3)
Si(4)	1.621(6)	0	1.620(3)
Si(5)	1.623(6)	0	1.628(3)

(*b*) (Ca)heu

	Ca^{2+} per unit cell	Na^+ per unit cell	Water molecules per unit cell
CS(1)	1.1	1.1	
CS(2)	1.8	0	
Structure refinement	2.9	1.1	20.6
Chemical analysis	3.1	1.1	24.0

(*c*) (Ag,Ca)heu

	Ca^{2+} per unit cell	Ag^+ per unit cell	Water molecules per unit cell
CS(1)	1.0	1.3	
CS(2)	2.0	0	
Structure refinement	3.0	1.3	17.5
Chemical analysis	3.1	1.3	25

One of the analysed crystals was previously used to determine the cell parameters and to collect X-ray diffraction data for both natural and exchanged zeolites.

Crystal Data.—Refined cell parameters are given in Table 1 for both compounds together with other crystal data of interest. The intensity data were collected on an automated Siemens diffractometer. A total of 1 863 [(Ca)heu] and 1 414 [(Ag, Ca)heu] independent reflections, having $I > 3\sigma(I)$, were corrected for the Lorentz-polarization factor.

Structure Determination and Refinement.—The choice of

TABLE 3

Fractional co-ordinates ($\times 10^4$) and thermal factors ($\times 10^2$ Å^2) of (Ca)heu with estimated standard deviations in parentheses

Atom *	*x*	*y*	*z*	*U*	Occupancy	No. of positions (Wyckoff notation)†
Si(1)	1 790(1)	1 702(1)	957(1)		1.0	8
Si(2)	2 123(1)	4 101(1)	5 011(1)		1.0	8
Si(3)	2 084(1)	1 907(1)	7 170(1)		1.0	8
Si(4)	650(1)	2 990(1)	4 120(1)		1.0	8
Si(5)	0	2 144(1)	0		1.0	4
O(1)	1 969(3)	5 000	4 586(7)		1.0	4
O(2)	2 322(2)	1 200(2)	6 140(5)		1.0	8
O(3)	1 835(2)	1 549(2)	8 855(5)		1.0	8
O(4)	2 369(2)	1 069(2)	2 530(4)		1.0	8
O(5)	0	3 250(3)	0		1.0	4
O(6)	819(2)	1 602(2)	618(4)		1.0	8
O(7)	1 278(2)	2 348(2)	5 488(5)		1.0	8
O(8)	96(2)	2 678(2)	1 851(5)		1.0	8
O(9)	2 102(2)	2 539(2)	1 771(5)		1.0	8
O(10)	1 156(2)	3 730(2)	4 012(5)		1.0	8
OW(11)	2 244(4)	5 000	−20(10)	6.1(0.2)	1.0	4
OW(12)	849(13)	0	8 721(31)	10.7(0.6)	0.5	4
OW(13)	773(3)	4 197(3)	9 687(8)	6.4(0.1)	0.9	8
OW(14)	0	5 000	5 000	7.6(0.3)	1.0	2
OW(15)	278(9)	868(9)	5 013(26)	6.2(0.4)	0.3	8
OW(16)	951(9)	0	2 879(23)	8.0(0.4)	0.50	4
OW(161)	702(38)	0	2 034(89)	17.0(2.1)	0.25	4
CS(1)	1 526(3)	0	6 612(7)		0.50	4
CS(2)	401(2)	5 000	2 106(5)		0.45	4

* OW = Water molecule, CS = cation site.

† ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 1.

the space group *C*2/*m* was decided after isotropic refinement of data with both *C*2/*m* and *Cm* space groups, in accord with the criteria stated by Alberti in the refinement of a natural heulandite [5] and clinoptilolites.[6] In addition we have found that the distribution of cations in the CS(2) and CS(2)′ sites (CS = cation site), obtained from refinement in the acentric space group, is much more symmetric than that previously found.[5] The occupancy factors were 45 and 55% while those of Alberti [5] are 20 and 80% respectively. The structures were solved starting from the available atomic parameters of framework atoms [5] (*C*2/*m* space group) and then water molecules and cations were located from Fourier maps. The isotropic refinement was carried out using Si^{3+} species with occupancy of 100%. The distribution of Al and Si species in the tetrahedra was then derived from the analysis of the Si–O bond lengths [7] and adjusted to satisfy the chemical analysis ratio (Table 2). The procedure followed was that described in refs. 5 and 6. The atomic scattering curves were calculated accordingly for both zeolites. The occupancies of cations and water molecules were refined during the isotropic refinement and were then held constant. During the final block-diagonal refinement

TABLE 4

Fractional co-ordinates ($\times 10^4$) and thermal factors ($\times 10^2$ Å^2) of (Ag, Ca)heu

