

The structures of the salt-bearing aluminosilicates, Species P and Q

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Auszug

Es wurden die Strukturen der salzhaltigen Aluminosilikate vom Typ P und vom Typ Q mit den Zellinhalten $\text{Ba}_{15}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}] \cdot 1,7\text{Ba}(\text{OH})_2 \cdot 12,5\text{BaCl}_2 \cdot 35\text{H}_2\text{O}$ bzw. $\text{Ba}_{15}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}] \cdot 1,6\text{Ba}(\text{OH})_2 \cdot 11,9\text{BaBr}_2 \cdot 30\text{H}_2\text{O}$ untersucht. Außerdem wurde die Struktur des Zeoliths $(\text{Na},\text{Ba}_{0,5})_{30}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}] \cdot 1,7(\text{Na}_2,\text{Ba})\text{Cl}_2 \cdot 72\text{H}_2\text{O}$ bestimmt, der aus P durch Herauslösen von BaCl_2 durch verdünnte Salpetersäure erhalten wurde. Das Untersuchungsergebnis bestätigte, daß das Gerüst aller drei Aluminosilikate auf dem des Zeoliths ZK-5 basiert. In allen drei Strukturen sind die nicht zum Gerüst gehörenden Ionen und Moleküle in den charakteristischen 18flächigen Hohlräumen nahezu identisch angeordnet. Die durch Auslaugung des BaCl_2 erhaltene Verbindung ist weitgehend durch die Form des Achtehnflächners bestimmt. Die drei Strukturen sind auch in den Anordnungen innerhalb der Sechszwanzigflächner ähnlich; deren größeres Volumen erlaubt jedoch eine stärkere Variation der Atomverteilung.

Abstract

Determinations have been made of the structures of the salt-bearing aluminosilicates, Species P and Q, having unit-cell compositions $\text{Ba}_{15}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}]1.7\text{Ba}(\text{OH})_2, 12.5\text{BaCl}_2, 35\text{H}_2\text{O}$ and $\text{Ba}_{15}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}]1.6\text{Ba}(\text{OH})_2, 11.9\text{BaBr}_2, 30\text{H}_2\text{O}$ respectively. The structure of the zeolite $(\text{Na},\text{Ba}_{0,5})_{30}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}]1.7(\text{Na}_2,\text{Ba})\text{Cl}_2, 72\text{H}_2\text{O}$ obtained from Species P by extraction of BaCl_2 with $\text{NaNO}_3 \cdot \text{aq}$ has also been determined. The structures confirmed that the aluminosilicate frameworks of all three phases were based upon that of zeolite ZK-5. Much of the non-framework scattering material was also located in the three structures. Within characteristic 18-hedral cavities the non-framework ions and molecules were almost identically arranged in Species P and Q and had a very similar configuration in the extracted Species P, so that this configuration appears to be determined largely by the form of the 18-hedron. The arrangement within 26-hedra also showed similarities between the three structures but here the greater volume permitted greater variations in configuration.

Introduction

In 1948 (BARRER) an account was given of the synthesis of two novel aluminosilicates, one rich in intercalated BaCl_2 (Species P) and the other in BaBr_2 (Species Q). The BaCl_2 was extracted from Species P to give a molecular sieve sorbent which, like chabazite or Linde Sieve 5A, could separate *n*-paraffins from iso-paraffins, cycloparaffins and aromatics (BARRER and RILEY, 1948). These syntheses were repeated subsequently by BARRER, HINDS and WHITE in 1953, and Species P and Q were then prepared and examined more fully by BARRER and MARCILLY (1970). It was shown that these phases had powder-diffraction patterns and unit cells very similar to those of the synthetic zeolite ZK-5 (KERR, 1963 and 1966). In addition aluminium-rich modifications, P' and Q', were prepared which were related to the more siliceous modifications in a manner recalling the relation between Linde Sieves X and Y. It was thought to be of considerable interest to determine and to compare the structures of Species P and Q with each other and with the zeolite obtained from Species P by extraction of BaCl_2 . The structures of all three phases could then be compared with the structure of Zeolite ZK-5 (MEIER and KOKOTAILO, 1965).

Experimental

Samples of the aluminosilicates Species P and Q, and the zeolite resulting from removal of BaCl_2 from Species P were available from the study of BARRER and MARCILLY (1970). The body-centred cubic cell dimensions were determined from Guinier photographs, calibrated with lead nitrate. These, together with the analytical results obtained by MARCILLY gave

	<i>a</i>	Cell contents
Species P	$18.65 \pm 0.03 \text{ \AA}$	$\text{Ba}_{15}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}] \quad 1.7 \text{ Ba}(\text{OH})_2, 12.5 \text{ BaCl}_2, 35 \text{ H}_2\text{O}$
Species Q	18.66 ± 0.03	$\text{Ba}_{15}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}] \quad 1.6 \text{ Ba}(\text{OH})_2, 11.9 \text{ BaBr}_2, 30 \text{ H}_2\text{O}$
Extracted P	18.78 ± 0.03	$(\text{Na}, \text{Ba}_{0.5})_{30}[\text{Al}_{30}\text{Si}_{66}\text{O}_{192}] \quad 1.7(\text{Na}_2, \text{Ba})\text{Cl}_2, 72 \text{ H}_2\text{O}$ with a maximum of 1.7 Ba per unit cell.

