Crystal Structure of Dehydrated Rb-Exchanged Zeolite A. Absence of Zero-Coordinated Rubidium. Preferential Ion Exchange of Barium Impurity

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Abstract: A new refinement of literature data for a dehydrated Rb-exchanged crystal of zeolite A lacked evidence for significant electron density at the supposed position for a zero-coordinate Rb atom. Electron microprobe analyses of new crystals exchanged with RbOH and $RbClO_4$ revealed zoning of Ba scavenged from impurities. All crystals became amorphous before complete Rb exchange was obtained. New structure determinations for Rb-exchanged crystals dehydrated at 350 °C revealed electron density only in six- and eight-ring sites, but the structural interpretation was ambiguous because of significant Ba, K, and Na impurities. Tetrahedral distances are consistent with Si, Al alternation.

The concept of *zero-coordinated* cations[1] was described in several reviews (e.g., ref 2 and 3), but positive evidence was not found in detailed crystal-structure analyses of dehydrated zeolite A[4] and its K-exchanged equivalent.[5] No chemical analysis was made of the Rb-exchanged crystal of zeolite A used for the structure analysis in which a zero-coordinated Rb atom was reported.[6] We report a new Fourier and least-squares refinement of the published data and present new crystallographic and chemical measurements of Rb-exchanged crystals. A Ba impurity in the Rb-bearing chemicals was found to exchange preferentially into zeolite A. Comparison is made of cation positions in (Rb,Ba,Na)-A with those for Ba_xNa_{12-2x}-A crystals.[7]

New Fourier and Least-Squares Refinement of Published Data

The published least-squares refinement of dehydrated Rb-exchanged zeolite A[6] was made with the pseudo space group ($Pm3m$, a = 12.261 Å) on a crystal ion exchanged with flowing 0.1 M aqueous RbOH at 25 °C for 8 days and dehydrated for 48 h at 350 °C and 1×10^{-5} torr. The crystal was not chemically analyzed, and was deduced to have a composition of $Rb_{11}Na_1Si_{12}Al_{12}O_{48}$ from least-squares refinement of X-ray data. Three equivalent Rb^+ ions were found at the centers of eight-rings of oxygen, five on 3-fold axes opposite six-rings in the large cavity, two on a 3-fold axis in the sodalite unit on opposite sides of the origin, and the remaining one on this 3-fold axis at 4.35 Å from the nearest oxygen. This eleventh Rb^+ ion was considered to be zero-coordinated because "its shortest approach to another ion exceeds the sum of the appropriate ionic radii by more than 1.5 Å".

Table I, column 4, shows the experimental conditions for the original data collection (denoted FS). The observed diffraction amplitudes were refined on a new model by difference-Fourier and least-squares methods (Table II), and no evidence was found for a significant electron-density peak at the supposed position for the zero-coordinated Rb(3). All contours in this region (Figure 1, FSp) were within the range of random error found for the remainder of the unit cell no matter what the details were of the refinements of the atomic positions taken from ref 6. In the original refinement a composition of $Rb_{11}Na_1Al_{12}Si_{12}O_{48}$ was assumed. Electron microprobe analyses of A crystals[5] gave somewhat less than 12 Al atoms per cell, and crystal-structure refinement in the $Fm\bar{3}c$ cell[4,5] consistently indicated less than 12 exchangeable cations. Hence it is concluded that there is no evidence in favor of a zero-coordinated Rb cation.