Atom	*x*	*y*	*z*	*U*	Occupancy	No. of positions (Wyckoff notation)
Si(1)	1 786(1)	1 706(1)	949(2)		1.0	8
Si(2)	2 139(1)	4 104(1)	5 050(2)		1.0	8
Si(3)	2 079(1)	1 912(1)	7 153(2)		1.0	8
Si(4)	659(1)	2 995(1)	4 142(2)		1.0	8
Si(5)	0	2 170(1)	0		1.0	4
O(1)	1 988(5)	5 000	4 620(11)		1.0	4
O(2)	2 324(3)	1 215(3)	6 136(8)		1.0	8
O(3)	1 843(4)	1 572(3)	8 847(8)		1.0	8
O(4)	2 332(3)	1 058(3)	2 492(7)		1.0	8
O(5)	0	3 251(5)	5 000		1.0	4
O(6)	813(3)	1 630(3)	568(7)		1.0	8
O(7)	1 280(3)	2 337(3)	5 478(8)		1.0	8
O(8)	115(3)	2 701(4)	1 848(8)		1.0	8
O(9)	2 124(3)	2 526(3)	1 835(8)		1.0	8
O(10)	1 184(3)	3 737(3)	4 124(8)		1.0	8
OW(11)	2 290(7)	5 000	7(17)	6.7(0.3)	1.0	4
OW(12)	791(56)	0	9 439(132)	21.9(3.5)	0.35	4
OW(13)	771(7)	4 215(6)	9 699(16)	6.5(0.3)	0.70	8
OW(14)	0	5 000	5 000	6.3(0.5)	0.95	2
OW(15)	94(51)	962(27)	4 735(117)	10.9(1.9)	0.20	8
OW(16)	829(28)	0	2 594(64)	14.7(1.4)	0.50	4
OW(161)	729(32)	0	789(75)	7.9(1.4)	0.25	4
CS(1)	1 573(2)	0	6 698(5)		0.57	4
CS(2)	401(3)	5 000	2 286(10)		0.50	4

the temperature factors of the framework atoms and cations were assumed to vary anisotropically, whereas those of the water molecules were assumed to be isotropic.

Atomic co-ordinates are given in Tables 3 and 4. Observed and calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 22743 (23 pp.).*

RESULTS AND DISCUSSION

Description of the Structure of (Ca)heu.—The Si, Al, and O atom framework is very close to that described by Alberti,[5] making allowance for the different Si : Al ratios. Two cationic sites are found occupied, confirming the previous assignment.[5] However, the structure determination and the chemical analysis of (Ag, Ca)heu (see below) suggest that CS(2) is only occupied by Ca^{2+} ions. Therefore the univalent cations, mainly Na^+ ions, are located in CS(1). Thus, the uniform distribution of univalent cations on the two sites, as already assumed,[5] is not supported. The CS(1) has a seven-fold co-ordination, being surrounded by five water molecules and two framework oxygen atoms, whereas CS(2) is co-ordinated by five water molecules and three framework oxygens, achieving an eight-fold co-ordination. These results compare well with those previously reported [5] (Table 5). Finally, the agreement between the crystallographic and chemical analyses concerning the exchange cations and water molecules is satisfactory, as shown in Table 2.

TABLE 5

Co-ordination bond lengths (Å) of the cation sites (CS) compared with those of ref. 5

	(Ca)heu	(Ag,Ca)heu	Value from ref. 5
CS(1)–O(2)	2.678(5)	2.686(6)	2.65(1)
–O(2)^{IV}			
–OW(11)^{II}	2.498(7)	2.37(1)	2.47(1)
–OW(12)	2.36(3)	2.9(1)	2.45(3)
–OW(15)	2.52(1)	2.93(7)	2.90(3)
–OW(15)^{IV}			
–OW(16)	2.67(2)	2.72(4)	2.66(1)
CS(2)–O(1)	2.553(5)	2.567(8)	2.59(2)
–O(10)	2.700(3)	2.693(6)	2.76(2)
–O(10)^{V}			
–OW(13)^{I}	2.608(5)	2.63(1)	2.56(1)
OW(13)^{VI}			
OW(13)^{VII}	2.394(5)	2.40(1)	2.40(1)
OW(13)^{III}			
OW(14)	2.550(4)	2.413(8)	2.62(1)

The Roman numeral superscripts refer to the following symmetry code:

I $x, y, z - 1$
II $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
III $-x, 1 - y, 1 - z$
IV $x, -y, z$
V $x, 1 - y, z$
VI $x, 1 - y, z - 1$
VII $-x, y, 1 - z$