The powder diffraction pattern for Species P was obtained with a General Electric XRD6 diffractometer, using a flat sample holder and $\text{CuK}\alpha$ radiation. Integrated intensities were obtained by measuring the areas under the diffractometer trace. Of the seventy reflections available, up to the limit of measurement $2\theta = 61^\circ$, fifty-eight were recorded above background.

For Species Q and extracted Species P the x-ray powder diffraction pattern was obtained with a Philips diffractometer, using a rotating flat sample holder and $\text{CuK}\alpha$ radiation. Integrated intensities were obtained from step-scan output.

For Species Q, of the one hundred and seventeen reflections available up to $2\theta = 83^\circ$, ninety-nine were recorded above background. Measurement up to $2\theta = 76^\circ$, for extracted Species P, gave eighty-one observed reflections out of a possible one hundred and four.

Refinement

Refinement of all three structures was carried out in space-group $Im\bar{3}m$, assuming statistical distribution of Si/Al. Methods of Fourier synthesis (BROUSSARD and SHOEMAKER, 1960) and least-squares refinement (BARRER and VILLIGER, 1969) for dealing with powder data, were employed.

The framework positions determined by MEIER and KOKOTAILO (1965) for ZK-5 (KERR, 1963) were used to provide starting phases for the calculation of electron density and difference electron density maps. An overall temperature factor of 5.0 \AA^2 was used initially, in order to reduce the effects of series termination. For the observed reflections:

	Species P	Species Q	Extracted Species P
Initial $R(I)$	1.17	1.05	0.85

where

$$R(I) = (\sum |I_{\text{obs}} - I_{\text{calc}}|) / \sum I_{\text{obs}}$$

$$I_{\text{calc}} = \sum_n M_i \cdot (LP)_i \cdot (sF_i)^2$$

n = number of non-equivalent lines contributing to a reflection.

M_i = multiplicity of the i th line

$(LP)_i$ = Lorentz and polarization factor

sF_i = scaled structure amplitude.

From successive electron-density maps and difference electron-density maps a number of non-framework positions were located, and the structures were partly refined. In Species P and Q the non-framework positions were assigned to barium or halogen, depending on the electron density and interatomic distances. In extracted Species P, all non-framework positions were assigned sodium scattering factors. Residuals were

	Species P	Species Q	Extracted Species P
$R(I)$	0.55	0.52	0.58

Full-matrix least-squares refinement of the structures was then begun. Initially unit weights were applied, and only small sets of parameters were allowed to vary. Non-framework atoms were retained if the thermal parameters and occupancy factors remained realistic. Refinement was considered complete when all shifts in parameters were less than half the relevant estimated standard deviations.

For Species P, slow convergence was achieved, and finally individual observational weights were applied. In the final cycles as many parameters as possible were varied to provide a reasonable estimate of standard deviations, though thermal parameters and occupancy factors were never included in the same cycle because of the possibility of correlation. At the completion of refinement

$$R(I) = 0.061$$

$$R(I) = 0.080 \text{ including unobserved reflections at half the minimum observed intensity.}$$

$$R(F) = (\sum ||F_{\text{obs}}| - |sF_{\text{calc}}||) / \sum F_{\text{obs}} = 0.070.$$

These low R factors probably reflect the low ratio of observations to variable parameters, rather than a particularly accurate structure.

Least-squares refinement of Species Q resulted in unsatisfactorily slow convergence. An examination of the structure-factor list revealed that for reflection 110 F_{calc} was much greater than F_{obs} . This reflection was omitted, and further refinement proceeded satisfactorily, giving as final results

$$R(I) = 0.150$$

$$R(I) = 0.169 \text{ including unobserved reflections}$$

$$R(F) = 0.133.$$

Refinement of extracted Species P, by least squares, and further electron-density maps, failed to reduce $R(I)$ below 0.50. Examination of the structure-factor lists showed that F_{obs} was always much less than F_{calc} for reflections 110 and 200. Removal of these two reflections and re-scaling led to an immediate improvement in $R(I)$ to 0.28. Further

Table 1

Atom	x	y	z	B	Fractional occupancy
<i>Species P</i>					
Si,Al	0.0814 (0.002)	0.1937 (0.002)	0.3211 (0.002)	12.6 Å ² (1.1)	
O(1)	0.1268 (0.003)	0.1268	0.3156 (0.005)	10.3 (5.0)	
O(2)	0.2574 (0.004)	0.2574	0.4039 (0.004)	6.5 (2.9)	
O(3)	0	0.1834 (0.004)	0.3400 (0.004)	2.0 (1.9)	
O(4)	1/4	0.1169 (0.006)	0.3831	7.7 (3.1)	
Ba(1)	0	1/4	1/2	5.8 (0.7)	0.60 (0.01)
Ba(2)	0	0.3877 (0.002)	0	2.4 (1.1)	0.39 (0.01)
Ba(3)	0.1194 (0.003)	0.1194	0	20.6 (3.6)	0.18 (0.01)
Ba(4)	0.1413 (0.001)	0.1413	0.1413	10.4 (1.8)	0.34 (0.01)
Cl(1)	0.4060 (0.002)	0.4060	0	9.7 (1.7)	0.87 (0.02)
Cl(2)	0	0.1540 (0.015)	0	3.2 (9.4)	0.20 (0.04)
Cl(3)	0	0.2543 (0.015)	0	16.0 (10.2)	0.30 (0.05)
<i>Species Q</i>					
Si,Al	0.0795 (0.002)	0.2031 (0.002)	0.3175 (0.002)	14.4 Å ² (1.3)	
O(1)	0.1206 (0.003)	0.1206	0.3253 (0.004)	7.8 (4.0)	