Table I. X-ray Diffraction Data and Structure Refinement

	exchange solution, time at 25 °C		
	PSa, 0.1 N RbOH, 4 days	PSb, 0.1 N RbOH, $RbClO_4$, 4 days	FSp, 0.1 N RbOH, 8 days
crystal size	82 μm	75 μm	100 μm
dehydration T, time	350 °C, 2 days	350 °C, 2 days	350 °C, 2 days
space group	$Fm\bar{3}c$	$Fm\bar{3}c$	$Pm\bar{3}m$
wavelength, Å	1.541 8	1.541 8	0.710 69
monochromator	graphite	graphite	graphite
cell dimension, Å	24.569 (1)	24.564 (2)	12.261 (2)
diffractometer	Picker FACS-1	Picker FACS-1	Syntex $P2_1$
orientation	2° from (110)	4° from (100)	?
scan technique	fixed θ-2θ	fixed θ-2θ	fixed θ-2θ
speed	1°/min	1°/min	1°/min
range	2.2°-2.8°	2.2°-2.8°	2.0°-2.5°
background	fixed 40 s	fixed 40 s	variable, scan/bkg = 1
total intensities	3330 (1818)[a]	3292 (1811)[a]	880
unique data set	576 (365)[a]	576 (365)[a]	880
significant data set	384 (333)[a] 2σ	323 (302)[a] 2σ	300 3σ
$\sin\theta/\lambda_{max}$	0.59	0.59	0.81
absorption coefficient	136.9 cm^{-1}	145.3 cm^{-1}	8.8 mm^{-1}
R	0.050 (0.047)[a]	0.043 (0.040)[a]	0.087 (0.077)[b]
weighted R	0.040 (0.044)[a]	0.035 (0.035)[a]	0.055 (0.081)[b]
S	3.1 (3.2)[a]	2.2 (2.2)[a]	2.9 (5.1)[b]

[a] Numbers in parentheses refer to pseudostructure. [b] New refinement of Firor-Seff data; see text.

New Experimental Data

Electron microprobe analyses of new Rb-exchanged crystals revealed the presence of K and Ba impurities. Although a series of experiments was made to determine suitable conditions for preparation of crystals for X-ray diffraction, a fully exchanged Rb–A crystalline specimen was not obtained. In general, crystals became unstable as the Rb content increased, but basic conditions inhibited degradation.

Crystals of zeolite 4A, prepared by a modification of Charnell's method,[8] were ion exchanged in a still aqueous solution of 0.1 M RbOH for 4 days at 25 °C with lot 062579 from Alfa Division. Electron microprobe analysis (ARL-EMX instrument, 15 kV, 1-μA beam current, 12-μm beam diameter, wavelength dispersion

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Table II. Atomic Populations, Positions and Displacements[a] of Dehydrated Rubidium-Exchanged Zeolite A

