Location of Cations in Metal Ion-exchanged Zeolites. Part 2.[1] Crystal Structures of a Fully Silver-exchanged Heulandite

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The crystal structure of a fully silver-exchanged heulandite is reported. The freshly prepared monoclinic crystals, space group *C*2/*m*, have cell parameters a = 17.736(9), b = 18.104(9), c = 7.447(6) Å, β = 116.2(1)°, Z = 1, and formula $Ag_{7.3}Al_{7.2}Si_{28.8}O_{72}\cdot 18H_2O$ (from electron microprobe analysis). The final R index was 0.068 using 1 602 independent reflections in the least-squares refinement. *X*-Ray analysis results suggest that Ag^+ has exchanged two sites CS(1) and CS(2) already occupied by Ca^{2+} and Na^+ in the natural heulandite. Furthermore, a new site, CS(3), with a low occupancy has been ascribed to Ag^+. However, the total amount of silver ions (4.1 per unit cell) detected from *X*-ray refinement is significantly smaller than that derived from chemical analysis. This suggests that the remainder of the Ag^+ ions are spread out in the zeolite pores. Since crystals after long exposure in air darken, a second crystal structure analysis was carried out using a crystal of (Ag)heu exchanged under different conditions and after exposure to air for two months. No significant difference was found with the above results.

RECENTLY we have reported the crystal-structure analysis of a natural and a partially Ag-exchanged heulandite,[1] hereafter (Ca)heu and (Ca,Ag)heu, showing the possibility of establishing the approximate distribution of cations over the same site, by means of single-crystal *X*-ray analysis before and after a controlled exchange. Thus the cation site CS(1) of the natural heulandite [2,3] is occupied by Ca^{2+} and Na^+ (1 : 1), while CS(2) is occupied only by Ca^{2+}. Furthermore, partial exchange by Ag^+ ions leads to the substitution of only Na^+ cations. Since we are interested in a systematic study of zeolites exchanged with transition metals, the next step was the preparation and the crystal-structure analysis of the fully Ag-exchanged heulandite (Ag)heu. In fact, in the latter case the complete exchange of Ca^{2+} ions should nearly double the ion contents in the unit cell, so that it was of interest to see whether new sites are occupied. It has been reported [4] that in fully exchanged Ag-A and K-A zeolites the univalent ions tend to spread out in many sites with small occupancy.

EXPERIMENTAL

Preparation of (Ag)heu.—The (Ag)heu was prepared starting from natural heulandite [5] (from N.E. Azerbaijan, Iran), the same employed in our previous work,[1] by using the hydrothermal method.[6] Two separate samples of (Ca)heu crystals, meshed between 250 and 500 μm, were exchanged under different conditions and analysed by means of wavelength-dispersive microprobe analysis carried out using a fully automated ARL SEMQ instrument (Table 1). Both exchanged samples were found to have the same diffraction pattern. Since the freshly exchanged colourless crystals slowly became dark grey on standing in air, we collected two sets of diffraction data, one using a freshly prepared single-crystal (sample II) and another using a dark grey crystal (sample I) prepared two months before.

Crystal Data, Structure Determination, and Refinement.—Refined cell parameters are given in Table 1 with other crystal data of interest. Reflections having $I > 3\sigma(I)$, after correction for Lorentz-polarization factors, were used in the subsequent calculations. The choice of the space group *C*2/*m* was decided in the same way as in previous work.[1,3] We have refined the structure using both sets of collected data. However, we will discuss the results obtained in the case of sample I, since no significant difference between the atomic co-ordinates of samples I and II has been detected despite the different colour and exchange conditions. Fourier maps calculated using the available parameters of framework atoms allow location of cations and water molecules. The distribution of Al and Si species and hence their atomic scattering factors were those used previously.[1] The occupancies of cations and water molecules were refined during the isotropic refinement [1] and were then held constant. Atomic co-ordinates are given in Table 2. Observed and calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 23085 (9 pp.).†

TABLE 1

Chemical analysis (%) [a] and crystal data [b]

	Sample [c]	
Species present	I	II
SiO_2	52.79	51.42
Al_2O_3	11.22	11.37
Ag_2O	25.99	26.95
H_2O	(10.00)	(10.26)
CaO	0.00	0.00
Na_2O	0.00	0.00
Formula per unit cell	$Ag_{7.3}Al_{7.2}Si_{28.8}O_{72}\cdot 18H_2O$	$Ag_{7.7}Al_{7.5}Si_{28.5}O_{72}\cdot 19H_2O$
M	3 267	3 328
a/Å	17.736(9)	17.725(6)
b/Å	18.104(9)	18.071(6)
c/Å	7.447(6)	7.461(4)
β/°	116.2(1)	116.1(1)
Z	1	1
U/Å^3	2 145.5	2 146.1
D_m/g cm^{-3}	2.53	2.55
D_c/g cm^{-3}	2.53	2.58
$F(000)$	1 596	1 624
μ/cm^{-1}	22	23
R	0.068	0.072
Space group	*C*2/*m*	*C*2/*m*
No. of independent reflections	1 602	1 724