Description of the Structure of (Ag, Ca)heu.—The framework of the partially silver-exchanged zeolite does not differ from that of (Ca)heu. Analogously, the occupancy and the co-ordination of CS(2) are unchanged (Tables 2 and 5). The only significant variation is found at CS(1), where a large increase in electron density may be detected on the Fourier map of the silver-exchanged heulandite. Comparison of electron density at CS(1) and CS(2) in (Ca)heu and (Ag, Ca)heu zeolites is shown in Figure 1. Furthermore, changes in co-ordinative bonds involving water molecules at CS(1) may be observed (Table 5), although it is difficult to ascertain what co-ordination is achieved by silver ions. However assuming an Ag–O distance >2.70 Å to be non-bonding,[8] silver ions interact with framework atoms O(2) [2.686(6) Å] and with OW(11), an oxygen atom of a water molecule [2.37(1) Å], which have occupancy factors of 100%. The water molecule OW(16) [2.72(4) Å] away from CS(1) probably completes a highly distorted tetrahedral co-ordination. Higher co-ordination numbers, however, cannot be ruled out. These results, together with those of the chemical analysis, strongly suggest that almost all silver ions are located in CS(1) where they have exchanged nearly all univalent alkali-metal ions.

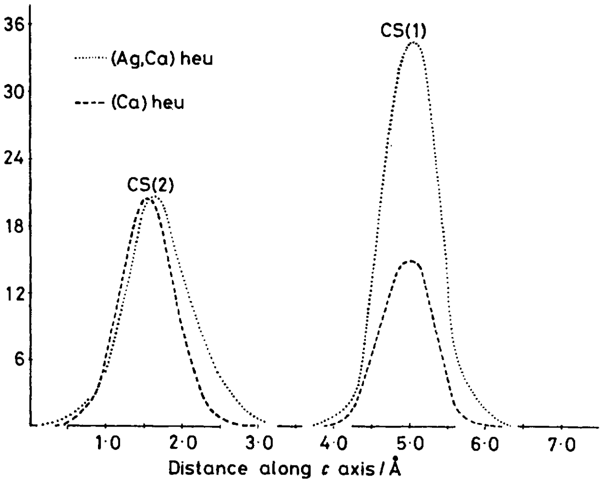

FIGURE 1 Electron density at the two cationic sites in the symmetry plane ($y = 0$) and along the c axis: CS(1), $x = 0.16$; CS(2), $x = 0.54$

The results above allow us to conclude that (*i*) no significant variation in the framework atoms occurs upon partial Ag^+ exchange, (*ii*) the univalent cations are mainly located in CS(1), and (*iii*) under the experimental conditions employed the Ag^+ ions exchange all univalent cations before any exchange of Ca^{2+} ions occurs.

From refinement of the cation-site populations and from chemical analyses, it may be assumed that CS(1) is occupied by approximately one Ca^{2+} ion and one univalent cation per unit cell, whereas CS(2) is occupied by approximately two Ca^{2+} ions per unit cell.

The structure of heulandite has been described by Merkle and Slaughter [9] and consists of well defined layers forming relatively open channels in three directions. Channels of 10- and 8-membered tetrahedral rings are parallel to c; two series of 8-membered rings are mutually parallel and at an angle of *ca.* 50° with respect to a. All the axes of these channels lie in the ac planes at $y = 0$ and $y = 0.5$. The atoms in the plane (x, 0, z) are shown in Figure 2, where the channel direction, the number of tetrahedra forming the channel rings, and the positions of cation sites are shown. Figure 2 also shows that the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton* 1979, Index issue.

10-membered tetrahedra channels are the only relatively open ones, CS(1) being located very near to its walls. All the other channels are blocked by the presence of cations distributed almost around their axes (Figure 2). These structural features and the unit charge of the ions may account for the finding that Ag^+ exchange in natural heulandite takes place by silver initially substituting the univalent cations in CS(1) which is the more accessible site.

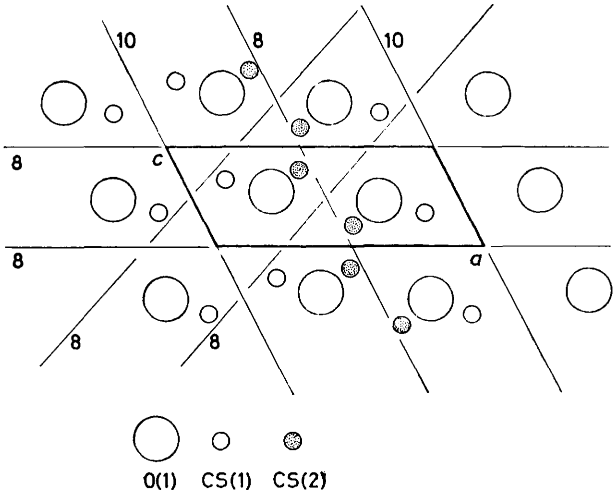

FIGURE 2 The content of the symmetry plane at $y = 0$, showing the distribution of oxygen atoms and cationic sites in this plane. The unit cell is also evident as well as the axes of the different types of channels

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