Table 1. (Continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Fractional occupancy
O(2)	0.2471 (0.004)	0.2471	0.3840 (0.004)	19.4 Å ² (4.9)	
O(3)	0	0.1705 (0.004)	0.3497 (0.004)	6.3 (2.6)	
O(4)	1/4	0.1178 (0.006)	0.3822	7.2 (2.6)	
Ba(1)	0	1/4	1/2	2.3 (0.6)	0.48 (0.01)
Ba(2)	0	0.3821 (0.002)	0	4.9 (1.3)	0.34 (0.02)
Ba(4)	0.1430 (0.002)	0.1430	0.1430	2.8 (1.5)	0.20 (0.01)
Br(1)	0.3998 (0.001)	0.3998	0	6.6 (0.8)	0.57 (0.02)
Br(2)	0	0.2065 (0.008)	0	5.3 (3.9)	0.18 (0.02)

Extracted Species P

Si,Al	0.0852 (0.001)	0.2000 (0.001)	0.3186 (0.001)	3.4 Å ² (0.4)	
O(1)	0.1203 (0.002)	0.1203	0.3271 (0.003)	2.1 (1.5)	
O(2)	0.2569 (0.002)	0.2569	0.3998 (0.003)	2.6 (1.8)	
O(3)	0	0.1837 (0.003)	0.3206 (0.003)	3.4 (1.6)	
O(4)	1/4	0.1093 (0.004)	0.3907	0.6 (1.8)	
A(1)	0	1/4	1/2	9.3 (3.5)	0.74 0.06

Table 1. (*Continued*)

Atom	x	y	z	B	Fractional occupancy
A(2)	0.4481 (0.003)	0.3752 (0.003)	0	13.3 Å ² (3.6)	0.58 (0.05)
A(3)	0	0	1/2	18.9 (9.9)	0.64 (0.10)
A(4)	0	0.3550 (0.006)	0	16.0 (3.8)	0.93 (0.07)
A(5)	0	0.2123 (0.006)	0.0374 (0.009)	14.1 (7.8)	0.27 (0.02)
A(6)	0.1136 (0.005)	0.1136	0.1136	8.5 (5.1)	0.43 (0.07)
A(7)	0.1582 (0.002)	0.1582	0.1582	4.8 (2.6)	0.65 (0.05)

refinement produced slow convergence. An attempt to assign some of the positions to water resulted in some unacceptably high occupancy factors, so this was abandoned. The final residuals were

$$R(I) = 0.128$$

$$R(I) = 0.137 \text{ including unobserved reflections}$$

$$R(F) = 0.109.$$

Final difference electron density maps were calculated for all three structures, and apart from peaks at 0,0,0 of about one half the height of a framework oxygen, no other detail was apparent. The position 0,0,0 proved unrefinable in all three structures giving divergent thermal parameters or zero occupancy.

Lack of agreement for the lowest-angle reflections in Species Q and extracted Species P indicates that the unlocated non-framework atoms are delocalized over the available space (SIMPSON and STEINFINK, 1969).

All computation was done on the C.D.C. Computers of the University of London. Electron-density maps were generated by the University of Washington X-Ray 63 System. The least-squares refinement

used a version of ORFLS (BUSING, MARTIN and LEVY, 1959) modified for powder data. Final atomic coordinates are listed in Table 1. Interatomic distances and angles, with estimated standard deviations, calculated by the programme ORFFE (BUSING, MARTIN and LEVY, 1964) are listed in Table 2. Observed and calculated intensities are listed in Table 3. Figures 1a, b and c and 2a, b and c which illustrate the configuration of much of the contents of the 18-hedra and 26-hedra of Species P, Q and extracted P, were drawn with the help of the programme ORTEP (JOHNSON, 1965).

Scattering factors were taken from *International tables for x-ray crystallography*, Vol. 3. Silicon, aluminium and oxygen were assumed

Table 2
Framework interatomic distances and angles

	Species P	Species Q	Extracted Species P
(Si,Al)—O(1)	1.51 (.05) Å	1.72 (.04) Å	1.64 (.03) Å
(Si,Al)—O(2)	1.75 (.05)	1.67 (.05)	1.66 (.03)
(Si,Al)—O(3)	1.57 (.05)	1.71 (.05)	1.63 (.02)
(Si,Al)—O(4)	1.70 (.06)	1.65 (.05)	1.71 (.04)
Mean	1.631	1.690	1.659
O(1)—O(2)	2.62 (.07) Å	2.81 (.07) Å	2.82 (.05) Å
O(1)—O(3)	2.63 (.05)	2.48 (.04)	2.56 (.03)
O(1)—O(4)	2.63 (.09)	2.64 (.07)	2.72 (.06)
O(2)—O(3)	2.78 (.08)	3.21 (.08)	2.63 (.05)
O(2)—O(4)	2.65 (.13)	2.41 (.12)	2.78 (.07)
O(3)—O(4)	2.64 (.08)	2.72 (.08)	2.74 (.05)
Mean	2.657	2.711	2.707
(Si,Al)—O(1)—(Si,Al)	157.0 (8.8)°	141.8 (6.8)°	136.2 (4.1)°
(Si,Al)—O(2)—(Si,Al)	148.3 (9.4)	129.7 (6.6)	143.8 (4.2)
(Si,Al)—O(3)—(Si,Al)	150.4 (7.9)	120.1 (5.9)	158.1 (5.2)
(Si,Al)—O(4)—(Si,Al)	156.3 (13.9)	155.7 (12.4)	136.3 (6.7)
Mean	153.0	136.8	143.6
O(1)—(Si,Al)—O(2)	106.6 (6.7)°	112.1 (5.3)°	117.3 (3.2)°
O(1)—(Si,Al)—O(3)	117.1 (6.3)	92.3 (4.0)	102.7 (2.8)
O(1)—(Si,Al)—O(4)	109.8 (5.9)	102.7 (3.6)	108.5 (2.6)
O(2)—(Si,Al)—O(3)	113.8 (5.9)	143.7 (5.3)	106.2 (2.9)
O(2)—(Si,Al)—O(4)	100.8 (6.4)	93.2 (6.1)	111.4 (3.0)
O(3)—(Si,Al)—O(4)	107.5 (7.6)	107.8 (6.3)	110.2 (4.3)
Mean	109.3	108.6	109.4

