

Structural Studies on the Ion-Exchanged Phases of a Porous Titanosilicate, $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}$

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A titanosilicate with the ideal formula, $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}$, containing unidimensional channels, was synthesized hydrothermally and converted to the hydrogen form by acid treatment. The hydrogen form was partially ion exchanged by sodium ions to obtain a 50% sodium ion exchanged phase. The crystals of the sodium phase, $\text{NaHTi}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}$, retain the symmetry and unit cell parameters of the parent disodium compound, space group $P4_2/mcm$, $a = b = 7.832(1) \text{ \AA}$, $c = 11.945(2) \text{ \AA}$, and $Z = 4$. The sodium ions are located on the ac faces of the crystal while the water molecules occupy the channels. Ion exchange of the acid form by potassium ions leads to a phase with a maximum potassium to proton ratio of about 2. In the acid, $\text{H}_2\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 1.5\text{H}_2\text{O}$, and potassium phases, $\text{K}_{0.5}\text{H}_{1.5}\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 1.5\text{H}_2\text{O}$ and $\text{K}_{1.38}\text{H}_{0.62}\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot \text{H}_2\text{O}$, the a and b axes are doubled while the c -axis dimension is retained. These doubled dimensions were transformed to a primitive tetragonal cell which has a volume twice that of the parent sodium form. The crystals belong to the space group $P4_2/mbc$ with $a = 11.039(1) \text{ \AA}$, $c = 11.886(1) \text{ \AA}$ for the acid phase, $a = 11.015(1) \text{ \AA}$, $c = 12.017(1) \text{ \AA}$ for the $\text{K}_{1.38}\text{H}_{0.62}$ phase, and $a = 11.0604(3) \text{ \AA}$, $c = 11.9088(3) \text{ \AA}$ for the $\text{K}_{0.5}\text{H}_{1.5}$ phase. The number of molecules in the unit cell in these three cases is 8. In the acid form, the channels are occupied by the water molecules, which are involved in hydrogen bonding among themselves as well as with the framework oxygens. In the $\text{K}_{0.5}\text{H}_{1.5}$ phase, all the K^+ ions are in the center of the tunnel. For the $\text{K}_{1.38}\text{H}_{0.62}$ phase, about 35% of the total potassium ions are located at the center of the channel and are bonded to the silicate oxygens. The remaining ions are found near the framework which is close to the positions of the sodium ions of the ac faces in the parent compound. These ions are bonded to both the framework and water oxygen atoms. The titanium atoms in all the phases are octahedrally coordinated, and they are grouped as clusters of four. These clusters are linked by the silicate groups along the a and b directions and by $\text{Ti}-\text{O}-\text{Ti}$ bonds along the c directions. This structural data provide a basis for explaining the observed ion exchange behavior and ion selectivity.

Introduction

There has been an ongoing search for the discovery and design of inorganic ion exchange materials for the selective removal and safe storage of radioactive species from nuclear waste solutions.^{1,2} The inorganic exchangers, unlike their organic counterparts, are resistant to radiation damage and have high selectivities for specific ions to be removed. A variety of ion exchange compounds including zeolites, metal phosphates, heteropoly acids, layered double hydroxides, and titanates have been tested and been used for the separation of specific ionic and molecular species.^{3–5} It was recently reported⁶ that a sodium titanosilicate compound is highly selective for Cs^+ and Sr^{2+} in the presence of 5.7 M sodium ion and 0.6 M hydroxide ion solutions. Subsequently, we were able to prepare this material in highly crystalline form and solve its three-dimensional structure from X-ray powder diffraction data.⁷ The compound is tetragonal, with $a = 7.8082(2) \text{ \AA}$, $c = 11.9735(4)$

 \AA , and $Z = 4$. The structure consists of clusters of four titanium–oxygen octahedra located around the unit cell corners which are linked by silicate groups along two of the unit cell axes. In the third direction, they are connected to each other by $\text{Ti}-\text{O}-\text{Ti}$ linkages. This arrangement leads to one-dimensional channels ideally suited for selective adsorption of Cs^+ ions. Half of the sodium ions reside within the framework bonded to four silicate oxygens and two water molecules. The remaining sodium ions reside in the tunnels, but there is insufficient room for the remaining four Na^+ ions. Instead, protons substitute for Na^+ and the actual formula is $\text{Na}_{1.64}\text{H}_{0.36}\text{Ti}_2\text{O}_3(\text{SiO}_4) \cdot 1.8\text{H}_2\text{O}$. Thus, the full complement of four Na^+ reside within the framework but only 2.56 Na^+ were located in the tunnels along with the water molecules. Treatment of the sodium phase with acid converts it to $\text{HTi}_2\text{O}_3\text{SiO}_4 \cdot 1.5\text{H}_2\text{O}$. This treatment creates cavities within the walls of the tunnels that behave as secondary exchange sites. To gain further insight into the ion exchange properties of this compound, we prepared a number of alkali metal ion exchanged phases and characterized them by application of Rietveld methods to their X-ray powder data. This paper also reports the results of silicon NMR studies and additional ion exchange data for these materials.

There exists a mineral, sodium titanosilicate, with a framework structure identical to that of the synthetic compound, which was determined by single-crystal methods.⁸ In the mineral, the titanium site is occupied by minor amounts of Nb atoms and

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Table 1. Crystallographic Data for the Titanosilicate Phases

	Na	H	K
formula	NaHTi ₂ O ₃ SiO ₄ ·2H ₂ O	H ₂ Ti ₂ O ₃ SiO ₄ ·1.5H ₂ O	K _{1.38} H _{0.62} Ti ₂ O ₃ SiO ₄ ·H ₂ O
fw	295.9	264.9	308.5
space group	<i>P</i> ₄ ₂ / <i>mcm</i> (No. 132)	<i>P</i> ₄ ₂ / <i>mbc</i> (No. 135)	<i>P</i> ₄ ₂ / <i>mbc</i> (No. 135)
<i>a</i> , Å	7.832(1)	11.039(1)	11.015(1)
<i>c</i> , Å	11.945(2)	11.886(1)	12.017(1)
Z	4	8	8
<i>V</i> , Å ³	732.7	1448.4	1458.0
<i>d</i> _{calcd} , g/cm ³	2.68	2.43	2.81
<i>μ</i> , cm ⁻¹	213.1	208.4	279.2
pattern range (2θ), deg	10–85	9.5–85	10–80
no. of reflns	161	274	272
no. of soft constraints	12	20	20
<i>R</i> _{wp} ^a	0.152	0.165	0.162
<i>R</i> _p ^a	0.119	0.120	0.121
<i>R</i> _f ^a	0.044	0.032	0.076

^a See ref 15 for definitions.

the channel is filled by partially occupied sites with water molecules, potassium ions, and sodium ions. Small amounts of other atoms such as Cs, Ba, Zr, and Fe were also detected by chemical analysis. It is interesting to note that the cluster of four metal octahedra observed in this titanate is found in the crystal structures of pharmacosiderite, [Fe₄(OH)₄(AsO₄)₃]·5H₂O,⁹ the Ge-zeolite [Ge₄O₄(GeO₄)KH₃·3H₂O, and the sodium germanogermanate Na[Ge₄O₄(GeO₄)(GeO₃)].^{10–13} As can be seen from their composition, all of these compounds contain exchangeable ions or protons. Thus, by proper choice of metal ions in the octahedra and bridging MO₄ (M = Si, P, As, Ge etc.) groups, it may be possible to design materials for the removal of specific metal ions. This study provides further structural insight into the origins of selectivity in these tunnel type compounds.