	PSap	PSbp	FSp[b]	FSp	PSaf		PSbf	
				Rb(1)				
position	8(g)	8(g)	8(g)	8(g)	64(g)		64(g)	
population	4.96 (4)	5.47 (3)	4.78 (9)	5	39.6 (3)		43.6 (3)	
x,y,z	0.2504 (1)	0.2516 (1)	0.2516 (3)	0.2514 (2)	0.12522 (5)		0.12577 (5)	
$\beta_{11},\beta_{22},\beta_{33}$	53 (1)	58 (1)	48 (2)	58 (13)	13.2 (0.2)		14.5 (0.2)	
$\beta_{12},\beta_{13},\beta_{23}$	21 (1)	16 (1)	16 (2)	19 (2)	5.1 (0.2)		4.0 (0.2)	
				Rb(2)				
position	3(c)	3(c)	3(c)	3(c)	24(d)		24(d)	
population	2.93 (3)	2.91 (2)	3.04 (7)	3	23.4 (2)		23.2 (2)	
x	0	0	0	0	0		0	
y,z	0.5	0.5	0.5	0.5	0.25		0.25	
β_{11}	109 (3)	117 (4)	120 (10)	116 (7)	27.2 (0.8)		29.2 (0.9)	
β_{22},β_{33}	111 (2)	128 (2)	131 (7)	125 (4)	27.9 (0.5)		32.0 (0.6)	
$\beta_{12},\beta_{13},\beta_{23}$	0	0	0	0	0		0	
				Rb(3)				
position				8(g)				
population				1				
x,y,z				0.3629 (47)				
$\beta_{11},\beta_{22},\beta_{33}$				1127 (153)				
$\beta_{12},\beta_{13},\beta_{23}$				−240 (126)				
				Rb(4)				
position	8(g)	8(g)	8(g)	8(g)	64(g)		64(g)	
population	1.15 (9)	1.23 (10)	1.34 (12)	1	9.3 (7)		9.8 (8)	
x,y,z	0.1226 (10)	0.1162 (13)	0.1226 (17)	0.1125 (13)	0.0614 (5)		0.0581 (6)	
$\beta_{11},\beta_{22},\beta_{33}$	$B = 2.2$ (3)	$B = 4.0$ (3)	$B = 4.0$ (6)	73 (10)	$B = 2.2$ (3)		$B = 4.0$ (3)	
$\beta_{12},\beta_{13},\beta_{23}$				9 (13)				
				Ba(5)				
position	8(g)	8(g)	8(g)	8(g)	64(g)		64(g)	
population	0.54 (6)	0.41 (6)	0.20 (6)	1	4.3 (4)		3.3 (5)	
x,y,z	0.1480 (12)	0.1419 (15)	0.1507 (17)	0.1456 (12)	0.0741 (6)		0.0710 (8)	
B	1.0 (4)	1.3 (6)	−1.3 (8)	3.4 (6)	1.1 (4)		1.4 (6)	
				Na				
position	8(g)	8(g)	8(g)	8(g)	64(g)		64(g)	
population	1.47 (11)	0.90 (11)	2.08 (35)	1	11.8 (9)		7.2 (8)	
x,y,z	0.1931 (11)	0.1845 (17)	0.1878 (32)	0.1904 (27)	0.0966 (5)		0.0922 (9)	
B	0.5 (5)	0.8 (8)	4.0 (1.6)	−0.5 (7)	0.4 (5)		0.6 (8)	
T	Si,Al	Si,Al	Si,Al	Si,Al	Si	Al	Si	Al
position	24(k)	24(k)	24(k)	24(k)	96(i)	96(i)	96(i)	96(i)
population	24	24	24	24	96	96	96	96
x	0	0	0	0	0	0	0	0
y	0.1861 (1)	0.1858 (1)	0.1854 (3)	0.1852 (2)	0.0945 (2)	0.1892 (3)	0.0946 (6)	0.1883 (7)
z	0.3764 (1)	0.3758 (1)	0.3752 (3)	0.3753 (2)	0.1873 (3)	0.0915 (2)	0.1874 (6)	0.0911 (7)
β_{11}	23.7 (1.2)	33.1 (1.2)	19 (2)	21 (2)	5.4 (1.1)	6.6 (1.3)	7.0 (1.8)	9.7 (2.2)
β_{22}	20.4 (1.1)	29.4 (1.2)	17 (2)	20 (2)	5.1 (1.1)	5.9 (1.3)	7.8 (1.5)	7.2 (2.0)
β_{33}	20.9 (1.1)	29.0 (1.2)	11 (2)	14 (2)	4.3 (1.1)	4.4 (1.2)	7.6 (1.9)	5.9 (1.6)
β_{12},β_{13}	0	0		0	0	0	0	0
β_{23}	2.3 (0.9)	1.8 (1.0)	5 (2)	4 (2)	0.6 (0.8)	1.2 (0.9)	−1.8 (1.9)	3.0 (1.9)
				O(1)				
position	12(h)	12(h)	12(h)	12(h)	96(i)		96(i)	
population	12	12	12	12	96		96	
x	0	0	0	0	0		0	
y	0.2435 (5)	0.2413 (5)	0.2408 (12)	0.2405 (8)	0.1219 (3)		0.1207 (3)	
z	0.5	0.5	0.5	0.5	0.2463 (8)		0.2432 (11)	
β_{11}	50 (6)	61 (6)	54 (13)	43 (11)	12.2 (1.3)		15.0 (1.5)	
β_{22}	48 (5)	55 (5)	44 (11)	49 (9)	11.8 (1.2)		13.6 (1.3)	
β_{33}	26 (5)	36 (5)	16 (9)	23 (9)	3.4 (1.6)		−2 (4)	
β_{12},β_{13}	0	0	0	0	0		0	
β_{23}	0	0	0	0	−2.6 (2.4)		−1.2 (1.8)	
				O(2)				
position	12(i)	12(i)	12(i)	12(i)	96(i)		96(i)	
population	12	12	12	12	96		96	
x	0	0	0	0	0		0	
y	0.2851 (4)	0.2871 (4)	0.2875 (9)	0.2871 (6)	0.1417 (6)		0.1411 (12)	
z	y	y	y	y	0.1435 (6)		0.1459 (11)	
β_{11}	49 (5)	54 (5)	39 (11)	44 (9)	12.0 (1.2)		13.2 (1.3)	
β_{22}	38 (3)	48 (3)	36 (7)	36 (6)	7 (4)		11.3 (3.5)	
β_{33}	β_{22}	β_{22}	β_{22}	β_{22}	11 (4)		9.4 (3.5)	
β_{12},β_{13}	0	0	0	0	0		0	
β_{23}	18 (4)	17 (4)	23 (8)	11 (7)	4.5 (1.0)		5.5 (1.5)	

