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# A Refinement of the Cation Positions in Synthetic Zeolite Type *A*

BY P. A. HOWELL

*The Research Laboratory of the Linde Company*
*Division of Union Carbide Corporation, Tonawanda, New York, U.S.A.*

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The structure of anhydrous synthetic sodium zeolite type *A* has been refined by the method of least squares. The refined structure has essentially the same Si, Al and O positions, as given by Reed & Breck (1956), but the 8 $Na_I$ ions near the six-membered oxygen rings randomly occupy 24 fold positions of the space group and the 4 $Na_{II}$ ions near the eight-membered oxygen rings randomly occupy another set of 24 fold positions. For the refined structure $R=0{\cdot}16$ versus 0·21 for the former model. That the cation positions were in error in the former model was suggested by the calculation of a coulombic potential map for the structure with the omission of cations.

## Introduction

Zeolite minerals present many interesting structural problems. One of these problems is the location of the cations in relationship to the Si, $AlO_{4/2}$ tetrahedra of the frameworks. We have approached this problem by calculating the coulombic potential at points in the unit cell of a zeolite due to the framework atoms alone. The lowest points on this function giving reasonable cation distances then represent points in space most likely to be occupied by the cations in the structure. Treating the structure of anhydrous synthetic sodium zeolite type *A* in this way we discovered that the cation positions, Reed & Breck (1956), did not lie in positions of low potential. By placing the cations in positions of lower potential and refining we have arrived at cation positions for zeolite type *A* which give better agreement with the X-ray data.

## Structure of zeolite type *A* as determined by Reed & Breck (1956)

The structure of anhydrous sodium zeolite type *A*, $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$, space group $O_h^1$–$Pm3m$, $a_0=$ 12·28 Å was determined by Reed & Breck (1956) using trial and error methods, powder data, and ten unique *hk*0 reflections for refinement of the (100) Fourier projection. The atomic coordinates given by their determination are shown in Table 1 along with the coordinates obtained in this investigation. Their Fourier projection on (100) along with its interpretation is given in Figs. 1(*a*) and (*b*). A recalculation of structure factors for their coordinates are given in Table 2 along with observed structure factors and structure factors for the best model of this investigation.

Table 1. *Atomic coordinates*

| Atom | No. in cell | Coordinates of Reed & Breck | | | Coordinates given by refinement | | |
|---|---|---|---|---|---|---|---|
| | | *x* | *y* | *z* | *x* | *y* | *z* |
| $O_I$ | 24 | 0·110 | 0·110 | 0·345 | 0·1133 | 0·1133 | 0·3444 |
| $O_{II}$ | 12 | 0 | 0·220 | 0·500 | 0 | 0·2214 | 0·5000 |
| $O_{III}$ | 12 | 0·289 | 0·289 | 0 | 0·2913 | 0·2913 | 0 |
| Si, Al | 24 | 0·370 | 0·183 | 0 | 0·3702 | 0·1864 | 0 |
| $Na_I$ | 8 | 0·188 | 0·188 | 0·188 | 0·2419 | 0·2419 | 0·1708 |
| $Na_{II}$ | 4 | 0·410 | 0·410 | 0 | 0·5000 | 0·4093 | 0·0397 |

## Experimental data

Slow speed X-ray spectrometer traces over the angular range 4–56° 2$\theta$ were obtained of activated synthetic sodium zeolite type *A* powder, Linde Company Lot 4541, using Ni filtered copper radiation and dry He to maintain the sample in an anhydrous condition. Observed structure factors were derived from the spectrometer line heights by applying the Lorentz, polarization and powder line multiplicity factors. For lines representing more than one reflection, *hkl* combination, the highest multiplicity factor, $P_{\text{max.}}$, was applied to the observed intensity. For such non-unique lines,

$$F_o = (\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}} ,$$

where the sum is over all the reflections contributing to the line. The $F_o$ are given in Table 2. From a comparison of these $F_o$ directly with the $F_o$ given by Reed & Breck, (1956), a discrepancy factor between the two sets of data of $R=0{\cdot}11$ was computed for 23 observed lines. Considering that the data were secured on different lots of material on different spectrometers at different times and the possible changes in intensity due to hydration, the agreement is considered to be satisfactory.

## Calculation of the coulombic potential and postulate of the trial model

The exchangeable cation positions in a zeolite will be a result of the attractive and repulsive forces between the cations and the Si, $AlO_{4/2}$ framework. Trial positions were therefore derived in the following way.