Experimental Section

Materials and Methods. All reagents were of analytical grade (Aldrich) and were used without further purification. Thermogravimetric analysis was carried out with a DuPont thermal analysis unit, Model No. 951, at a heating rate of 10 °C/min under a nitrogen atmosphere. The IR spectrum was recorded on a Digilab FTS-40 FTIR unit by the KBr disk method. The solids were dissolved in HF, and the titanium and silicon contents were determined using a SpectraSpec PCP-AEC spectrometer. ²⁹Si NMR spectra were recorded on a Bruker MSL-300 spectrometer.

Synthesis of Na₂Ti₂O₃SiO₄·2H₂O. A 30 mL solution of 2 M TiCl₄ was kept in a Teflon vessel and while being stirred it was mixed with 40 mL of a 30% H₂O₂ solution, 150 mL of distilled water, and 40 mL of 10 M sodium hydroxide. To this reaction mixture was added 4.3 g of silicic acid dissolved in 200 mL of 1 M sodium hydroxide. The contents were then treated hydrothermally at 200 °C for 10 days. A highly crystalline white powder was isolated by filtration, washed with water, and dried at 70–80 °C. Its X-ray diffraction powder pattern was that of Na_{1.64}H_{0.34}Ti₂O₃SiO₄·1.8H₂O, described previously.⁷

The sodium form was converted to the hydrogen form by successive treatment with 0.05–0.1 M HCl. The protons in this form were then partially substituted for sodium, potassium, cesium, and lithium ions by treating with 0.05 M chloride or hydroxide of the respective metal ion at a certain pH. Adsorption of alkali metal ions by the hydrogen form was studied using a 0.05 N metal chloride or metal hydroxide solution at a volume to mass ratio of 200:1 (mL/g) at room temperature. After equilibrium was attained (5 days), the pH of these model solutions was measured using a Corning 340 pH meter. Final concentration of the alkali metal ions in solution was measured using a Varian SpectraAA-300 atomic absorption spectrometer.

Potentiometric Titrations. Potentiometric titrations were carried out by the batch method. Between 50 and 100 mg portions of the exchanger were weighed into polyethylene bottles and equilibrated with appropriate volumes of 0.05 M MCl–HCl or 0.05 M MCl–MOH (M = Li⁺, Na⁺, K⁺, Cs⁺). The volume to mass ratio (*V:m*) was 200:1

(mL/g); equilibration time was 5 days at ambient temperature. The ionic strength was maintained constant throughout the titration. The cation uptake (*A*) was determined by AAS analysis of the filtered equilibrium solutions according to eq 1, where *C*₀ and *C*_e are initial and final concentrations, respectively.

$$A = (C_0 - C_e)V/m \quad (1)$$

X-ray Data Collection, Structure Solution, and Rietveld Refinement. X-ray powder data for the sample packed into a flat aluminum sample holder were collected by means of a Rigaku computer-automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. Data were collected at room temperature between 8.5 and 85° in 2θ with a step size of 0.01° and a count time of 10 s/step. The powder pattern was indexed by Ito methods.¹⁴ The solution, which indexed all the peaks in the monosodium phase, corresponded to a tetragonal cell with *a* = 7.83 and *c* = 11.94 Å, and the systematic absences were consistent with the space group *P*₄₂/*mcm*, as in the case of the parent disodium compound.⁷ The unit cells for the acid and potassium forms are also tetragonal but with the cell dimensions of *a* = 11.039(1), *c* = 11.886(1) Å, *a* = 11.0604(3), *c* = 11.9088(3) Å, and *a* = 11.015(1), *c* = 12.017(1) Å for the acid phase, K_{0.5}H_{1.5} phase, and K_{1.38}H_{0.62} phase, respectively. The systematic absences for these three phases indicated the space group *P*₄₂/*mbc*.

Atomic positions for the framework atoms reported⁷ for the disodium form were used for the refinement of the monosodium form. In the case of the acid and potassium forms, the positions were obtained by transformation of the coordinates. The positions of the alkali metal ions and water molecules in these structures were obtained by difference Fourier maps, followed by initial Rietveld refinement of the full patterns.¹⁵ The atomic positions were refined with soft constraints consisting of both Ti–O (2.00(2) Å) and Si–O (1.63(2) Å) bond distances and O–O (2.66(2) Å) nonbonded distances in the silicate tetrahedra. No constraints were applied for the refinement of alkali metal ions and water oxygen positions. During the final cycles of refinement, the weight of the soft constraints was reduced, but they could not be lifted without reducing the stability of the refinement. All the atoms were refined isotropically. The background was subtracted by means of a cosine Fourier series background function¹⁵ consisting

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Table 2. Positional and Thermal Parameters for the Sodium Titanosilicate, NaHTi₂O₃SiO₄·2H₂O

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} , Å ²
Ti1	0.1440(2)	0.1440(2)	0.1530(2)	0.009(1)
Si1	0	0.5	0.25	0.013(5)
Na1	0	0.5	0.5	0.146(1)
O1	0.1271(4)	0.3886(4)	0.1698(3)	0.024(4)
O2	0.1148(4)	0.1148(4)	0.3340(4)	0.012(4)
O4	0.1455(7)	0.1455(7)	0	0.009(5)
O5	0.2782(7)	0.2782(7)	0.5	0.014(5)
O6	0.5	0.5	0.115	0.044(6)

$${}^a U_{\text{iso}} = B_{\text{iso}}/8\pi^2.$$

Table 3. Positional and Thermal Parameters for the Acid Phase, H₂Ti₂O₃SiO₄·1.5H₂O

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} , Å ²
Ti1	0.1528(2)	0.0177(2)	0.1505(2)	0.045(2)
Si1	0.2220(3)	0.2780(3)	0.25	0.016(3)
O1	0.2309(5)	0.1660(5)	0.1650(5)	0.028(2)
O2	0.1153(5)	0.0169(6)	0.3327(5)	0.016(3)
O3	0.2724(6)	-0.0955(6)	0.1792(5)	0.009(2)
O4	0.1446(8)	0.0106(8)	0	0.070(3)
O5	0.2794(8)	0.0525(7)	0.5	0.010(3)
O6 ^a	0.5	0	0.084(1)	0.053(8)

$${}^a \text{Occupancy} = 0.5.$$

Table 4. Positional and Thermal Parameters for the Potassium Phase, K_{1.38}H_{0.62}Ti₂O₃SiO₄·H₂O

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} , Å ²
Ti1	0.1435(2)	-0.0012(3)	0.1505(3)	0.003(1)
Si1	0.2530(7)	0.2470(7)	0.25	0.013(1)
O1	0.2510(9)	0.1312(9)	0.1620(7)	0.017(1)
O2	0.1195(5)	-0.0338(6)	0.3249(5)	0.045(1)
O3	0.2573(9)	-0.1353(9)	0.1769(9)	0.048(1)
O4	0.1482(9)	0.0135(13)	0	0.005(1)
O5	0.0913(12)	0.3029(15)	0	0.016(2)
K1	0	0.5	0.25	0.089(1)
K2 ^a	0.1463(10)	0.7381(8)	0	0.135(1)

$${}^a \text{Occupancy} = 0.88.$$

of nine parameters. The peak shape was reproduced by use of pseudo-Voigt functions with parameters L_x and L_y . Neutral-atom scattering factors were used for all atoms.¹⁶ No corrections were made for anomalous dispersion, absorption, or preferred orientation. The refinement results show that the cations and the lattice water molecules in these phases exhibit relatively larger thermal parameters, possibly due to disorder and/or partial occupancy.

