tions of the octahedron are reversed, the $Br(3^{i})$—Mn—$Br(2^{ii})$ and $Br(3^{i})$—Mn—Br(1) angles being 88·6 (7) and 91·4 (6)° respectively, whilst the $Br(3^{i})$—Mn—$Br(3^{ii})$ angle is 90·0 (3)°. This difference between the structures is probably due to the less favourable radius ratio for the close-packing of the Rb and halogen ions in the heptabromodimanganate. This in turn has led to a more uneven distribution of Rb—halogen separations and given Br(3) a somewhat greater z parameter than Cl(3) in the structure of $Rb_3Mn_2Cl_7$.

The mean Mn–Br and Br–Br lengths, 2·68 and 3·78 Å respectively, agree very well with the corresponding values (2·68 and 3·79 Å) in $RbMnBr_3$.

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Cation-Site Location in a Natural Chabazite

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Abstract. (Ca,Sr) chabazite, $Ca_{1.4}Sr_{0.3}Al_{3.8}Si_{8.3}O_{24}\cdot 13H_2O$ from electron microprobe analysis, rhombohedral, $R\bar{3}m$, $a = 9{\cdot}421\,(4)$ Å, $\alpha = 94{\cdot}20\,(1)°$, $U = 829$ Å^3, $Z = 1$, μ(Mo $K\alpha$) = 0·82 mm^{-1}; final R = 0·071 for 578 independent reflections. The location of three cation sites along the [111] direction and of water molecules in the zeolitic cage is discussed and compared with that previously attributed on the basis of a two-dimensional analysis.

Introduction. Chabazite is a natural zeolite of group 4, its framework being built up by double six-membered rings (D6R), linked by tilted four-membered rings (Fig. 1). The framework contains large ellipsoidal cavities of 6·7 × 10 Å, entered by eight-membered rings (Breck, 1974). The ion-exchange properties and the role played by exchangeable cations in molecule-sieving properties justify the interest for a structural study of chabazites (Mortier, Pluth & Smith, 1977*a*,*b*; Pluth, Smith & Mortier, 1977; Barrer, 1978). On the other hand only two-dimensional X-ray diffraction analyses have been reported for hydrated natural chabazites (Smith, Rinaldi & Dent Glasser, 1963; Smith, Knowles & Rinaldi, 1964). From these results it was suggested that cations occupy but one site at $x = 0{\cdot}357$, $y = 0{\cdot}494$, $z = 0{\cdot}577$, so that the crystal should contain two calcium ions and 13 water molecules per unit cell.

To verify such an arrangement of cations and water molecules, we have undertaken the three-dimensional X-ray analysis of a natural chabazite as the first step of a structural study of chabazites exchanged with transition-metal ions. The natural sample was from north-east Azerbaijan, Iran (Comin-Chiaramonti, Pongiluppi & Vezzalini, 1979). Wavelength dispersive microprobe analysis was carried out on eight single crystals of chabazite, using a fully automated ARLSEMQ instrument.

The mean chemical analysis and the atomic ratios evaluated for 24 O atoms are given in Table 1. The chemical analysis indicates that the chabazite is particularly rich in strontium.

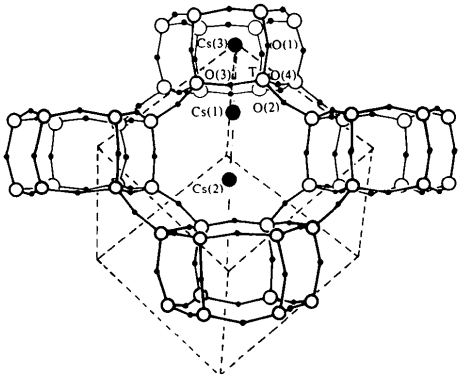

Fig. 1. A view of a model of the natural chabazite with the unit cell. The numbering scheme for the framework atoms and cationic sites is shown.

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Table 1. *Chemical analysis*

		Observed range
SiO_2	47·9%	(45·2–50·3%)
Al_2O_3	18·9	(18·0–21·3)
CaO	7·6	(7·2–7·7)
SrO	3·0	(2·6–3·7)
Na_2O	0·1	(0·02–0·13)
K_2O	0·1	(0·04–0·14)
H_2O	(22·4)*	
E	+11·9†	

Formula per unit cell: $Ca_{1.4}Sr_{0.3}Al_{3.8}Si_{8.3}O_{24}.13H_2O$ based on the above analysis.

* The water content has been obtained by difference.

† The 'balance error' E is calculated by the formula $E = (Al - Al_{theor})/Al_{theor} \times 100$ where $Al_{theor} = Na + K + 2(Sr + Ca)$.