The potential due to the major attractive force,

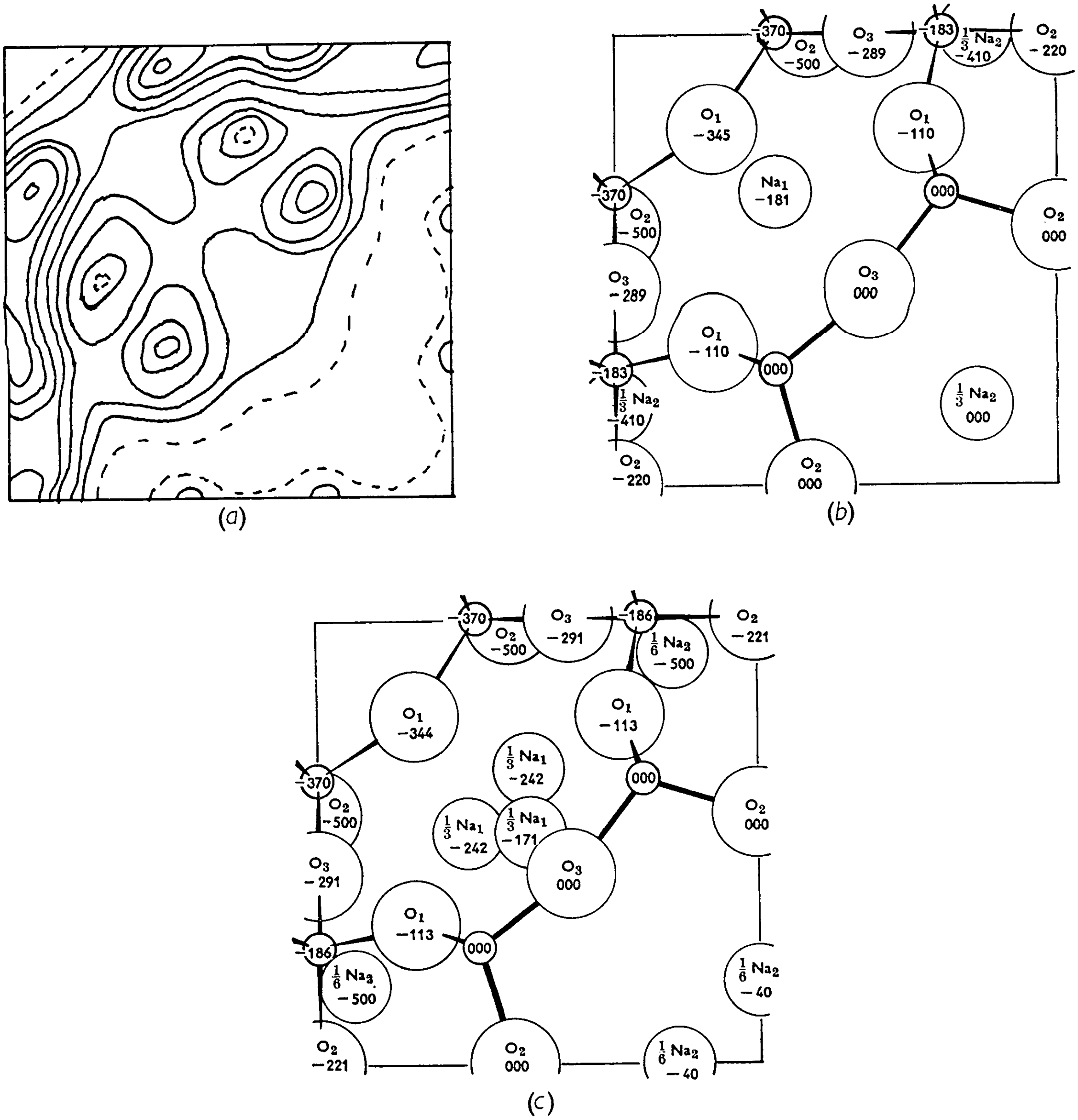

Fig. 1. (*a*) Fourier projection on (100), $\frac{1}{4}$ of unit cell, shown. Dotted line indicates electron density of one. Other contours are at intervals of two electrons per Å$^2$. Reed & Breck (1956). (*b*) Interpretation of Fourier projection shown in (*a*). Reed & Breck (1956). (*c*) Interpretation of Fourier projection shown in (*a*) according to the refined model.

coulombic, was calculated for various points within the asymmetric unit using the formula

$$V_j = \sum_{i=1}^{N} Q_i/r_{ij}\,.$$

$Q_i$ is the charge on the *i*th atom of the framework and $r_{ij}$ is the distance from the *i*th atom to point *j*. In the calculation the sum was taken over the 120 framework atoms (48 Si, Al and 72 O) surrounding the large, $\alpha$, cage in the structure using a charge of $+3{\cdot}5$ for Si, Al positions and $-2{\cdot}0$ for O positions. A typical section of such a potential map is given in Fig. 2, which indicates that the cation positions of Breck & Reed are not at positions of low potential.