Results

Crystallographic and experimental parameters are given in Table 1, final positional and thermal parameters in Tables 2–4, and bond lengths and angles in Tables 5–7. The final Rietveld refinement difference plots are shown in Figure 1.

The sodium titanosilicate, either synthetic or mineral, crystallizes in the tetragonal space group $P4_2/mcm$ with $a = b \sim 7.8$ Å and $c \sim 12.0$ Å. The same space group and similar unit cell dimensions were observed for the monosodium titanosilicate described here. However, when the sodium titanosilicate is converted to the acid form and subsequently to its potassium phases, the crystals undergo distortion. This is reflected in doubling of the a (and b) axis. The resulting lattice is still tetragonal with a very similar c dimension, but the other two dimensions (a , b) are doubled to about 15.6 Å. These dimensions lead to a C -centered lattice with 4 times the volume

Table 5. Bond Lengths (Å) and Bond Angles (deg) for the Sodium Phase, NaHTi₂O₃SiO₄·2H₂O

atoms	dist		atoms	dist
Ti1–O1	1.930(3)	2×	Ti1–O2	2.186(4)
Ti1–O2	2.046(3)	2×	Ti1–O4	1.828(2)
Si1–O1	1.634(3)	4×		
atoms	angle range		av	
O–Ti1–O (cis)	76.9(2)–97.2(2)		89.7	
O–Ti1–O (trans)	165.4(2)–172.0(3)		167.6	
O–Si1–O	98.3(2)–115.4(3)		107.9	
atoms	dist		atoms	distances
Na1–O1	2.422(3)	4×	O5--O2	2.685(6) 2×
Na1–O5	2.786(1)	2×	O5--O6	2.814(7) 2×
Na1–O4	3.001(3)	2×	O6--O6	2.75(2)

Table 6. Bond Lengths (Å) and Bond Angles (deg) for the Acid Phase, H₂Ti₂O₃SiO₄·1.5H₂O

atoms	dist		atoms	dist
Ti1–O1	1.859(6)		Ti1–O2	2.205(5)
Ti1–O2	2.109(6)		Ti1–O2	2.171(7)
Ti1–O3	1.850(7)		Ti1–O4	1.793(2)
Si1–O1	1.599(5)	2×	Si1–O3	1.632(6) 2×
atoms	angle range		av	
O–Ti1–O (cis)	73.9(3)–104.3(3)		89.3	
O–Ti1–O (trans)	159.2(3)–166.0(4)		161.5	
O–Si1–O	107.7(6)–109.4(3)		109.5	
atoms	dist		atoms	dist
O5--O2	2.72(1)	2×	O5--O6	2.70(1) 2×
O6--O3	2.95(1)	2×		

Table 7. Bond Lengths (Å) and Bond Angles (deg) for the Potassium Phase, K_{1.38}H_{0.62}Ti₂O₃SiO₄·H₂O

atoms	dist		atoms	distance
Ti1–O1	1.884(9)		Ti1–O2	2.142(6)
Ti1–O2	2.236(7)		Ti1–O2	1.821(6)
Ti1–O3	1.963(9)		Ti1–O4	1.817(3)
Si1–O1	1.657(8)	2×	Si1–O3	1.571(9) 2×
atoms	angle range		av	
O–Ti1–O (cis)	71.6(3)–102.1(5)		89.7	
O–Ti1–O (trans)	159.4(4)–172.9(4)		164.5	
O–Si1–O	101.1(10)–115.3(10)		109.3	
atoms	dist		atoms	dist
K1–O1	3.28(1)	4×	K1–O3	3.18(1) 4×
K2–O1	2.54(1)	2×	K2–O3	2.82(1) 2×
K2–O5	2.66(1)		K2–O5	2.98(1)
K2–O4	3.03(2)		K2–O2	3.29(1) 2×
O5--O3	2.79(1)	2×	O5--O2	2.99(1) 2×

of the parent compound. In the tetragonal system, however, this lattice can be transformed to a primitive cell by taking the diagonal [110] of the 15.6 Å edges as the new a and/or b of the new unit cell. The relationship between the unit cell dimensions of the parent and H (and K) phases is shown in Figure 2. The resulting unit cell therefore has an a dimension of about 11 Å and $c \sim 12$ Å, and the unit cell volume is twice that of the parent compound. The systematic absences in this new unit cell correspond to the space group $P4_2/mbc$.

In sodium titanosilicate, Na_{1.64}H_{0.36}Ti₂O₃SiO₄·1.8H₂O, 1 mol of sodium ions is located in the ac faces of the framework at 0, $1/2$, 0 and 0, $1/2$, $1/2$, etc. The titanium atoms occur in clusters of four centered about the 4_2 axis at the edges of the unit cell with their centers at $z = 1/4$ and $3/4$. They are connected to each other by four oxygen atoms (O2) to form cubes. The cubes in turn are connected to each other in the a and b directions through the silicate groups with the Si atoms at $z = 1/4$ and $3/4$. The Ti–O cubes are linked in the c direction by O4; the