A rhombohedral crystal (0·3 × 0·5 × 0·3 mm) was selected for data collection on an automated Siemens diffractometer using Mo $K\alpha$ radiation. The reflections of one hemisphere were collected in the range $3{\cdot}5 \leq \theta \leq 28°$. A total of 578 independent reflections, having $I > 3\sigma(I)$, were corrected for the Lorentz–polarization factor. In accordance with Smith, Rinaldi & Dent Glasser (1963), the space group $R\bar{3}m$ was selected. A Fourier map calculated using the contributions of the framework atoms, as located in the two-dimensional analysis (Smith *et al.*, 1964), revealed the remaining unit-cell content (see below). The structure was refined by full-matrix least-squares techniques with anisotropic temperature factors for the cations and the framework atoms. Occupancies and temperature factors of the cations and water molecules were refined separately. Several cycles of refinement carried out with constant occupancies were followed by more cycles in which temperature factors were held constant. This was done to increase the possibility of a good convergence towards a physically meaningful result, owing to the strong correlation between temperature factor and occupancy of the various sites. The final R was 0·071. The atomic scattering factors were those of Moore (1963) and the calculations were done using the XRAY system (Stewart, Kundell & Baldwin, 1970). Atomic scattering factors of neutral O and O^- for water sites and the oxygen framework were used. For T and cation sites Al^{2+}/Si^{3+} and Ca^{2+}/Sr^{2+} atomic scattering factors mixed according to the chemical analysis were employed. Atomic coordinates are listed in Table 2, bond lengths and angles of interest in Table 3.*

Discussion. The chabazite framework is that already described for other hydrated chabazites (Pluth *et al.*, 1977; Smith *et al.*, 1964). The distribution of Al and Si in the TO_4 tetrahedra was derived from the elemental analysis which gave an Al/T ratio of 0·31. Such a distribution is in agreement with the T—O bond lengths. In fact the mean T—O distance of 1·647 (3) Å corresponds to an Al/Si ratio of 0·28 (Smith & Bailey, 1963).

A view of the unit cell with the numbering scheme for the crystallographically independent atoms is reported in Fig. 1.

The two highest peaks in the electron density map, not belonging to framework atoms, were located along the [111] diagonal at $x = y = z = 0{\cdot}204$ [CS(1)] and $x = y = z = 0{\cdot}407$ [CS(2)]. Their electron density values are about twice [CS(1)] and equal [CS(2)] to the value of the framework O atom with unitary occupancy factor. Consequently Ca^{2+}, Sr^{2+} ions, in the ratio derived from the chemical analysis, were located in the above twofold sites on the triad axis with occupancy

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36209 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional coordinates* (×10⁴) *and thermal parameters with e.s.d.'s in parentheses*

Anisotropic temperature factors have been deposited. O(5), O(6) and O(7) are the O atoms of water molecules refined isotropically. The equivalent temperature factors, B_{eq} (Å²), for the remaining atoms have been calculated by $B_{eq} = \frac{1}{3}(B_{11}a^{*2}a^2 + B_{12}a^*b^*ab\cos\gamma + \ldots)$.

	x	y	z	B_{eq}	Occupancy factor ($f°$)	Number of positions (Wyckoff notation)
T	1044 (1)	3338 (1)	8749 (1)	1·04 (3)	1·0	12
O(1)	2638 (5)	−2638 (5)	0	3·0 (2)	1·0	6
O(2)	1548 (4)	−1548 (4)	5000	2·1 (2)	1·0	6
O(3)	2515 (5)	2515 (5)	8946 (8)	2·7 (2)	1·0	6
O(4)	248 (5)	248 (5)	3277 (7)	2·5 (2)	1·0	6
O(5)	4180 (13)	4180 (13)	7599 (19)	5·4 (3)	0·57	6
O(6)	5000	5000	0	5·8 (6)	0·50	3
O(7)	2024 (47)	3101 (48)	4913 (51)	9·9 (1·1)	0·23	12
CS(1)	2038 (8)	2038 (8)	2038 (8)	6·4 (3)	0·53	2
CS(2)	4065 (8)	4065 (8)	4065 (27)	4·2 (4)	0·24	2
CS(3)	0	0	0	5 (2)	0·11	1