The repulsive forces were taken into account by restricting possible cation positions to surfaces at a constant distance (2·30 Å equal to the sum of the oxygen plus sodium ionic radii) away from the centers of the framework oxygen atoms. The points of lowest coulombic potential on such surfaces were then taken as the cation locations for the first trial model. These positions were:

8 $\mathrm{Na_I}$ at 0·260, 0·260, 0·184
4 $\mathrm{Na_{II}}$ at 0·368, 0·118, 0·500

Interestingly, they explain a peak on the (100) Fourier Fig. 1(*a*) at 0, ½, 0·34 which is not explained by the Breck & Reed model.

## Refinement of the structure

The 8 $\mathrm{Na_I}$ cations are in 24 fold positions of type *m* of space group $O_h^1 Pm3m$ and the 4 $\mathrm{Na_{II}}$ cations are in 24 fold positions of type *l*. Random occupancy of these positions was assumed. These cation positions were then refined using the method of least squares Hughes (1941), a selected list of 17 unique reflections with equal weighing factors, no temperature factor, and assuming that the Si, AlO framework contributions given by Reed & Breck (1956) were correct. Initial refinements were carried out by hand but at a later stage structure factors and least-squares terms were computed using a Burroughs 205 computer.

Table 2. *Observed and calculated structure factors*

A. Unique observed spectrometer lines

| *hkl* | $F_o$(a) | Reed & Breck $F_c$(b) | Refined model $F_c$(c) |
|---|---|---|---|
| 1·0·0 | 118 | 177 | 155 |
| 1·1·0 | 106 | −117 | −127 |
| 1·1·1 | 94 | −117 | −110 |
| 2·1·0 | 64 | −91 | −86 |
| 2·2·0 | 51 | −64 | −46 |
| 3·1·1 | 115 | 96 | 113 |
| 2·2·2 | 33 | −22 | −31 |
| 3·2·0 | 48 | −19 | −41 |
| 3·2·1 | 73 | 70* | 55 |
| 4·2·0 | 52 | −40 | −46 |
| 4·2·1 | 30 | 29 | 18 |
| 3·3·2 | 108 | −109* | −88 |
| 4·2·2 | 50 | 17 | 35 |
| 5·2·1 | 26 | 19* | 34 |
| 4·4·0 | 80 | 70* | 78 |
| 5·3·1 | 34 | −42* | −28 |
| 5·4·1 | 41 | −52 | −44 |

* Miscalculated in Reed & Breck paper.

B. Non-unique observed spectrometer lines

| | | Reed & Breck | | Refined model | |
|---|---|---|---|---|---|
| *hkl* | $F_o = (\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}}$(a) | $F_c$(d) | $(\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}}$(b) | $F_c$(d) | $(\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}}$(c) |
| 3·0·0 | 84 | 68 | 80 | 85 | 84 |
| 2·2·1 | | 80 | | 80 | |
| 4·1·0 | 118 | −106 | 113 | −88 | 104 |
| 3·2·2 | | −80 | | −81 | |
| 4·1·1 | 55 | −29 | 28 | −47 | 64 |
| 3·3·0 | | −22 | | −83 | |
| 5·0·0 | 55 | 175 | 70 | 113 | 46 |
| 4·3·0 | | − 3 | | − 8 | |
| 5·1·1 | 36 | −28 | 55 | −28 | 33 |
| 3·3·3 | | −113 | | −54 | |
| 5·2·2 | 57 | 84 | 65 | 65 | 49 |
| 4·4·1 | | 29 | | 3 | |
| 5·3·0 | 52 | −47 | 48 | −15 | 51 |
| 4·3·3 | | 46 | | 66 | |
| 6·0·0 | 70 | 212 | 82 | 167 | 69 |
| 4·4·2 | | 47 | | 42 | |
| 6·2·1 | 44 | 3 | 45 | 18 | 47 |
| 5·4·0 | | 40 | | 68 | |
| 4·4·3 | | 85 | | 61 | |
| 6·3·0 | 23 | −29 | 20 | 41 | 25 |
| 5·4·2 | | −23 | | −23 | |
| 7·1·0 | 72 | −95 | 78 | −83 | 60 |
| 5·5·0 | | 210 | | 138 | |
| 5·4·3 | | −15 | | −10 | |
| 7·2·0 | 40 | −44 | 39 | −75 | 64 |
| 6·4·1 | | −56 | | −85 | |