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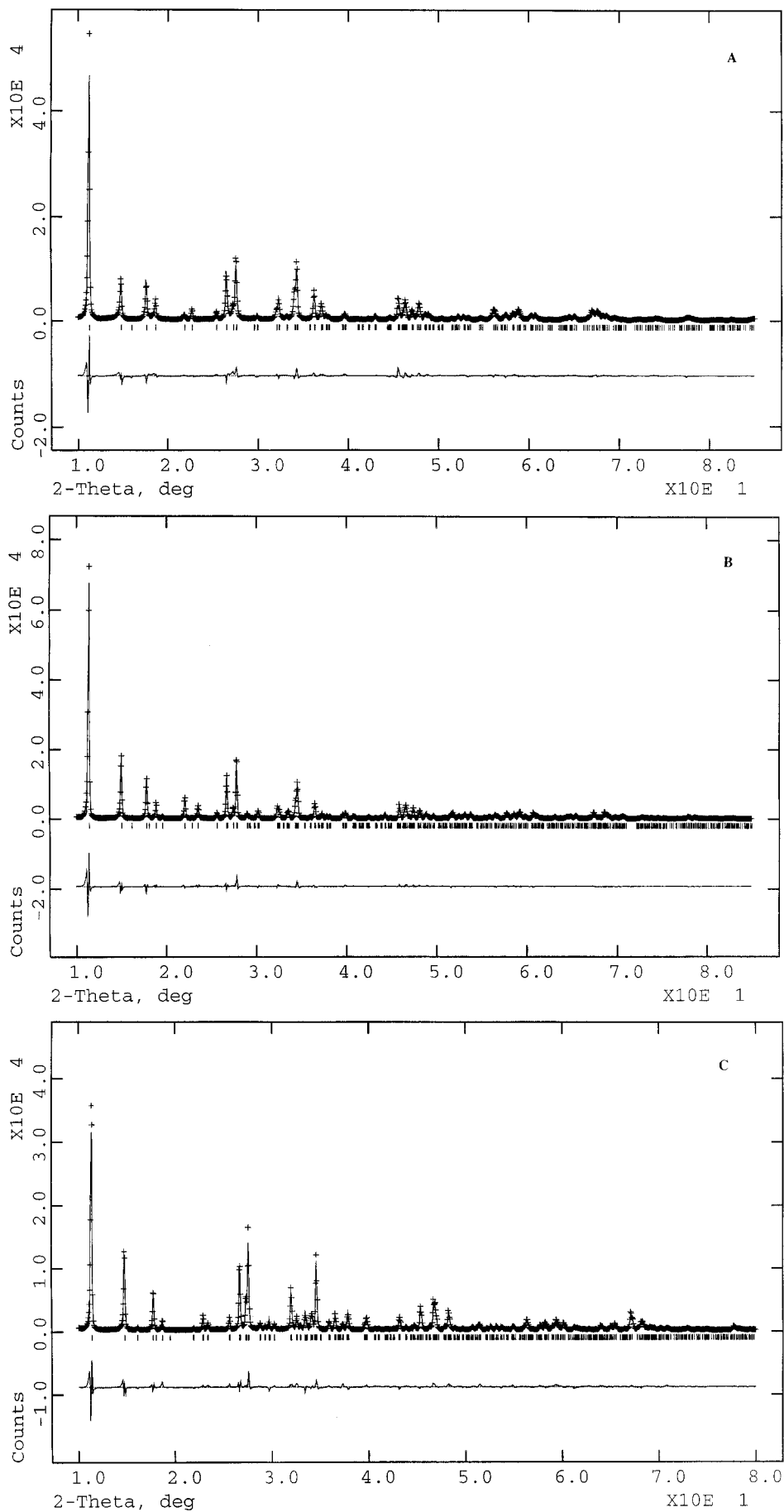


Figure 1. Observed (+) and calculated (-) profiles for the Rietveld refinement for (A) sodium, (B) acid, and (C) potassium phases. The bottom curve is the difference plot on the same intensity scale.

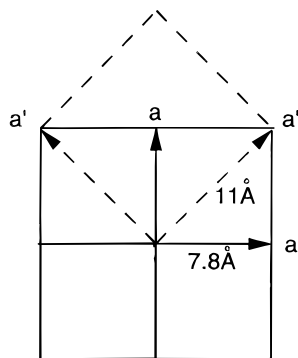


Figure 2. Relationship between the unit cell dimensions of the space groups $P4_2/mcm$ and $P4_2/mbc$.

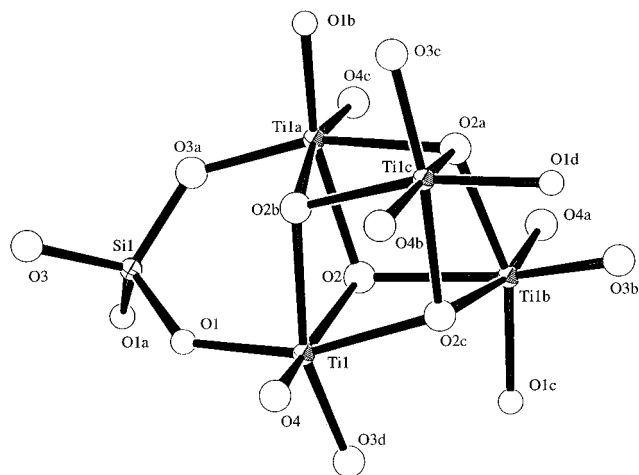


Figure 3. A section of the titanosilicate structure showing the cluster of four titanium octahedra. Silicate oxygen atoms connect this cluster to titania octahedra along the a and b axes while O4 links these clusters along the c axis.

connectivity is Ti–O4–Ti. In all, there are 4 formula units per unit cell.⁷ The Ti atoms in all the structures have a distorted octahedral coordination. The arrangement of octahedra to form a cubelike structure is shown in Figure 3. The metal atoms are about 3.1 Å apart. In the case of the sodium phase, the silicate oxygens O1 and O3 are symmetry related but in the space group $P4_2/mbc$ this symmetry is relaxed so that O1 and O3 are independent. The labeling of other atoms remains the same for Na-, H-, and K-forms. There are two sites for sodium ions. In the ideal formula $Na_2Ti_2O_3SiO_4$, half of the sodium ions would reside in the framework and half in the tunnel. The sodium ions in the framework are halfway along the a and b axes at $z = 0$ and $1/2$. The silicon atoms are also halfway along the a and b axes at $z = 1/4$ and $3/4$ and form four Si–O–Na bonds to the sodium ions. Two water molecules inside the tunnel complete the octahedral coordination of these sodium ions in site 1. The remaining sodium ions reside within the tunnels. However, there is insufficient room for the water molecules and four sodium ions in the allocated space. Thus, only 64% of the sites are occupied by sodium ions and the positive charge requirement for neutrality is compensated by the presence of protons. The selectivities for Na^+ are different in the two sites.

In the monosodium phase, the structure is as described in the preceding paragraphs. The sodium ions occupy all the framework sites. The sodium and silicon atoms alternate along the c -axis with a Na–Si distance of about 3.0 Å. The sodium ions are six-coordinated where four of the coordination sites are from the silicate oxygen (O1) atoms and two from water oxygen atoms. These oxygens link the sodium and silicon atoms

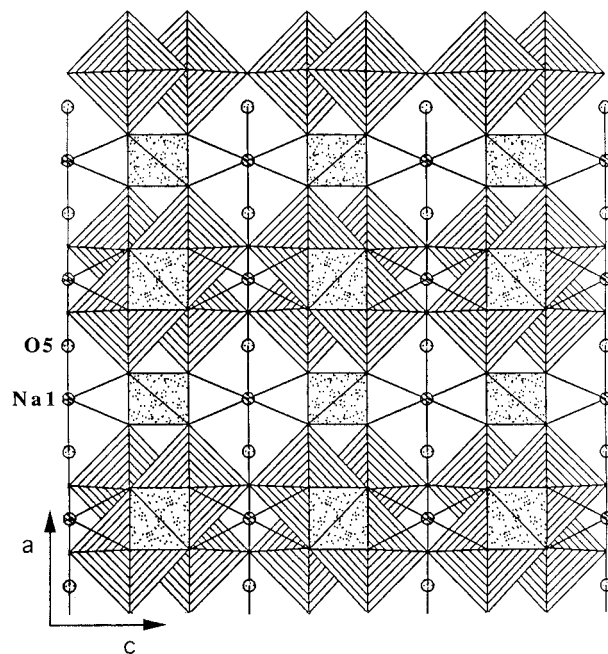


Figure 4. Plot of the titanosilicate structure down the b axis showing the arrangement of silicon tetrahedra and sodium (Na1) octahedra in the ac and bc faces. The water oxygens connect the sodium ions to form linear chains. Solid lines depict groupings of four titanium octahedra; the stippled squares are silicate groups.