[a] Values in parentheses were obtained by difference. [b] $\theta_{max.}$ 28°; λ(Mo-K_α) = 0.710 7 Å. [c] Sample I: 5 days at 160 °C in Ag[NO_3] (1 mol dm^{-3}); Sample II: 12 days at 210 °C in Ag[NO_3] (1 mol dm^{-3}).

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 2

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

Atom	x	y	z	U	Occupancy	No of positions (Wyckoff notation)
Si(1)	1 785(1)	1 711(1)	972(3)		1.0	8
Si(2)	2 158(1)	4 107(1)	5 078(3)		1.0	8
Si(3)	2 078(1)	1 910(1)	7 144(3)		1.0	8
Si(4)	671(1)	2 987(1)	4 177(3)		1.0	8
Si(5)	0	2 197(2)	0		1.0	4
O(1)	1 997(6)	5 000	4 652(13)		1.0	4
O(2)	2 322(4)	1 209(4)	6 159(9)		1.0	8
O(3)	1 860(4)	1 574(4)	8 912(9)		1.0	8
O(4)	2 291(4)	1 037(4)	2 468(9)		1.0	8
O(5)	0	3 231(5)	5 000		1.0	4
O(6)	801(3)	1 651(4)	491(9)		1.0	8
O(7)	1 245(4)	2 306(4)	5 472(10)		1.0	8
O(8)	143(4)	2 737(4)	1 850(9)		1.0	8
O(9)	2 149(4)	2 507(4)	1 969(9)		1.0	8
O(10)	1 223(3)	3 702(4)	4 269(10)		1.0	8
OW(11)	2 351(10)	5 000	7(23)	7.9 (0.4)	1.00	4
OW(12)	611(76)	0	8 206(180)	14.9 (4.2)	0.20	4
OW(13)	779(16)	4 217(16)	9 693(36)	9.2 (0.8)	0.45	8
OW(14)	0	5 000	5 000	7.8 (0.9)	0.66	2
OW(15)	70(40)	986(24)	5 464(74)	7.0 (1.4)	0.20	8
OW(16)	772(25)	717(24)	3 303(57)	13.6 (1.3)	0.40	8
OW(17)	0	4 144(36)	0	10.4 (1.9)	0.30	4
CS(1)	1 615(3)	0	6 758(7)		0.41	4
CS(2)	375(2)	5 000	2 550(7)		0.43	4
CS(3)	877(18)	0	925(40)		0.13	4

RESULTS AND DISCUSSION

The zeolite framework is close to that previously reported [1] for (Ca)heu and (Ca,Ag)heu. The Si–O bond lengths are reported in Table 3. The main differences

TABLE 3

Relevant interatomic distances (Å)

(*a*) Mean Si–O *

Si(1)	1.621(6)	Si(4)	1.619(5)
Si(2)	1.662(5)	Si(5)	1.625(6)
Si(3)	1.626(6)		

(*b*) Ag–O distances <3 Å

Ag(1)–O(2)	2.652(8)	Ag(2)–O(1)	2.600(9)
–O(2)^{V}		–O(13)^{II}	2.44(3)
–O(12)	2.5(2)	–O(13)^{IV}	
–O(16)	2.68(4)	–O(14)	2.203(5)
–O(16)^{V}		–O(17)	2.31(4)
–O(11)^{IV}	2.30(1)	–O(17)^{V}	
Ag(3)–O(12)^{I}	1.9(1)		
–O(16)	2.27(6)		
–O(16)^{V}			

(*c*) Ag · · · Ag contacts

Ag(1) · · · Ag(3)	3.87(4)	Ag(2) · · · Ag(2)^{III}	3.434(7)
Ag(1) · · · Ag(3)^{V}	3.95(3)	Ag(3) · · · Ag(3)^{VII}	2.79(4)

The Roman numeral superscripts refer to the following symmetry code:

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

* The mean estimated standard deviations of the individual values are in parentheses.

are in water molecules and cation sites. Water molecules OW(11)—OW(16) occupy the same or slightly displaced positions detected in (Ca)heu and (Ca,Ag)heu, generally with a lower occupany. A new peak on the Fourier map with occupancy factor of 0.3 was attributed to a water molecule, OW(17). The low electron density suggests this choice, although cation sites with a very low population cannot be excluded. On the contrary, the peak at $x = 0.073$, $y = 0$, and $z = 0.079$, already assigned in (Ca,Ag)heu to a water molecule with an