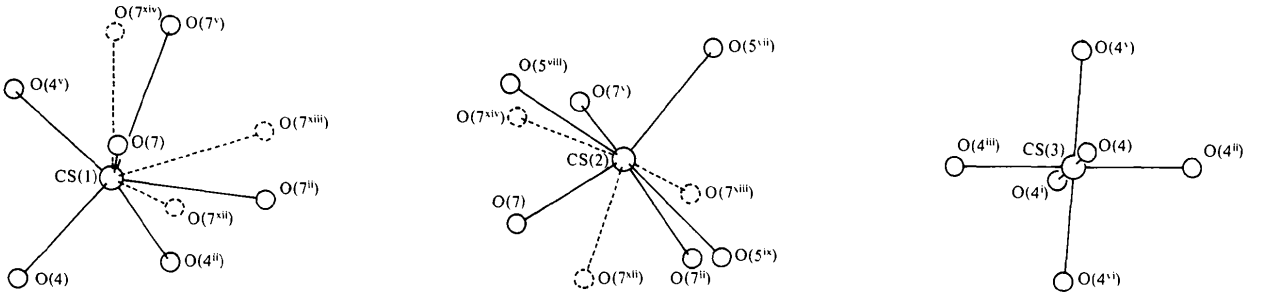

Fig. 2. Coordination of water molecules around the cationic sites. The dashed lines indicate the alternative coordination for three of the O(7) atoms.

factors (f) of 0·53 [CS(1)] and 0·24 [CS(2)] respectively as derived from the final refinement. Both CS(1) and CS(2) show a highly distorted octahedral coordination (see Fig. 2) with CS–O distances in the range 2·29–2·88 Å.

Furthermore, a low electron density peak was detected at the centre of the D6R cage. This peak was assumed as a third cation site CS(3) with an occupancy factor of 0·11.

In fact the coordination is nearly octahedral, with CS(3) surrounded by six framework O atoms at distances of 3·07 Å. Furthermore this site has already been interpreted as a cation site in some fully dehydrated chabazites (Mortier *et al.*, 1977*a*,*b*; Pluth *et al.*, 1977). Simultaneous occupancy of CS(1), CS(2) and CS(3) is ruled out by electrostatic repulsion between ions about 3·0 Å apart. However, the occupancies of the cations are such as to permit a statistical location in the sites, since f[CS(1)] + f[CS(2)] = 0·77 < 1 and f[CS(1)] + f[CS(3)] = 0·64 < 1. The total number of cations in the unit cell of 1·65 is in good agreement with that of 1·7 derived from analytical data.

The sites CS(1) and CS(3) assigned to the cations are close to those assigned in the dehydrated Ca chabazites (Mortier *et al.*, 1977*a*,*b*). The site CS(2) is not occupied in the dehydrated form, since such a position does not provide any bonding interaction with framework O atoms. On the contrary the above assignment is in contrast with the results of a previous analysis of the hydrated form, which located water molecules in all these sites (Smith, Rinaldi & Dent Glasser, 1963). Finally, water molecules were located in the remaining three low peaks. Their final occupancies are reported in Table 2. The total number of water molecules in the unit cell is 7·7, while 13 molecules should be present according to the chemical analysis.

This difference may derive partly from the strong correlation between temperature factors and occupancy during the refinement and partly from the fact that the water content has been obtained by difference and all the errors of the chemical analysis contribute. Furthermore, the existence of further water sites having an occupancy too low to be detected on the Fourier maps cannot be excluded.

Table 3. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

T–O(1^{xi})	1·643 (2)	CS(2)–O(5^{vii})	2·88 (2)
T–O(2^{x})	1·653 (2)	CS(2)–O(5^{viii})	
T–O(3)	1·642 (4)	CS(2)–O(5^{ix})	
T–O(4^{iv})	1·649 (4)	CS(2)–O(7)	2·28 (5)
CS(1)–O(4)	2·685 (6)	CS(2)–O(7^{ii})	
CS(1)–O(4^{ii})		CS(2)–O(7^{v})	
CS(1)–O(4^{v})		CS(2)–O(7^{xii})	
CS(1)–O(7)	2·82 (5)	CS(2)–O(7^{xiii})	
CS(1)–O(7^{ii})		CS(2)–O(7^{xiv})	
CS(1)–O(7^{v})		CS(3)–O(4)	3·069 (7)
CS(1)–O(7^{xii})		CS(3)–O(4^{i})	
CS(1)–O(7^{xiii})		CS(3)–O(4^{ii})	
CS(1)–O(7^{xiv})		CS(3)–O(4^{iii})	
		CS(3)–O(4^{v})	
		CS(3)–O(4^{vi})	
O(1^{xi})–T–O(2^{x})	107·9 (2)	O(3)–T–O(4^{iv})	107·7 (3)
O(1^{xi})–T–O(3)	111·8 (2)	O(1)–T^{xv}–T^{xvii}	146·5 (2)
O(1^{xi})–T–O(4^{iv})	112·1 (1)	O(2)–T^{xvi}–T^{xix}	140·9 (2)
O(2^{x})–T–O(3)	106·1 (1)	O(3)–T–T^{xii}	149·1 (2)
O(2^{x})–T–O(4^{iv})	111·1 (3)	O(4)–T^{xvii}–T^{xix}	147·6 (2)