along the c direction (Figure 4). The water oxygen, O5, connects the sodium ions along the a and b directions by $-O5-Na-O5-Na-$ links. These bonds are linear, since the angle $O5-Na-O5$ is 180° . Chemical analysis showed that the compound has the formula $Na_{1.1}H_{0.9}Ti_2O_3SiO_4 \cdot 2H_2O$, indicating that it contains 10% more sodium ions than the amount obtained from the X-ray study. These excess sodium ions would then occupy the channel sites as in the parent compound. However, they could not be located, since the occupancy is very small. The channel is also occupied by the water molecules. Both water oxygens have mm site symmetry. These water molecules are involved in extensive H-bonding among themselves and also with the framework oxygen atoms (Table 4). We have also carried out Rietveld analysis of the phase containing only 0.88 mol of sodium ions in the formula. The results show that all the sodium ions occupy the Na1 site as described above and that the positions of water molecules in these partially substituted sodium phases are very similar.

In space group $P4_2/mbc$ the symmetry constraints on the atoms are relaxed. The titanium atom occupies a general position, and the silicon atom is located on a 2-fold axis. There are two independent oxygen atoms for the silicate group, as opposed to one single atom in the lower symmetry structure. The symmetry constraints on the framework oxygen atoms are also relaxed.

A polyhedral representation of the structure of the acid phase, $H_2Ti_2O_3SiO_4 \cdot 1.5H_2O$, is shown in Figure 5. The framework of the acid form contains only the silicate and cubelike arrangements of the Ti octahedra. The positions normally occupied by sodium ions on the ac face which links the silicate groups along the c axis are empty. This indicates that the structure is not dependent on the these sodium ions for maintenance of its integrity although this site is highly specific to Na^+ ions as demonstrated by the results reported above. The tunnels contain 1.5 mol of water molecules, among which the O5 position is fully occupied and its position corresponds very closely to that of O5 in the monosodium phase. Water molecule oxygen O6 is found at the center of the channel and is disordered

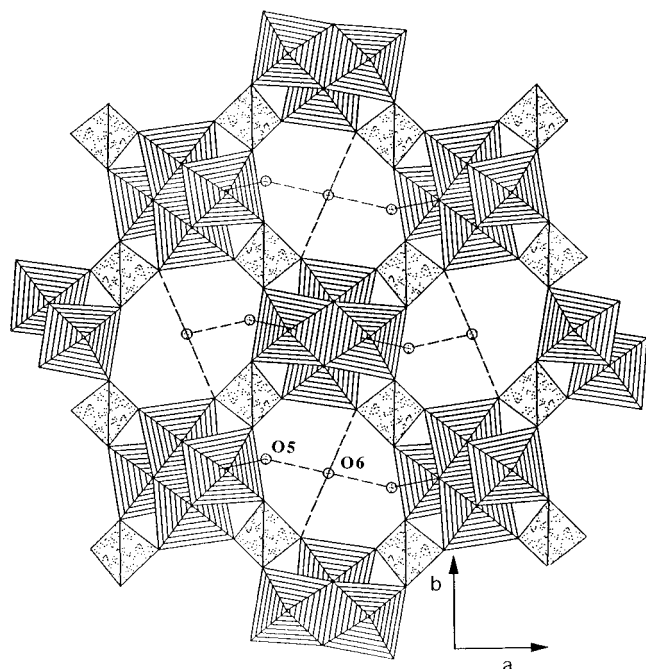


Figure 5. Structure of the acid phase as viewed down the *c*-axis. Hydrogen bonds are shown by dotted lines. Water oxygens O5 and O6 are hydrogen-bonded to framework oxygens O2 and O3, respectively. The representation of polyhedra is same as in Figure 4.

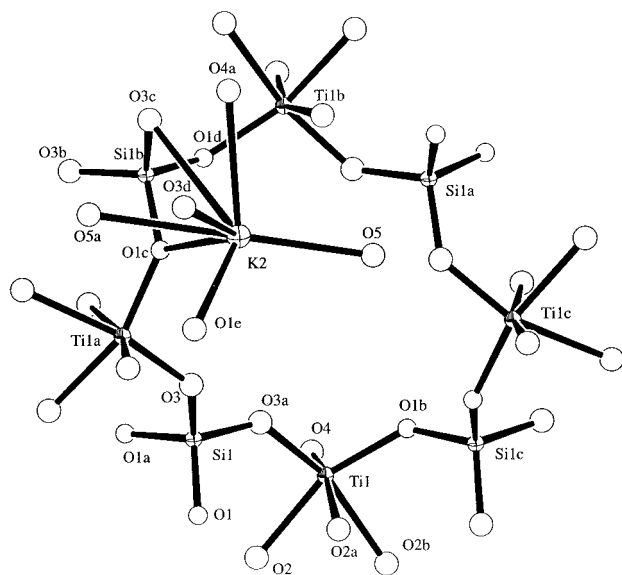


Figure 6. Coordination of the potassium (K2) ions which occupy sites close to the framework.

over two positions ($O6 - -O6' = 2.0 \text{ \AA}$) about a mirror plane. It is involved in hydrogen bonding with the silicate oxygen, O3, as well as with the other water molecule oxygen, O5, as shown in the Figure. O5 is also hydrogen-bonded to the framework oxygen atom, which in this case is O2.

The composition for the K-form, $K_{1.38}H_{0.62}Ti_2O_3SiO_4 \cdot H_2O$, obtained from Rietveld analysis agrees very well with a formula, $K_{1.35}H_{0.65}Ti_2O_3SiO_4 \cdot H_2O$, derived from chemical analysis. The structure contains two independent K^+ ion positions and one water molecule. Potassium ion K1 is in the channel center at $z = 1/4$ and $3/4$ and is fully occupied and accounts for $1/2$ mol of K^+ . K2 is near the framework, as shown in Figure 6, and its occupancy refined to about 88% of its expected value. The position of the water molecule is very close to that of O5 in the previously described phases. As in the case of the H-form, site 1 of the sodium atoms in the *ac* face is empty. However, the