Table 2. (Continued)
Non-framework distances and angles

<i>Species P</i>			
Cl(1)—O(1)	3.55 (.10) Å	Cl(3)—Ba(2)	2.49 (.32) Å
Cl(1)—O(3)	3.84 (.07)	Cl(3)—Ba(3)	3.36 (.25)
Cl(1)—O(4)	3.66 (.11)	Cl(3)—Ba(4)	4.28 (.16)
Cl(1)—Ba(1)	3.40 (.01)		
Cl(1)—Ba(2)	3.25 (.04)	Ba(1)—O(3)	3.23 (.08)
Cl(1)—Cl(1)	3.51 (.08)	Ba(1)—O(4)	3.08 (.19)
		Ba(2)—O(1)	3.61 (.11)
Cl(2)—O(1)	4.50 (.27)	Ba(2)—O(3)	3.54 (.08)
Cl(2)—O(3)	4.87 (.26)	Ba(3)—O(2)	3.71 (.13)
Cl(2)—Cl(2)	4.06 (.48)	Ba(3)—O(3)	4.29 (.10)
Cl(2)—Ba(4)	3.73 (.04)	Ba(3)—Ba(4)	2.70 (.04)
Cl(2)—Ba(3)	2.32 (.10)	Ba(3)—Ba(3)	3.15 (.10)
Cl(2)—Cl(3)	1.87 (.40)	Ba(4)—O(1)	3.27 (.10)
		Ba(4)—O(2)	2.80 (.10)
Cl(3)—O(1)	3.54 (.15)		
Cl(3)—O(3)	3.78 (.16)		

<i>Species Q</i>			
Br(1)—O(1)	3.30 (.07) Å	Br(2)—Ba(2)	3.28 (.15) Å
Br(1)—O(3)	3.62 (.07)	Br(2)—Ba(4)	3.95 (.06)
Br(1)—O(4)	3.57 (.09)	Ba(1)—O(3)	3.17 (.09)
Br(1)—Ba(1)	3.36 (.01)	Ba(1)—O(4)	3.11 (.17)
Br(1)—Ba(2)	3.44 (.03)	Ba(2)—O(1)	3.35 (.09)
Br(1)—Br(1)	3.74 (.05)	Ba(2)—O(3)	3.24 (.08)
Br(2)—O(1)	3.88 (.13)	Ba(4)—O(1)	3.45 (.07)
Br(2)—O(3)	4.16 (.12)	Ba(4)—O(2)	2.94 (.10)

<i>Extracted Species P</i>			
A(1)—O(3)	3.59 (.07) Å	A(4)—O(3)	3.51 (.07) Å
A(1)—O(4)	2.90 (.10)	A(4)—A(5)	2.77 (.12)
A(1)—A(2)	2.54 (.06)	A(5)—O(1)	3.49 (.12)
A(2)—O(1)	3.49 (.06)	A(5)—O(3)	3.42 (.18)
A(2)—O(3)	3.68 (.07)	A(5)—A(6)	3.17 (.11)
A(2)—O(4)	3.30 (.07)	A(5)—A(7)	3.87 (.11)
A(2)—A(2)	1.94 (.12)	A(5)—A(5)	0.99 (.26)
A(2)—A(4)	3.72 (.10)	A(7)—A(6)	1.45 (.18)
A(3)—A(4)	2.72 (.12)	A(7)—O(1)	3.33 (.07)
A(2)—A(3)	2.73 (.06)	A(7)—O(2)	2.50 (.06)
A(4)—O(1)	3.24 (.06)		

to be half-ionized, and appropriate averages were taken. The ionized values for chlorine, bromine and sodium, and the unionized value for barium were used.