Table 2 (*cont.*)

C. Unique non-observed spectrometer lines

| | | Reed & Breck | Refined model |
|---|---|---|---|
| *hkl* | $F_o$(a) | $F_c$(b) | $F_c$(c) |
| 2·0·0 | < 17 | 1 | −12 |
| 2·1·1 | < 11* | 24 | 33 |
| 3·1·0 | < 14 | 1 | 20 |
| 4·0·0 | < 36 | −16 | 26 |
| 3·3·1 | < 20 | 16 | − 3 |
| 6·1·0 | < 29 | 25 | 14 |
| 6·2·0 | < 31 | −34 | − 5 |
| 5·3·3 | < 31 | 18 | −17 |
| 6·2·2 | < 32 | −10 | −28 |
| 6·3·1 | < 23 | − 3 | 9 |
| 4·4·4 | < 59 | 15 | −29 |
| 6·4·0 | < 36 | − 6 | − 2 |

* Observed by Reed & Breck $F_o=29$.

D. Non-unique non-observed spectrometer lines

| *hkl* | $F_o=(\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}}$(a) | $(\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}}$(b) | $(\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}}$(c) |
|---|---|---|---|
| 5·1·0 4·3·1 | < 16 | 13 | 18 |
| 5·2·0 4·3·2 | < 18 | 7 | 20 |
| 6·1·1 5·3·2 | < 22 | 15 | 20 |
| 7·0·0 6·3·2 | < 24 | 9 | 32 |
| 7·1·1 5·5·1 | < 36 | 35 | 30 |
| 7·2·1 6·3·3 5·5·2 | < 26 | 27 | 29 |

(a) Scaled to fit refined model, for comparison with Reed & Breck model multiply by 1·023.
(b) Includes temperature factor $\exp -5{\cdot}7\ (\sin\theta/\lambda)^2$.
(c) Includes temperature factor $\exp -5{\cdot}1\ (\sin\theta/\lambda)^2$.
(d) Geometric structure factor without the inclusion of a temperature factor.

When the cation positions appeared to be fairly well determined, the entire list of 68 possible structure factors was computed using the atomic scattering factors of Freeman (1958). At this point, a plot of $\ln \Sigma|F|_{\text{obs.}}/\Sigma|F_c|$ versus $(\sin\theta/\lambda)^2$ for various ranges of $\sin\theta/\lambda$ indicated that a fairly large temperature factor is required for the structure. Discrepancy factors for the observed spectrometer lines indicated the thus far refined cation positions to be better than those of Reed & Breck ($R=0{\cdot}17$ versus 0·21 for 29 observed lines). In the calculation of $R$ for non-unique lines $(\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}}_{\text{calc.}}$ was compared with $(\Sigma PF^2/P_m)^{\frac{1}{2}}_{\text{obs.}}$. One further least-squares refinement was then carried out using the 17 unique observed reflections and varying the 10 positional parameters weighting the indicated shifts according to the scattering power of the atoms involved. The resulting coordinates are given in Table 1 and Fig. 1(*c*). Structure factors for this model are given in Table 2. Discrepancy factors for this model are compared with those of Reed & Breck (1956) in Table 3. Nearest neighbor distances are given in Table 4.

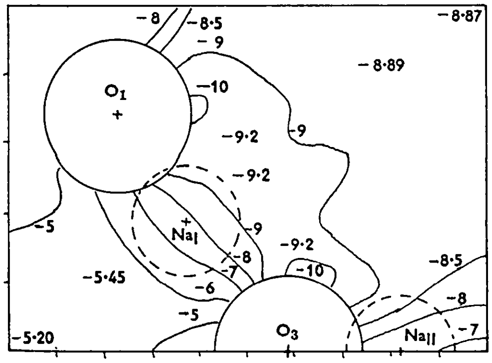

Fig. 2. Potential section on (110). The circles about $O_1$, $O_3$, $Na_I$, and $Na_{II}$ represent the ionic radii. The function was not computed within circles about $O_1$ and $O_3$ and has been adjusted to a reasonable scale.