Table II (*Continued*)

	PSap	PSbp	FSp[b]	FSp	PSaf	PSbf
				O(3)		
position	24(m)	24(m)	24(m)	24(m)	192(j)	192(j)
population	24	24	24	24	192	192
x	0.1117 (2)	0.1122 (2)	0.1117 (6)	0.1122 (4)	0.0534 (4)	0.0555 (9)
y	x	x	x	x	0.0583 (4)	0.0567 (9)
z	0.3556 (3)	0.3543 (3)	0.3521 (8)	0.3530 (6)	0.1777 (2)	0.1772 (2)
β_{11}	40 (2)	51 (2)	43 (5)	44 (4)	9 (2)	17 (4)
β_{22}	β_{11}	β_{11}	β_{11}	β_{11}	7 (2)	8 (3)
β_{33}	53 (4)	62 (4)	53 (9)	50 (7)	12.8 (0.8)	15 (1)
β_{12}	15 (3)	12 (3)	15 (6)	9 (6)	4.9 (0.7)	3 (1)
β_{13}	5 (2)	5 (2)	6 (5)	−1 (4)	2.6 (1.5)	1 (4)
β_{23}	β_{13}	β_{13}	β_{13}	β_{13}	−0.1 (1.4)	2 (3)

[a] Estimated standard deviations given in parentheses to same significance level as parameters. Isotropic B given in Å^2. Anisotropic displacement factor given as $10^4 \exp[-\Sigma_{j=1}^{3}\Sigma_{i=1}^{3}\beta_{ij}h_ih_j]$. [b] Firor and Seff's data refined with this model.