Table 3. Observed and calculated intensities $\times 10^{-2}$

a Species P											
h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}
1 1 0	5036	5041	6 3 1	337	271	7 5 2	360	362	10 2 2	155	120
2 0 0	566	573	4 4 4	151	150	8 4 0	197	301	6 6 6		
2 1 1	316	<30	7 1 0			9 1 0			10 3 1		
2 2 0	204	181	5 4 3	820	754	8 3 3	5	<30	9 5 2	302	301
3 1 0	120	120	6 4 0	419	332	8 4 2	309	392	7 6 5		
2 2 2	137	<30	7 2 1			9 2 1			8 7 1		
3 2 1	1459	1358	7 2 1			7 6 1	459	392	7 7 4	350	422
4 0 0	159	241	6 5 2	1941	2115	6 5 2			8 5 5		
4 1 1			6 5 3			6 6 4	97	90	10 4 0		
3 3 0	4130	4226	6 4 2	637	664	9 3 0			8 6 4	73	<30
4 2 0	2269	2234	7 3 0	227	211	7 5 4	119	60	10 3 3	39	<30
3 3 2	171	150	7 3 2	469	633	8 5 1			9 6 1		
4 2 2	2834	3049	8 0 0	688	633	9 3 2	51	90	10 4 2	141	<30
5 1 0			7 4 1			7 6 3			8 7 3		
4 3 1	1148	1117	8 4 4			8 4 4	133	150	11 1 0	272	332
5 2 1	267	<30	8 1 1	1933	1962	7 7 0			9 5 4		
4 4 0	620	724	5 5 4			9 4 1	454	362	11 2 1		
5 3 0			8 2 0	469	513	8 5 3			9 6 3	7	<30
4 3 3	4048	4075	6 4 4			10 0 0			10 5 1		
6 0 0	686	724	6 5 3	170	211	8 6 0	284	392	8 8 0	655	754
4 4 2			8 2 2			7 7 2	49	<30	11 3 0	162	90
6 1 1	6213	6068	6 6 0	68	60	10 1 1			9 7 0		
5 3 2			7 4 3	144	150	10 2 0	221	271	8 8 2	79	<30
6 2 0	100	150	8 3 1			9 4 3	267	271	10 4 4		
5 4 1	738	724	6 6 2	228	301	9 5 0					
6 2 2	5441	5313									

b Species Q											
h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}
1 1 0	29042	5189	7 4 3			8 8 0	607	634	11 7 2		
2 0 0	1703	1780	7 5 0	321	210	11 3 0	148	184	13 2 1	167	187
2 1 1	196	<4	8 3 1			9 7 0			10 7 5		
2 2 0	33	25	6 6 2	154	181	8 8 2	42	26	12 4 4	25	<4
3 1 0	116	117	7 5 2	301	264	10 4 4			13 5 0		
2 2 2	60	63	8 4 0	65	139	11 3 2			12 5 3	32	61
3 2 1	564	476	9 1 0	69	46	9 2 0	434	523	9 9 4		
4 0 0	128	126	8 3 3			10 5 3			12 6 0	84	25
4 1 1	784	1060	8 4 2	104	274	7 7 6			10 8 4		
3 3 0			9 2 1			10 6 0	51	57	13 3 2		
4 2 0	1321	904	7 6 1	286	258	8 6 6			10 9 1	122	250
3 3 2	122	133	6 5 5	40	<4	11 4 1	19	17	11 6 5		
4 2 2	2532	2594	6 6 4			8 7 5			12 6 2	101	107
5 1 0	499	416	9 3 0			10 6 2	208	163	13 4 1		
4 3 1	159	147	7 5 4	252	256	9 6 5	5	13	11 8 1	54	<4
4 4 0	208	298	8 5 1			12 0 0			11 7 4		
5 3 0			9 3 2	12	11	8 8 4	176	174	10 9 3	0	<4
4 3 3	4799	4920	7 6 3			11 4 3			8 8 8	32	<4
6 0 0	342	270	8 4 4	295	227	9 7 4			13 4 3		
4 4 2			7 7 0			11 5 0	347	292	11 8 3		
6 1 1	6732	6695	9 4 1	31	86	12 1 1			15 5 0	180	317
5 3 2	70	33	8 5 3			9 8 1			12 7 1		
6 2 0	785	662	10 0 0	361	480	12 2 0	25	<4	12 5 5		
5 4 1	4360	3901	8 6 0			10 7 1			9 8 7		
6 2 2	299	<4	7 7 2	62	38	11 5 2	341	315	14 0 0	11	<4
6 3 1	372	378	10 1 1			10 5 5			12 6 4		
7 1 0			10 2 0	219	202	12 2 0			14 1 1		
5 5 0	2476	2052	8 6 2			10 6 4	105	64	13 5 2	142	119
5 4 3			9 4 3	185	119	12 3 1	121	146	9 9 6		
6 4 0	191	232	9 5 0			9 8 3			10 7 7		
7 2 1			10 2 2	108	59	10 7 3	259	299	10 10 0	89	70
6 3 3	1595	2066	6 6 6			11 6 1			10 8 6		
5 5 2			10 3 1			12 4 0	44	30	10 8 6		
6 4 2	386	302	9 5 2	231	266	12 3 3			12 7 3	21	<4
7 3 0	196	187	7 6 5			8 7 7	140	159	11 9 0		
7 3 2			8 7 1	683	604	9 9 0			14 2 2	63	<4
6 5 1	296	212	7 7 4			11 5 4			10 10 2		
8 0 0	747	810	8 5 5			12 4 2			14 3 1		
7 4 1			10 4 0	79	38	10 8 0	53	23	13 6 1	14	34
8 1 1	1237	1818	8 6 4			8 8 6			11 9 2		
5 5 4			10 3 3	305	352	9 9 2			10 9 5		
8 2 0	746	699	10 4 2	77	68	11 6 3	78	21	12 8 0	73	<4
6 4 4			8 7 3			10 8 2	7	<4	13 5 4	29	49
6 5 3	95	93	11 1 0	216	378	11 7 0			11 8 5		
8 2 2	10	<4	9 5 4			13 1 0			14 4 0	30	35
6 6 0			11 2 1			12 5 1	114	108	12 8 2		
			9 6 3	59	122	9 8 5			14 3 3		
			10 5 1			10 6 6	205	264	13 6 3	21	12