## Discussion of the structure

The discrepancy factors given in Table 3 show that the new model is closer to the true structure of anhydrous sodium zeolite type *A* than the former model. The shifts of the last least-squares refinement indicate that the atoms are probably within 0·05 Å of their correct positions but some of them may be as far as 0·2 Å from their true positions. The temperature factor ($B=5{\cdot}13$) would indicate average temperature displacements of 0·2–0·3 Å in the structure. Keeping these limitations in mind the distances in Table 4 are quite reasonable. Smith (1954) has found for an average aluminosilicate structure with Si/Al = 1, the Si, Al–O distance 1·69 Å. The $Na_I$–O distances appear to be short; Wunderlich (1959), however, observed sodium oxygen distances of 2·29 Å in sodium hydroxide hydrates. The following minimum ring opening distances are observed in the structure: between the oxygen of the eight member rings 4·2 Å, between the oxygen of the six member rings 2·0 Å, between a sodium of type II and oxygen across the eight member ring 2·3 Å. These distances are consistent with the known adsorption properties of the material.

Table 3. *Discrepancy factors*

| Class of reflection | No. of reflections | No. of spectrometer lines | $R$ Reed & Breck | $R$ This investigation |
|---|---|---|---|---|
| Unique observed | 17 | 17 | 0·24 | 0·18 |
| Non-unique observed | 26 | 12 | 0·14 | 0·12 |
| All observed | 43 | 29 | 0·21 | 0·16 |

$R = \Sigma |F_o| - |F_c| / |F_o|$ where $|F_o|$ or $|F_c|$ for a non-unique line $= (\Sigma PF^2/P_{\text{max.}})^{\frac{1}{2}}$.

For the unobserved reflections (25 reflections, 18 lines), three calculate to be slightly above the observational limit, one of these 2·1·1 was observed by Reed & Breck.

For the unique observed reflections the framework atoms alone give an $R = 0{\cdot}30$.

Table 4. *Nearest neighbor distances for the refined model*

| | $d_{ij}$ | Average distance |
|---|---|---|
| Distances within the framework tetrahedra | | |
| Si, Al–$O_{I}$ | 1·69 Å | 1·66 Å |
| Si, Al–$O_{II}$ | 1·65 | |
| Si, Al–$O_{III}$ | 1·61 | |
| $O_{I}$–$O_{I}'$ | 2·78 | 2·71 Å |
| $O_{I}$–$O_{II}$ | 2·71 | |
| $O_{I}$–$O_{III}$ | 2·67 | |
| $O_{II}$–$O_{III}$ | 2·70 | |
| Sodium–oxygen distances | | |
| $Na_{I}$–$O_{III}$ | 2·27 Å | |
| $Na_{I}$–$O_{I}$ | 2·14 | |
| $Na_{II}$–$O_{II}$ | 2·36 | |

Thus far, the refinement has been carried out using the pseudo unit cell for zeolite *A* rather than the true unit cell with $a_0 = 24{\cdot}56$ Å. The larger cell of lower symmetry is required because of a very weak reflective indexing $\frac{5}{2}.\frac{3}{2}.\frac{1}{2}$ on the basis of the small cell and is necessary to allow alternation of $SiO_{4/2}$ and $AlO_{4/2}$ tetrahedra according to the ideas of Loewenstein (1942). Also zeolite *A* is not strictly stoichiometric. Chemical analysis of Lot 4541 gives the atom ratios $Na/Al = 0{\cdot}95 \pm 0{\cdot}04$ and $Si/Al = 0{\cdot}98 \pm 0{\cdot}02$. Si/Al ratios less than 1·0 have been noticed previously for zeolite *A*, Reed & Breck (1956), and the suggestion was made by Barrer & Meier (1958) that an extra $NaAlO_2$ unit is occluded at the center of the $\beta$ cage. The Na/Al ratio less than one may indicate cation defects in the structure or a few per cent of hydrogen exchange. Because of these many factors, further refinement of the structure does not seem justified until single crystal data is available.

It is a pleasure to acknowledge the help of Mr L. G. Dowell who aided in the experimental phases of this investigation; Mr L. D. Potts who wrote the program for the Burroughs 205 computer; and Dr D. W. Breck who aided and supported the refinement of the structure.

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# Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about* 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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## Relationships between the crystal chemistry of pyroxenes and amphiboles.

By E. J. W. Whittaker, *Ferodo Ltd., Chapel-en-le-Frith, Stockport, England*

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In a recent paper (Whittaker, 1960) it has been shown that the composition ranges of the orthorhombic amphiboles, and the different $\beta$ angles and $a \sin \beta$ values of the various series of monoclinic amphiboles, depend to a large extent on the radii of the metal ions occupying certain sites in the structure. It is therefore natural to enquire whether the same or a similar dependence can be observed in the related field of the pyroxenes.

The amphibole structure may be regarded as a packing together of narrow strips of talc-like structure. The