Symmetry code: (i) $-x,-y,-z$; (ii) z,x,y; (iii) $-z,-x,-y$; (iv) $y, z, 1 + x$; (v) y,z,x; (vi) $-y,-z,-x$; (vii) $1 - x, 1 - y, 1 - z$; (viii) $1 - z, 1 - x, 1 - y$; (ix) $1 - y, 1 - z, 1 - x$; (x) $-y, 1 - z, 1 - x$; (xi) $z, x, 1 + y$; (xii) y,x,z; (xiii) z,y,x; (xiv) x,z,y; (xv) $y, z - 1, x$; (xvi) $1 - z, -x, 1 - y$; (xvii) $z - 1, x, y$; (xviii) $1 - z, -y, -x$; (xix) $x, z - 1, y$.

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Palladium Metaborate

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Abstract. PdB_2O_4, tetragonal, $I\bar{4}2d$, $a = 11{\cdot}672$ (2), $c = 5{\cdot}698$ (1) Å, $V = 776$ (1) Å^3, $Z = 12$, $M_r = 192{\cdot}02$, $D_c = 4{\cdot}92$ Mg m^{-3}, μ(Mo $K\alpha$) = 2·117 mm^{-1}. 476 non-equivalent reflections with $I > 3\sigma(I)$ were measured up to $\sin\theta/\lambda = 0{\cdot}66$ Å^{-1}; $R(F) = 0{\cdot}020$. The structure is isotypical with its Cu analogue. The average Pd—O bond distance is 2·033 (5) Å.

Introduction. By applying hydrostatic pressure of about 40 × 10^8 Pa to a 1:1 mixture of $Pd(NO_3)_2.2H_2O$ and B_2O_3 at 1073 K for 6 h followed by rapid quenching the first borate of palladium was obtained in the form of idiomorphic, dark-brown to black crystals of up to 500 μm. The crystal form is a combination of the predominant tetragonal scalenohedron and the tetragonal prisms {100}. The morphological aspect of the crystals is that of a tetrahedron. Preliminary investigations showed the strong relationship between this new compound and the already known CuB_2O_4 (Martínez-Ripoll, Martínez-Carrera & García-Blanco, 1971). In a preliminary report this relationship was stated and interplanar distances were given (Depmeier, Schmid & Haenssler, 1980). Lattice parameters obtained from powder work and given in that report agree very well with the single-crystal results given here. The latter have been obtained from a least-squares refinement of the 2θ values of 54 reflections situated between 7·959 and 54·983° and centred on a Philips PW 1100 diffractometer with Zr-filtered Mo $K\alpha$ radiation. This was also used for the data collection with a crystal of the form of a tetrahedron with edge lengths of about 0·25 mm. Four equivalent reflections were measured up to $\sin\theta/\lambda = 0{\cdot}66$ Å^{-1}, yielding a total of 1994 reflections. Two test reflections measured after every 100 min showed no significant change during the data collection. The equivalent reflections were averaged, resulting in 478 non-equivalent reflections, 476 of which with $I > 3\sigma(I)$ were classed as observed and were used for the refinement. No absorption correction was applied ($\mu R \sim 0{\cdot}4$). The atomic positions of CuB_2O_4 (Martínez-Ripoll, Martínez-Carrera & García-Blanco, 1971) were used as a starting point and this model refined immediately. The occurrence of negative temperature-factor coefficients was overcome by performing an isotropic-extinction correction. The final R value was $R(F) = 0{\cdot}020$ with anisotropic temperature-factor coefficients for Pd and O, but isotropic temperature factors for B. All calculations were carried out with the XRAY system (1976) on the Univac 1100 computer of the University of Geneva. Table 1 lists the final atomic positions and Table 2 the bond lengths and angles.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36356 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* (×10^4) *and equivalent Debye–Waller factors* (×10^3) (*isotropic U for boron*)

	Wyckoff notation	Point symmetry	x	y	z	U_{eq}/U (Å^2)
Pd(1)	4(*b*)	$\bar{4}$	0	0	5000	3·1 (2)
Pd(2)	8(*d*)	2	802 (1)	2500	1250	3·1 (2)
O(1)	16(*e*)	1	1619 (3)	702 (3)	4978 (7)	3 (1)
O(2)	8(*d*)	2	2498 (5)	2500	6250	3 (1)
O(3)	8(*d*)	2	2500 (4)	893 (5)	8750	6 (1)
O(4)	16(*e*)	1	737 (3)	1878 (3)	7922 (6)	3 (1)
B(1)	16(*e*)	1	1843 (5)	1490 (5)	6979 (10)	5 (1)
B(2)	8(*d*)	2	8 (7)	2500	6250	1 (1)

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