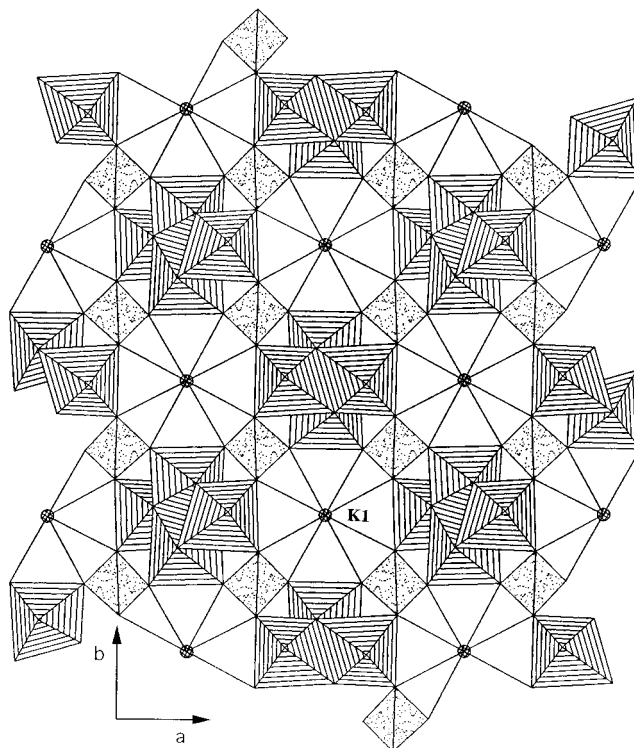


Figure 7. Structure of the potassium phase down the *c* axis showing the coordination of the potassium (K1) ions at the center of the cavity. Potassium ions are represented by filled circles. The representation of polyhedra is same as in Figure 4.

K^+ ion K2 is very close to this site (1.2 \AA away from the ideal site $0.24, 0.75, 0$) although it is located in the pore away from the Si–Si axis along the *c* direction. The coordination of this K^+ ion and its position with respect to the pore are shown in Figure 6. It is strongly bonded to two O1 atoms ($K-O1 = 2.54(1) \text{ \AA}$), two O3 atoms ($K-O3 = 2.82(1) \text{ \AA}$), and two water oxygens ($K-O5 = 2.66(1), 2.98(1) \text{ \AA}$). In addition, it is $3.03(2) \text{ \AA}$ away from an O4 atom and $3.29(1) \text{ \AA}$ from two symmetry-related positions of O2 that are not shown in the figure. The other potassium atom K1 is located at the center of the cavity (Figure 7) and is bonded to the oxygen atoms of the silicate group. This is also the preferred position for the cesium ion. The ions are eight-coordinated by symmetry-related positions of O1 and O3 atoms. The $K-O1$ ($3.28(1) \text{ \AA}$) and $K-O3$ ($3.18(1) \text{ \AA}$) bond lengths are slightly long for eight-coordinated potassium ions. However, in this case the distances are governed by the cavity size, which is ideally suited for the Cs^+ ions. In the Cs^+ -exchanged phase, all eight silicate oxygens are $3.18(1) \text{ \AA}$ from the ions.⁷

In order to determine the sequence by which the two K^+ sites are filled, we synthesized the phase $K_{0.5}H_{1.5}Ti_2O_3SiO_4 \cdot 1.5H_2O$. The unit cell dimensions for this phase are $a = 11.0604(3)$ and $c = 11.9088(3) \text{ \AA}$, with $Z = 8$. Rietveld refinement led to reliability factors of $R_{wp} = 0.146$, $R_p = 0.112$, and $R_F = 0.046$ for 237 independent reflections. In this phase, which contains 25% of the theoretically allowed two potassiums per formula, all the K^+ ions are in the center of the cavity. Since in the more fully exchanged phase $K_{1.38}H_{0.62}$ this site is completely filled, we assume that this site is preferred and the second site close to the framework is filled only to the amount allowed by the space available.

The Li^+ -exchanged phase, on the other hand, crystallizes in the same space group as the sodium phases. Analytical data indicate a composition $Li_{1.7}H_{0.3}Ti_2O_3SiO_4 \cdot \sim 2.3H_2O$ at maximum exchange. The unit cell dimensions are $a = 7.860(2)$ and

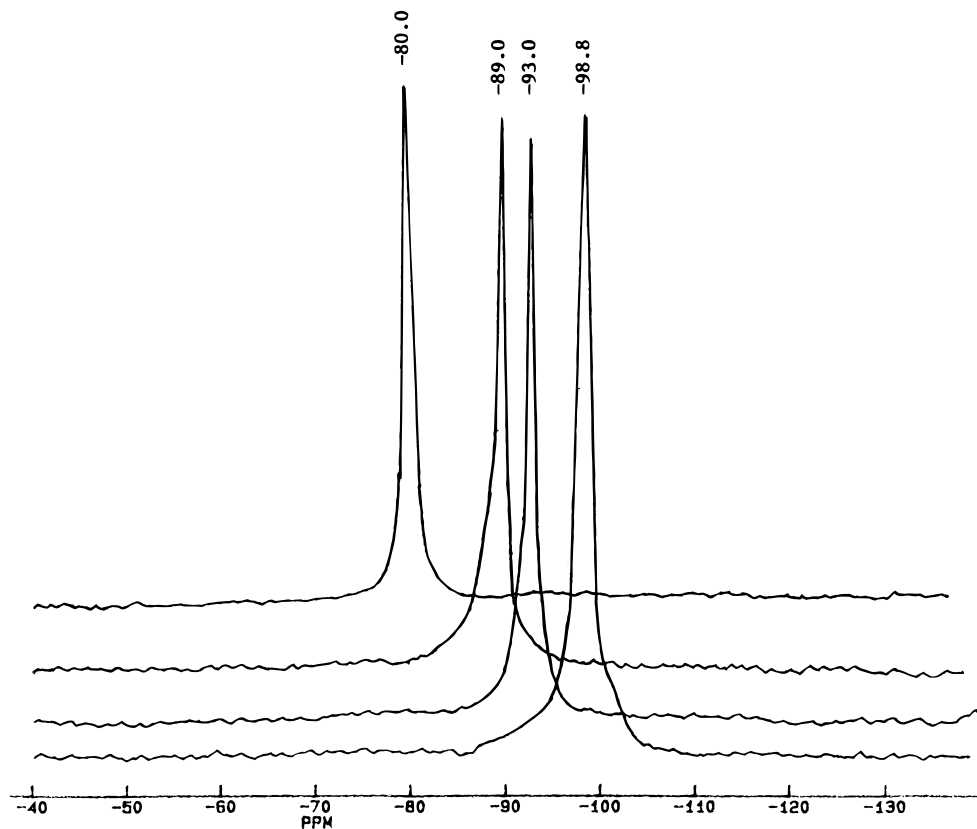


Figure 8. ^{29}Si magic angle spinning NMR spectra of titanosilicate samples.

$c = 11.876(4)$ Å. The structure was refined by the Rietveld method, in a manner similar to that for the other structures, which led to $R_{\text{wp}} = 0.131$, $R_p = 0.102$, and $R_F = 0.043$. Because of its relatively poor crystallinity, it was not possible to locate and refine the positions of all water oxygens and Li^+ ions. However, one of the water molecules is found very close to the position of O5 in the sodium phase. Another water molecule was located at the center of the cavity (0.5, 0.5, 0.25). The other water oxygens are disordered near this central water oxygen molecule. The lithium ion was located very close to the silicate group on a mirror plane (0.132(2), 0.557(2), 0.0) and is bonded to the water oxygens (O5), silicate oxygens (O1), and also the disordered water oxygens. The results however clearly show that the lithium ions have not occupied the sites of the sodium ions on the ac face; instead, they are shifted toward the center of the cavity similarly to potassium ions (K2).