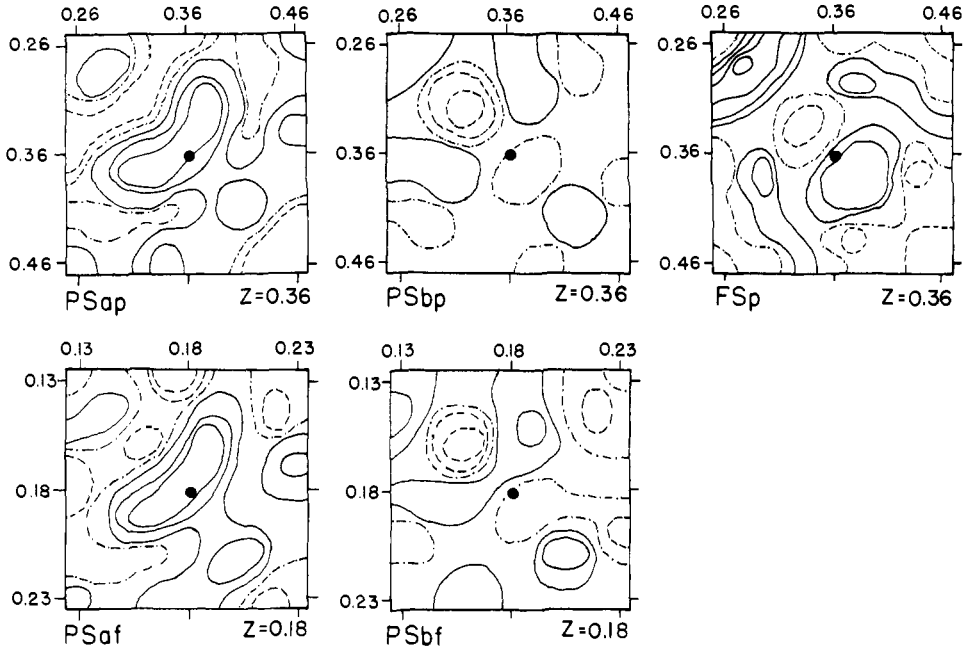

Figure 1. Difference-Fourier map for the region around the position (dot) for the supposed zero-coordinate cation Rb(3). Sections are given for the Pluth–Smith crystals a and b for refinement in both the pseudocell (p) and the 24-Å cell (f) and for the Firor–Seff crystal. Positive, negative, and zero contours are shown respectively by continuous, dashed, and dot–dash lines. Contour levels 0.1 e/Å^3 for all PS data, 0.2 e/Å^3 for FS data.

with the following standards: Rb, $RbAlSi_2O_6$ glass; Ba, paracelsian; Na, Al, and Si, An 70 glass; K, Asbestos microcline) showed that the crystals were chemically zoned and contained Na and Ba. The presence of Ba was surprising, but atomic absorption spectrophotometry showed that the 0.1 M RbOH solution contained 3.85 ± 0.09 μg/mL Ba (2.8×10^{-5} M $Ba(OH)_2$). Scanning electron microprobe analysis showed that Ba is concentrated in the outer rim (~15 μm across) of a crystal used for collection of diffraction data. An average bulk composition is close to $K_{0.2}Na_{0.4}Ba_{0.6}Rb_{9.9}Al_{11.4}Si_{12.6}O_{48}$. The correction procedures for X-ray emission from Rb atoms in a complex matrix are somewhat uncertain for Rb analysis, for which an error up to 1 atom might be possible, but the analysis of Ba is correct to ±0.1 atom. The persistence of the Ba zoning some weeks after ion exchange and dehydration indicates that ion exchange of Rb and Ba at room temperature is sluggish. Sodium appeared to be unzoned.

Prior to the electron microprobe analysis, the zoned crystal was dehydrated at 350 °C and 10^{-5} torr for 2 days, and X-ray diffraction data were collected at room temperature for the 24-Å unit cell with space group $Fm\bar{3}c$ under conditions listed in Table I, column PSa. Computer refinements gave puzzling results until the electron microprobe determinations were obtained. Satisfactory refinement was then obtained with a mixed-cation model, but the amount of inferred Na and Ba is quite uncertain just from the X-ray refinement. No peak was found in the supposed position (Figure 1) for the zero-coordinated Rb. Coordinates and populations are given in Table II (columns PSap and PSaf).