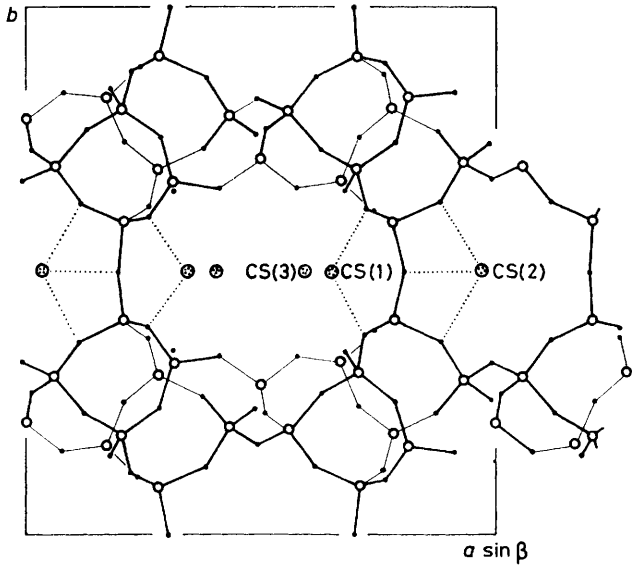

FIGURE 1 The Si,Al framework viewed along the c axis showing the cation sites for (Ag)heu

occupancy factor of 0.25, is found slightly displaced in (Ag)heu at (0.091, 0, 0.100) but with a noticeably higher electron density. This suggests that such a peak was wrongly assigned to water in (Ca,Ag)heu, owing to its low electron density, actually being a third cation site, CS(3) (see Figure 1). Its population increases with the increas-

TABLE 4

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

(*a*) (Ca)heu	Ca^{2+} per unit cell	Na^{+} per unit cell	Water molecules per unit cell	Density/g cm^{-3}
CS (1)	1.1	1.1		
CS (2)	1.8	0		
Structure refinement	2.9	1.1	20.6	2.15 (calc.)
Chemical analysis	3.1	1.1	24.0	2.15 (meas.)

(*b*) (Ca,Ag)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	2.15 (calc.)
Chemical analysis	3.1	1.3	25	2.18 (meas.)

(*c*) (Ag)heu *	Ag^{+} per unit cell	Water molecules per unit cell	
CS (1)	1.8 (1.7)		
CS (2)	1.8 (1.7)		
CS (3)	0.5 (0.5)		
Structure refinement	4.1 (3.9)	15.7 (15)	2.53 (2.58) (calc.)
Chemical analysis	7.3 (7.8)	18 (19)	2.53 (2.55) (meas.)

* Values for sample II in parentheses.

ing exchange of silver ions and reaches an occupancy factor of 0.12 in (Ag)heu. On the other hand, site CS(3) is not located far from the third site found at (0, 0, 0) in two natural clinoptilolites,[7] which have the same Si,Al framework and the same CS(1) and CS(2) sites of heulandite. However, in a recent determination of two other clinoptilolites [8] a site (0.094, 0, 0.074) was assigned to a water molecule with an occupancy factor of 0.34. Sites CS(1) and CS(2) have been located nearly in the same positions found in (Ca,Ag)heu both with an occupancy factor of 0.42. It must be pointed out that imposed higher occupancies for the Ag^{+} ion followed by a refinement lead to significantly larger values R. The Ag–O co-ordination bond lengths (<2.7 Å) are given in Table 3.[1] For both Ag(1) and Ag(2) the co-ordination does not exceed six, with a largely distorted octahedral stereochemistry, while only three short distances are found for Ag(3), although many other long contacts near to 3 Å with the O(6) and O(4) oxygen atoms are detected.

A comparison of site occupancies, derived from chemical and crystallographic analyses for (Ca)heu, (Ca,Ag)heu and (Ag)heu is reported in Table 4; for (Ag)heu, the corresponding figures for sample II are given in parentheses. The electron density at the cation sites in (Ag)heu, (Ca)heu, and (Ca,Ag)heu is reported in Figures 2 and 3 respectively. Taking into account data of Table 4 and Figures 2 and 3 a qualitative progression of the exchange of cations in the natural heulandite by silver ions may be suggested. At first Ag^{+} ions exchange with Na^{+} ions in site CS(1) with a significant increase of the electron density which, in contrast, remains unchanged at CS(2). Probably some Ag^{+} ions start to occupy the site CS(3). When the exchange is complete, the electron density at CS(1) does not change significantly; in fact data of Table 4 show that 1.0 Ca^{2+} per unit cell of (Ca,Ag)heu is replaced by 0.5 Ag^{+}. Such an exchange of Ca^{2+} and Ag^{+} cations should not provoke a large variation of the electron density at CS(1). However, the electron density increases in the CS(3) as well as in site CS(2) where it reaches nearly the same value of that in CS(1), 2 Ca^{2+} per unit cell being replaced by 1.8 Ag^{+} (Table 4).