Table 3. (Continued)
e Extracted Species P.

h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}	h k l	I _{calc}	I _{obs}
1 1 0	7322	1200	6 4 4	132	105	10 4 0	30	49	12 4 0	5	<6	14 1 1		
2 0 0	8453	5969	8 2 0			8 6 4			11 5 4			13 5 2	58	22
2 1 1	55	74	6 5 3	60	63	9 6 1	203	134	8 7 7	89	97	9 9 6		
2 2 0	332	338	6 6 0	386	488	10 3 3			9 9 0			10 7 7		
3 1 0	1210	1146	8 2 2			10 4 2	0	14	12 3 3			14 2 0		
2 2 2	1836	1651	7 5 0			11 1 0			10 8 0			10 10 0	31	<6
3 2 1	173	170	7 4 3	173	242	8 7 3	308	280	12 4 2	235	256	10 8 6		
4 0 0	232	244	8 3 1			9 5 4			8 8 6			11 9 0	10	<6
3 3 0			6 6 2	78	33	11 2 1			11 6 3			12 7 3		
4 1 1	1980	2044	7 5 2	0	<6	10 5 1	162	179	9 7 6	38	30	14 2 2	36	<6
4 2 0	2403	2409	8 4 0	5	<6	9 6 3			9 9 2			10 10 2		
3 3 2	1715	1599	9 1 0	196	194	8 8 0	363	388	10 8 2	1	<6	14 3 1		
4 2 2	1771	1740	8 3 3			11 3 0	285	275	11 7 0			13 6 1		
5 1 0			8 4 2	92	118	9 7 0			13 1 0			11 9 2	142	182
4 3 1	457	400	7 6 1			10 4 4			12 5 1	32	<6	10 9 5		
5 2 1	1141	1404	6 5 5	206	240	8 8 2	1	<6	9 8 5			11 7 6		
4 4 0	64	92	9 2 1			11 3 2			10 6 6	46	30	12 8 0	5	<6
5 3 0			6 6 4	34	15	9 7 2			11 7 2			13 5 4	137	72
4 3 3	2116	2478	9 3 0			10 5 3	187	243	10 7 5	32	<6	11 8 5		
6 0 0			8 5 1	13	18	7 7 6			13 2 1			14 4 0	73	60
4 4 2	110	103	7 5 4			10 6 0	204	184	12 4 4	0	<6	12 8 2		
5 3 2			9 3 2	71	59	8 6 6			13 3 0			14 3 3	23	<6
6 1 1	3267	3721	7 6 3			11 4 1			12 5 3	408	486	13 6 3		
6 2 0	1217	1569	8 4 4	6	21	8 7 5	51	37	10 7 5			14 4 2		
5 4 1	235	308	7 7 0			10 6 2	74	86	12 6 0	70	61	10 10 4	114	128
6 2 2	1884	1769	9 4 1	198	300	9 6 5	52	<6	10 8 4			12 6 6		
6 3 1	969	1073	8 5 3			12 0 0			10 9 1			13 7 0		
4 4 4	25	20	10 0 0			8 8 4	59	22	13 5 2	149	218	11 9 4	19	<6
7 1 0			8 6 0	490	452	11 5 0			11 6 5			12 7 5		
5 5 0	687	718	10 1 1			11 4 3			12 6 2	79	69	14 5 1		
5 4 3			7 7 2	138	80	9 7 4	77	86	13 4 1			11 10 1	56	72
6 4 0	68	88	10 2 0	351	330	12 1 1			11 8 1	1	<6	13 7 2		
7 2 1			8 6 2			9 8 1			9 9 4			12 8 4	22	<6
5 5 2	841	1072	9 5 0	29	18	12 2 0	84	35	10 9 3	9	<6			
6 3 3			9 4 3			10 7 1			8 8 8	2	17			
6 4 2	0	31	10 2 2	60	<6	11 5 2	141	175	13 5 0					
7 3 0	298	301	6 6 6			10 5 5			12 7 1					
6 5 1			10 3 1			10 6 4			13 4 5					
7 3 2	72	115	9 5 2	384	529	12 2 2	40	21	11 8 3	420	522			
8 0 0	9	<6	7 6 5			12 3 1	40	13	9 8 7					
7 4 1			8 7 1			9 8 3			12 5 5					
5 5 4	182	155	7 7 4	58	45	11 6 1			14 0 0	56	<6			
8 1 1			8 5 5			10 7 3	28	21	12 6 4					

Description of the structure

The framework of these three compounds is almost the same as that determined for ZK-5, and is built up of 26-hedral cavities, linked through pairs of six-membered rings, forming hexagonal prisms, and intermediate 18-hedral cavities, which also occur in paulingite (GORDON, SAMSON and KAMB, 1966).

The high standard deviations in the atomic parameters prevent any detailed analysis of bond lengths and angles in the four related structures. The positions of the framework atoms in extracted Species P differ by less than three times their estimated standard deviation from the positions in ZK-5. Both Species P and Species Q show some significant positional differences from one another, and from the sodium forms, which are probably due to accommodation of divalent ions and included salts. These differences follow no obvious pattern.