Attempts to obtain ion exchange with $RbCl_2$ and $RbClO_4$ solutions were unsuccessful because crystals became amorphous although retaining cubic shape. Ion exchange was achieved by controlling the pH at ~11 by a solution of 50% RbOH and 50% $RbClO_4$ with Rb molality of 0.1. A crystal exchanged for 4 days at 25 °C was dehydrated at 350 °C for 2 days, and X-ray diffraction data were collected at room temperature by using conditions listed in Table I (PSb). The crystal remained intact, and although fractures were visible, the X-ray diffractions were broadened but not split. Electron microprobe analysis showed strong zoning from a Ba-rich rim ($K_{0.2}Na_{0.4}Ba_{0.8}Rb_{9.5}Al_{11.4}Si_{12.6}O_{48}$) to a Ba-free core ($K_{0.2}Na_{0.4}Rb_{10.5}Al_{11.3}Si_{12.7}O_{48}$) with a bulk composition near $K_{0.2}Na_{0.4}Ba_{0.6}Rb_{9.8}Al_{11.4}Si_{12.6}O_{48}$. X-ray data were also collected for two crystals ion exchanged with a 0.1 M solution of 98% $RbClO_4$ and 2% RbOH for 1 h and 4 h at room temperature. The first crystal with 9 Rb and 2 Na was highly crystalline, and the second with ~10.7 Rb and 0.9 Na showed broad peaks. Samples exchanged for 6 h to 2 days showed various degrees of decomposition. Refinements yielded parameters similar to those for crystals a and b, and are not listed here.

Refinement procedures followed those in ref 4. All diffractions obey $Fm\bar{3}c$ except for 111 with intensity 194 ± 46 (1σ) in crystal A and 71 ± 40 in crystal B.

Discussion of New Structure Refinements

Just as for refinement of the original FS data, the difference-Fourier maps for the PSa and PSb data sets both for the

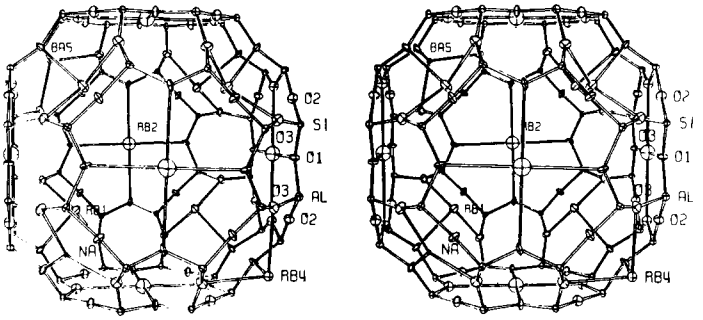

Figure 2. Stereoplot of representative positions for cations in the large cage of dRb-A zeolite (PSaf refinement). Displacement ellipsoids at 30% probability level.

Table III. Interatomic Distances (A) and Angles (deg) of Dehydrated Rubidium-Exchanged Zeolite A