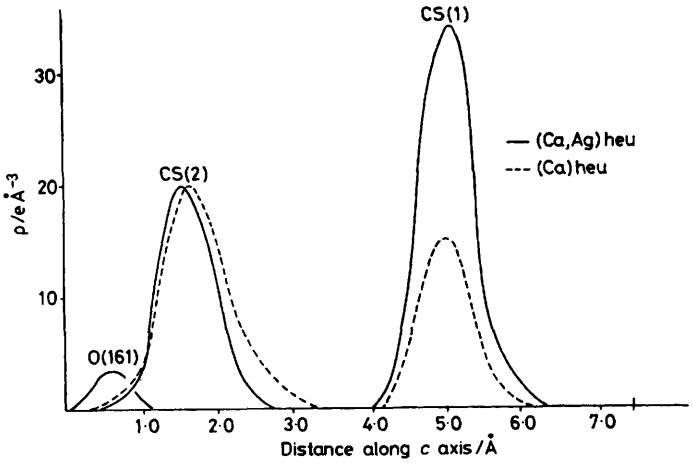

FIGURE 2 Electron density in (Ca)heu and (Ca,Ag)heu at the cation sites in the symmetry plane ($y = 0$) and along the c axis: CS(1), $x = 0.16$; CS(2), $x = 0.54$. The electron density at the site assigned to OW(161) in (Ca,Ag)heu is also reported, $x = 0.07$

However it must be emphasised that only 56% (sample I) of exchanged Ag^{+} ions is detected by X-ray data refinement in the three cationic sites, although the chemical analysis indicates a complete exchange as confirmed by the value of the measured density (Table 4). Such a difference is highly significant, even if the occu-

pancy of each site may be larger than that suggested by the crystallographic analysis. In fact the refined cation occupancy is often found [1,3,7] to be lower than that derived from chemical analysis, probably because of the correlation between thermal factors and occupancies

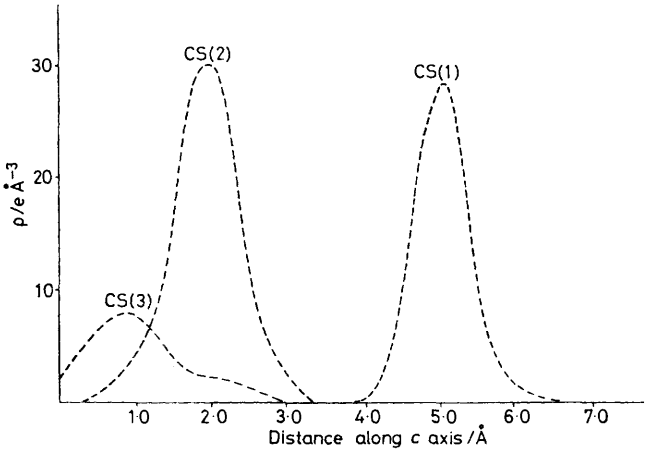

FIGURE 3 Electron density in (Ag)heu at the three cation sites in the symmetry plane ($y = 0$) and along the c axis: CS(1), $x = 0.16$; CS(2), $x = 0.54$; CS(3) $x = 0.09$

during the refinement. Furthermore, the new site assigned to O(17) could be attributed to silver ions, although a small increase of silver content is expected owing to its low electron density. Taking into account that no significant variation is observed in the frameworks of (Ag)heu and (Ca)heu, the above results may be interpreted assuming that some silver ions are spread out in the channels of the zeolite together with some water, giving no detectable contribution to the diffraction pattern. A proportion of the 'disordered' Ag^+ ions, probably less tightly bound, may undergo a reduction process to metallic silver which may be ultimately responsible for the observed crystal darkening. Since it is likely that there will be an even distribution of reduced Ag atoms no significant variation of the diffraction pattern is expected upon darkening.

Finally, it is interesting to observe that sites CS(1) and CS(2) in both heulandites [1,2,3] and clinoptilolites [7,8] have always been found with occupancy factors around 0.5. This suggests that there is a limit to their occupancy, so that when the Si : Al ratio or the exchange by univalent cations increases the number of cations in the cell, other sites are populated. In fact, in a natural heulandite (Si : Al = 2.9 : 1) completely exchanged with potassium,[9] five cation sites have been detected. The electrostatic potential of the framework, the co-ordination geometry of sites, and short cation–cation contacts may be responsible for such a limit [for (Ag)heu see Table 3].

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