Interatomic distances within the framework show quite a wide range. The mean values of (Si,Al)—O are

Species P	1.63 Å
Species Q	1.69 Å
Extracted Species P	1.66 Å
ZK-5	1.625 Å (MEIER and KOKOTAILO, 1965).

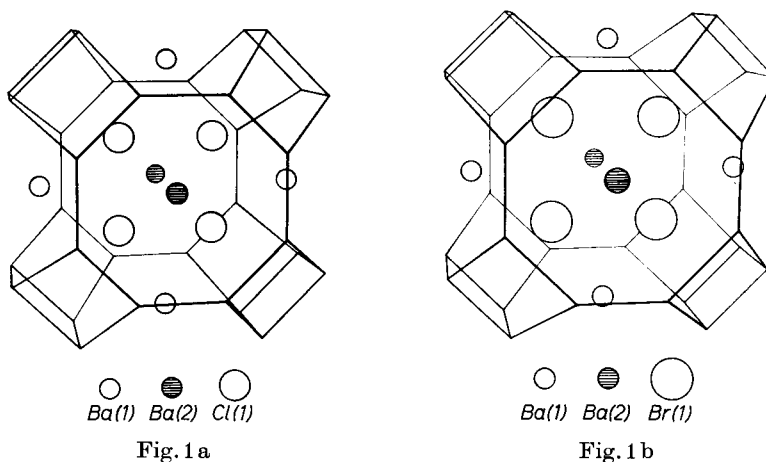


Fig. 1a. Distribution of located non-framework atoms in the 18-hedron of Species P.

Fig. 1b. Distribution of located non-framework atoms in the 18-hedron of Species Q.

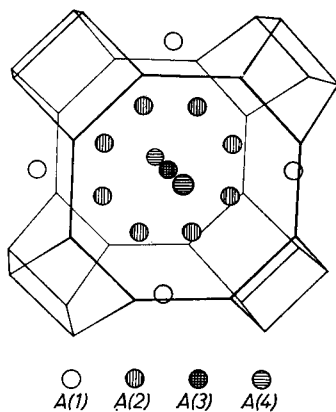


Fig. 1c. Distribution of located non-framework atoms in the 18-hedron of extracted Species P.

Of these, the value for extracted Species P is closest to the value 1.65 Å predicted for an Si:Al ratio of 2:1 (SMITH and BAILEY, 1963). In the three structures determined, none of the individual bonds differs significantly from the relevant mean value.

Thermal parameters for the atoms of Species P and Q are much higher than is normal for framework silicates. This is due to lack of

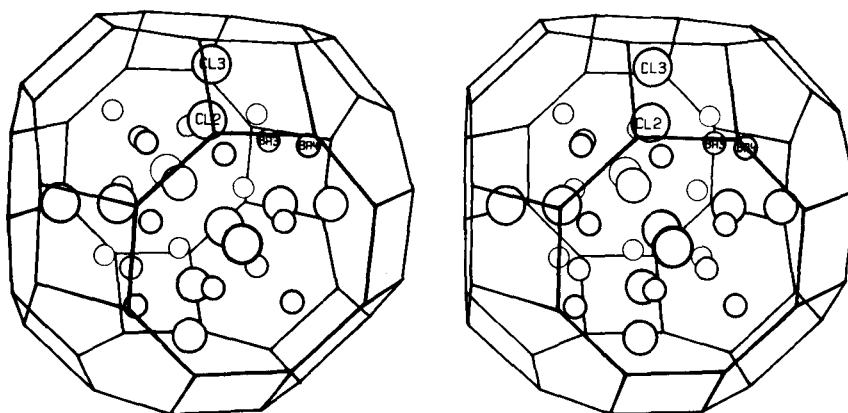


Fig. 2a. Stereoscopic pair showing the distribution of located non-framework atoms in the 26-hedron of Species P

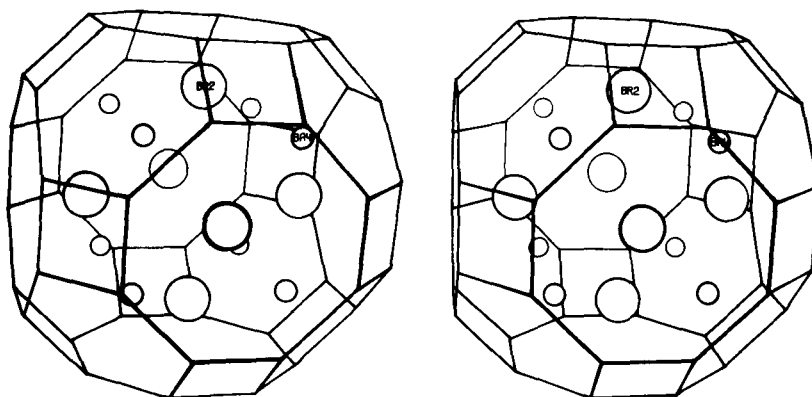


Fig. 2b. Stereoscopic pair showing the distribution of located non-framework atoms in the 26-hedron of Species Q

absorption correction (SRIVASTAVA and LINGAFELTER, 1966). The absence of heavy atoms in extracted Species P results in more reasonable thermal parameters.