					PSaf		PSbf	
	PSap	PSbp	FSp[a]	FSp	Si	Al	Si	Al
T-O(1)	1.674 (3)	1.671 (3)	1.674 (7)	1.673 (5)	1.597 (21)	1.751 (21)	1.515 (25)	1.833 (26)
T-O(2)	1.654 (2)	1.654 (2)	1.651 (4)	1.652 (2)	1.582 (21)	1.730 (21)	1.531 (39)	1.776 (40)
T-2 O(3)	1.669 (2)	1.669 (2)	1.665 (3)	1.664 (2)	1.602 (13)	1.735 (13)	1.669 (28)	1.668 (27)
mean	1.667	1.666	1.664	1.663	1.596	1.738	1.596	1.736
Rb(1)-3 O(3)	2.734 (4)	2.729 (4)	2.721 (11)	2.716 (7)	2.736 (5)		2.731 (5)	
Rb(1)-3 O(2)	3.135 (2)	3.151 (2)	3.147 (4)	3.114 (3)	3.135 (2)		3.151 (2)	
Rb(2)-4 O(1)	3.151 (6)	3.178 (6)	3.179 (15)	3.181 (10)	3.150 (7)		3.179 (7)	
Rb(2)-4 O(2)	3.734 (7)	3.698 (7)	3.684 (15)	3.692 (7)	3.733 (7)		3.701 (8)	
Rb(4)-3 O(3)	2.869 (12)	2.926 (16)	2.821 (22)	2.949 (17)	2.866 (12)		2.926 (16)	
Rb(4)-3 O(2)	3.200 (12)	3.294 (14)	3.231 (21)	3.327	3.200 (11)		3.292 (15)	
Ba(5)-3 O(3)	2.627 (10)	2.660 (14)	2.560 (16)	2.608 (12)	2.624 (10)		2.660 (14)	
Ba(5)-3 O(2)	2.996 (9)	3.066 (12)	3.007 (16)	3.034	2.996 (9)		3.064 (13)	
Na-3 O(3)	2.446 (4)	2.435 (5)	2.408 (11)	2.411 (7)	2.446 (4)		2.436 (5)	
Na-3 O(2)	2.860 (4)	2.883 (4)	2.880 (9)	2.874 (6)	2.861 (4)		2.883 (5)	
O(1)-T-O(2)	107.8 (3)	107.1 (3)	106.7 (7)	106.9 (5)	108.0 (5)	107.3 (5)	106.7 (1.3)	107.4 (1.2)
O(1)-T-O(3)	111.7 (2)	111.4 (2)	112.1 (4)	111.6 (4)	111.5 (4)	112.2 (4)	111.9 (6)	111.0 (7)
O(2)-T-O(3)	107.4 (2)	107.7 (2)	107.5 (5)	107.4 (4)	107.9 (4)	106.8 (4)	108.4 (7)	106.9 (8)
O(3)-T-O(3)	110.7 (3)	111.4 (3)	110.7 (7)	111.6 (5)	109.8 (5)	111.3 (5)	109.4 (9)	113.3 (1.0)
T-O(1)-T	130.2 (4)	131.8 (4)	132.1 (9)	132.2 (6)	129.9 (4)		131.5 (5)	
T-O(2)-T	175.4 (5)	172.4 (5)	171.3 (1.1)	171.8 (7)	175.4 (5)		172.5 (5)	
T-O(3)-T	151.3 (3)	150.3 (3)	149.7 (7)	149.6 (3)	151.3 (3)		150.5 (4)	

[a] Firor and Seff's data refined with this model.

pseudocell (p) and the true cell (f) show no electron density above the random experimental error for the supposed zero-coordinate position for Rb (Figure 1). Assignment of extra framework electron density to the cations is ambiguous because of the presence of Rb, Ba, K, and Na (see Figure 2). Within the uncertainty of the electron microprobe analysis, there are only 11 cations per pseudocell, and these are accommodated in the eight six-ring and three eight-ring sites. The specific assignments of cation populations in Table II are ambiguous because K–O, Ba–O, and Rb–O distances should be fairly similar. For the eight-ring sites, the electron density is in the middle, and not off-center, and refinements are consistent with about one Rb per site. For the six-ring sites, the electron density was split into four sites: Rb(4) and Ba(5) projecting into the sodalite unit, Na lying near the center of the six-ring, and Rb(1) projecting into the large cage. Because of strong correlations between population factors and because of large contrast in scattering factors, the populations and positions of these sites, especially the "Na" site, are quite uncertain in spite of the apparently small errors from the computer refinement. The refinement of unanalyzed fully dehydrated Ba-exchanged crystals of zeolite A[7] showed Ba in two sites: off-center in an eight-ring, and projecting from a six-ring into the large cage. For the present structures of Rb-exchanged zeolite A, a little Ba could be "obscured" by Rb in the eight-ring site, but a large amount (e.g., 1 atom out of 3) would have been detected if it had been off-center. Occupancy by Ba of the Rb(1) site is permitted by the present data. Detailed speculation on the six-ring sites is futile, and readers are specifically cautioned to treat the data for cations in Tables II and III merely as a convenient model for computer refinement.

Alternation of Si and Al is indicated by the T–O distances for refinement in the 24-Å cell, but the accuracy is lower that reported in ref 4 and 5. This confirms the evidence discrediting the 3:1 ordering model.[9]

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Supplementary Material Available: A listing (Table IV) of the observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(9) Cheetham, A. K.; Fyfe, C. A.; Smith, J. V.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 823–825.