NMR Data. Solid state MAS NMR data were obtained for the ^{29}Si nucleus as a function of cation loading. In the absence of any alkali metal ions in the structure, the silicon atoms resonate at -98.8 ppm. As the cations are introduced, this resonance shifts downfield as a result of deshielding of the silicon atoms by location of the cations between the Si atoms. The shifts accompanying sodium ion uptake are given in Figure 8. The downfield shift was found to be directly proportional to the amount of sodium ion exchanged, as shown in Figure 9. The chemical shifts for partially exchanged Na^+ phases containing 2.1 and 3.0 mequiv of Na/g are -93 and -89 ppm, respectively. When the exchanger has achieved the maximum uptake of Na^+ as in $\text{Na}_{1.64}\text{H}_{0.36}$, the ^{29}Si resonance occurs at -80 ppm, a shift of 18 ppm relative to the acid. Similar dependence is found for K^+ but with a slightly different slope of the straight line. One might expect to see a more radical change in the slope of the straight line when all the sites in the center of the tunnels are filled and the K^+ begins to fill the sites close to the framework. However, this is not the case,

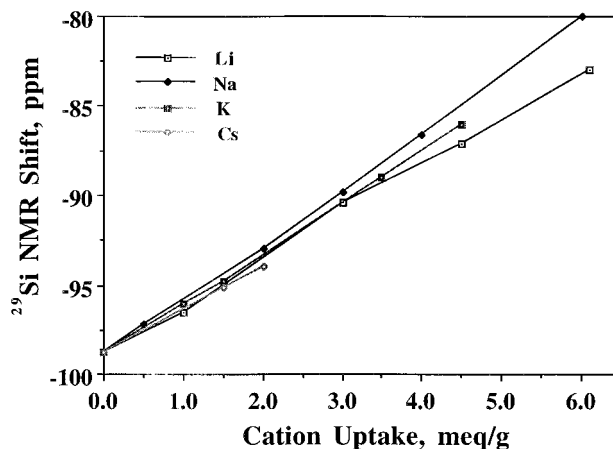


Figure 9. Effect of cation loading on the ^{29}Si NMR chemical shift.

indicating a uniform dispersion of the ions. The difference in slope observed for K^+ may result from its initial positioning in the tunnel centers rather than the framework. We note that Cs^+ , which cannot fit into the framework sites but only into the tunnel sites, has an even larger slope difference than K^+ . Finally the shift due to lithium ions at first duplicates the K^+ curve but then exhibits a more drastic change in slope. This change occurs at about 3 mequiv/g of Li^+ loading or close to half-exchange and may signal a change in filling of exchange sites. The small size of Li^+ and its increased hydration (Figure 10) may account for the observed lower chemical shift. Lithium ions apparently fill the sites close to the framework first because, placed at the center of the tunnels, the ions are too far away from the silicon oxygens to form bonds. Once these sites are filled, the lithium ions occupy the sites near the tunnel center. These Li^+ ions are surrounded by water molecules that form hydrogen bonds to the hydration shell of the Li^+ ions located in the near framework sites.

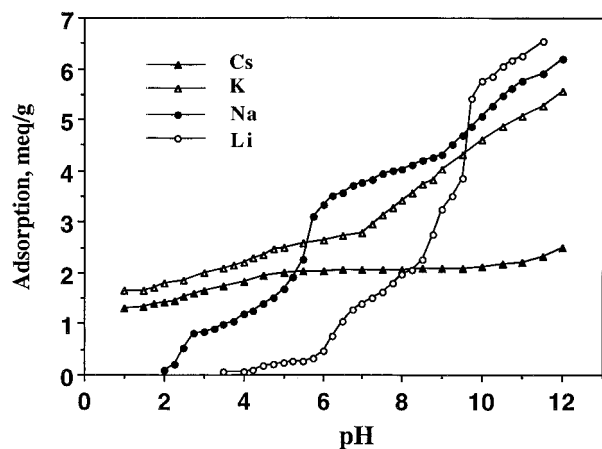


Figure 10. Potentiometric titration of titanosilicate with alkali metal hydroxides.

Ion Exchange Behavior. The results of the potentiometric titrations are shown in Figure 10. The Na^+ and Cs^+ curves were presented previously.¹⁷ Both K^+ and Cs^+ are taken up at pH values below zero, showing the very high selectivity for these ions in the presence of large amounts of hydrogen ion. Cesium ion is actually the more preferred ion, but less Cs^+ is taken up than K^+ . This seeming anomaly arises from the fact that Cs^+ cannot fit into the framework sites but only into the tunnel sites⁷ and even in these sites can only occupy half of them because of its large size. Ion uptake in mequiv/g was calculated on the basis of the anhydrous phase $\text{H}_2\text{Ti}_2\text{O}_3\text{SiO}_4$, for which the Cs^+ capacity should be 2.1 mequiv/g. It is seen that this capacity is attained at a pH of 12. Potassium ions also fill this tunnel site (site 2) first. Because K^+ is smaller than Cs^+ , more K^+ ions can fill the site 2 positions. We note that there is a slope change at a K^+ uptake of 2.8 mequiv/g (pH \sim 7). This value represents half the total K^+ uptake (5.6 mequiv/g or 1.38 mol). At this point, the near framework sites (site 1) may begin to fill up as well as any remaining positions at site 2.

Sodium ions, in contrast to the larger ions, begin to exchange by filling the voids within the framework, since they can fit nicely into these spaces. We note also that they are not exchanged until a pH of 2, indicating a lower selectivity than for Cs^+ and K^+ . An even lower selectivity is expected for Li^+ , as it is poorly exchanged until pH 6. Thus, the selectivity sequence determined earlier,¹⁷ $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$, is confirmed by the X-ray data. However, the maximum loading at high pH is just the reverse of this sequence and is determined by the ion size as explained in the Discussion.

Discussion

The reasons for the observed ion exchange behavior of the titanosilicate have been clarified by the structural analysis reported here and in the previous study. There are several exchange sites to consider in explaining the behavior toward different ions. One exchange site is in the framework (designated site 1) at $0, \frac{1}{2}, \frac{1}{2}$ in the sodium form. This is a 4-fold site with sodium ions in each face at $c = 0$ and $\frac{1}{2}$. Since there are four molecules per unit cell, in the formula idealized as $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4$, there are theoretically 8 Na^+ ions per unit cell. Half of them can then occupy site 1. The second sodium site (site 2') is in the tunnel at approximately 0.435, 0.435, 0.06. This is an 8-fold site, but only half of the sites in any one unit

cell can be occupied; otherwise, the sodium ions would be too close to each other. This site is less preferred because Na^+ forms long bonds with framework oxygens, $\text{Na}-\text{O}1 = 2.74(2)$ Å, and with water molecules. If all four of these Na-site 2' positions were occupied, the theoretical or idealized formula $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4$ would be realized. However, only 64% occupancy was obtained for this site in the hydrothermally prepared compound and slightly less was obtained by titration of the proton phase (Figure 10). The charge discrepancy is compensated by protons, as the formula of the synthesized product is $\text{Na}_{1.64}\text{H}_{0.36}\text{Ti}_2\text{O}_3\text{SiO}_4$.