Non-framework positions were located in the 18-hedra and in the 26-hedra of each of the three structures. Assignment of these positions to barium or halogen in Species P and Q took account of the interatomic contact distances, and the number of electrons present at each position. No positions could definitely be assigned to the water molecules. In extracted Species P, no differentiation was made between

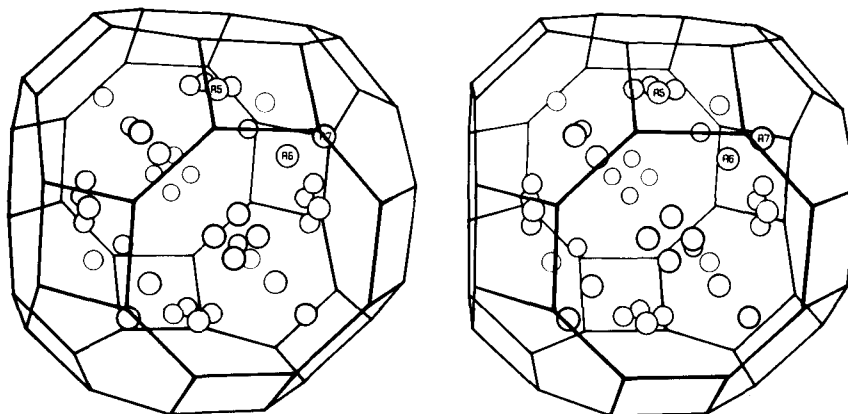


Fig. 2c. Stereoscopic pair showing the distribution of located non-framework atoms in the 26-hedron of extracted Species P

sodium and water, and sodium scattering factors were applied to all positions.

In the 18-hedra, all three compounds displayed a similar non-framework arrangement, shown in Fig. 1 a, b and c. In Species P and Q, Ba(1) is at the centre of the puckered 8-rings shared by two 18-hedra, making two sets of four barium-oxygen contacts:

Species P	Ba(1)—O	3.08 Å, 3.23 Å
Species Q	Ba(1)—O	3.11 Å, 3.17 Å .

In extracted Species P this position is occupied by A(1), probably sodium, making contacts of 2.90 Å and 3.59 Å with framework oxygen atoms.

Four halogen atoms occur in Species P and Q, at $x, x, \frac{1}{2}$ in the 18-hedra, such that two approach each Ba(1) from each side, at 3.40 Å in Species P, and 3.36 Å in Species Q. In extracted Species P, these positions are split into pairs, giving eight locations at $x, y, \frac{1}{2}$ for A(2), which must be disordered so that only four are occupied at any time.

In Species P and Q, a pair of bariums Ba(2) occurs along the four-fold axis, within the 18-hedra close to the planar 8-rings. This position is occupied by A(4) in extracted Species P, and an additional location A(3) occurs at $0, 0, \frac{1}{2}$, the centre of the 18-hedra.

The arrangement of non-framework atoms within the 26-hedra is illustrated in Figures 2 a, b and c. It is simplest in Species Q, and most complex in extracted Species P. In all three structures a position is

observed on the [111] axis, equivalent to that assigned by MEIER and KOKOTAILO to sodium in ZK-5. This is assigned to Ba(4) in Species P and Q, and is close to three of the six oxygen atoms in the 6-ring, giving for Ba(4)—O the distances:

Species P	2.80 Å,	3.27 Å
Species Q	2.94 Å,	3.45 Å .

These distances compare with Ba—O 2.67 Å in celsian (NEUNHAM and MEGAW, 1960) and 3.02 Å in harmotome (SADANAGA, MARUMO and TAKEUCHI, 1961). In extracted Species P, two positions occur along the [111] axis, A(7) which is certainly sodium, at 2.50 Å and 3.33 Å from the framework oxygen atoms, compared with Na—O 3.14 Å and 3.55 Å in ZK-5, and A(6) which is closer to the centre of the 26-hedra, and cannot coexist with A(7).

In Species Q, the only other position in the 26-hedra occurs on the fourfold axis, close to the planar 8-ring. This is assigned to Br(2). An additional position, at $x,x,0$, occurs in Species P and is assigned to Ba(3). This position can only be occupied when Ba(4) is vacant. The halogen located on the fourfold axis is also split into a pair of positions Cl(2) and Cl(3), which appear to represent stable positions of the chloride, depending on whether Ba(2) or Ba(3) is present. The less complicated arrangement in Species Q may be due to the larger size of the bromine ion restricting its movement.

The position close to the planar 8-ring, in extracted Species P, shifts off the fourfold axis, producing a set of four disordered positions assigned to A(5), only one of which can be occupied at one time. Within the 18-hedral cavity the arrangement of non-framework atoms is almost identical in Species P and Q, and is quite similar for extracted Species P, indicating that the final configuration is dictated largely by the cavity. The arrangement in the 26-hedra is similar for the three structures, though the greater free volume allows much greater freedom of arrangement.

Even when the non-framework atoms are heavy, it may not be possible to locate all the scattering material in these open structures. The percentage of non-framework scattering material located in the three structures was

Species P	68%
Species Q	47%
Extracted Species P	70% .

To account for the observed molecular sieve behaviour of extracted Species P (BARRER and RILEY, 1948), dehydration must move the atoms from positions A(2), A(3), A(5) and A(6). The two most probable sodium positions A(1) and A(7) would have little effect on sorption, even if they did not move significantly during dehydration.

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