Potassium ion prefers a site within the tunnel of the expanded cell (designated site 2) at $0, \frac{1}{2}, \frac{1}{4}$. This site is completely filled when the composition is $\text{K}_{0.5}\text{H}_{1.5}\text{Ti}_2\text{O}_3\text{SiO}_4$, as shown by the X-ray data. The second site for potassium is also within the tunnel because the large K^+ ions cannot fit within the cavity in the framework as can Na^+ ions. However, the K^+ in this second site is near the framework; we shall designate it as site 1'. The occupancy is only 0.88, which added to the 0.5 gives a total of 1.38 K^+ in the formula. This smaller amount of K^+ relative to Na^+ prevents crowding within the tunnel.

Cesium ion, on exchange with the sodium ion phase, only displaced a small amount of the sodium ions,⁷ the final composition being $\text{Na}_{1.49}\text{H}_{0.31}\text{Cs}_{0.2}\text{Ti}_2\text{O}_3\text{SiO}_4$. Two different sites were occupied, the first being $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$, a site that is equivalent in this small cell to the $0, \frac{1}{2}, \frac{1}{4}$ position (site 2) in the larger $\text{K}_{0.5}\text{H}_{1.5}$ structure. The second Cs^+ site was $\frac{1}{2}, \frac{1}{2}, 0.131$ (site 2'), so labeled because it was close to but not exactly equal to the sodium site 2'. Both sites were equally occupied by Cs^+ but were too close to each other to have both positions filled in the same unit cell. This limited the occupancy to one or the other site so the maximum amount of Cs^+ that could be taken up by the sodium phase was $\text{Na}_{1.5}\text{Cs}_{0.5}$ (2.1 mequiv/g). The problem with attainment of this level of Cs^+ in the tunnels is the crowding that would result in fitting in an additional equal number of sodium ions (0.5) to satisfy charge balance. Instead, the titanosilicate retains the 0.31 mol of protons originally present, probably as TiOH , and retains much of the smaller sodium ion originally in the tunnels.

A greater amount of Cs^+ is taken up if the exchanger phase is in the hydrogen form, $\text{H}_2\text{Ti}_2\text{O}_3\text{SiO}_4$. Even in acid solution, about 1.5 mequiv of Cs^+ /g (pH 4) is taken up and a maximum uptake of 2.1 mequiv/g is reached at pH 12. This latter value is equivalent to a formula of $\text{Cs}_{0.5}\text{H}_{1.5}\text{Ti}_2\text{O}_3\text{SiO}_4$, which is exactly the formula required by filling only one of the two tunnel sites. Thus, the limitations of space prevent a larger uptake of Cs^+ . This behavior contrasts to that of potassium ion. Potassium ion initially fills the tunnel site at $\frac{1}{4}c$ and $\frac{3}{4}c$ with bond distances of 3.18 and 3.28 Å (Table 7). These bond distances are somewhat long for eight-coordinate K^+ ($r = 1.51$ Å) but are more suitable for Cs^+ . Thus, we tentatively assume that the affinity in this site of the proton form of the exchanger is greater for Cs^+ than for K^+ as has been measured by K_d values.¹⁷ However, because of the smaller size of K^+ , a small amount of K^+ also fits into the site closer to the framework (site 1'). This would allow a somewhat greater uptake of K^+ than of Cs^+ because there are two tunnel sites competing against protons for exchange and two different equilibrium constants for the sites. At the point where the slope of the titration curve (Figure 10) increases, the exchanger has taken up 2.77 mequiv of K^+ /g, or $\text{K}_{0.65}\text{H}_{1.35}$. Thus, we assume that at this point the site in the center of the tunnels ($\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$) is filled and an additional 0.15 mol of K^+ is already present in site 1'. The filling of two sites simultaneously by Cs^+ is not possible due to size constraints.

(17) Bortun, A. I.; Bortun, L. N.; Clearfield, A. *Solvent Extr. Ion Exch.* **1996**, *14*, 341.

The selectivity for Na^+ is lower than that for Cs^+ and K^+ , as shown by the much higher pH at which sodium ion begins to exchange. However, it must be remembered that Na^+ enters the framework site (site 1) first. In this site it forms four strong bonds ($\text{Na}-\text{O} = 2.42 \text{ \AA}$) to silicate oxygens and two weaker bands ($\text{Na}-\text{O} = 2.79 \text{ \AA}$) to water oxygens. The tunnel sites are less favorable for Na^+ , as the shortest bonds are 2.72 \AA in these sites. Lithium ion does not fit well into either site and is therefore the least preferred ion, as shown by the high pH (4) at which it begins to exchange. Thus, the selectivity sequence is $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$, in harmony with the K_d values. This selectivity sequence also obtains in alkaline solution even though the total uptake is in the reverse order. The total amount of ion taken up depends upon ion size, not selectivity.

There is a seeming contradiction in the uptake results when exchange occurs from mixed ion solutions. In the presence of sodium ion, much less Cs^+ is taken up. It was shown that the maximum uptake of Cs^+ from a 0.05 M solution in the presence of 0.05 M Na^+ is about 0.5 mequiv/g, down from 2.1 mequiv/g.¹⁷ Apparently, both sodium and cesium ions can be exchanged simultaneously since they occupy different sites. However, with sodium in the framework sites and Cs^+ in the tunnel center, there is insufficient room for water to shield the repulsion between the two positively charged ions. But all the framework sodium sites fill up (up to pH 12) and the Cs^+ sites do not. Cesium ion can only diffuse down the tunnels whereas Na^+

can also diffuse in directions at right angles to the tunnel directions. The smaller Na^+ must fill its sites more rapidly than Cs^+ because of its greater rate of diffusion. The large Cs^+ must encounter significant electrostatic repulsive forces when sodium is present in the framework sites, presenting a large barrier to its diffusion. In contrast, sodium ion moving through the tunnels and faces could diffuse more rapidly, encountering less electrostatic repulsions, and in competition with Cs^+ not only fills up the framework sites but is also found in the tunnels. This further reduces the Cs^+ occupancy. Thus, while Cs^+ is thermodynamically favored over Na^+ as shown from K_d values, we attribute its low occupancy to less favorable kinetic and size factors. Additional studies to develop these concepts further are in progress.

Many nuclear waste streams are alkaline and contain high levels of Na^+ , lesser but significant amounts of K^+ , and small amounts of Cs^+ (10^{-3} M or less). Thus, in spite of the low uptake of Cs^+ , the high K_d values allow Cs^+ to be removed from such solutions by the titanosilicate, albeit with a very low capacity.

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