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High-Pressure and -Temperature Ion Exchange of Aluminosilicate and Gallosilicate Natrolite

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ABSTRACT: The simultaneous application of high pressure and high temperature has been used to achieve direct ion exchange of large cesium cations for the small sodium cations found in the zeolite natrolite by putting it into a superhydrated state with increased pore size. The larger cations remain trapped upon pressure release, and thus, this method is a means of producing new cationic forms of zeolites.

Ion exchange is a fundamental chemical process in many important materials, including aluminosilicate zeolites and related framework solids, layered phosphates, and certain polymer resins.[1] For zeolites, ion exchange is the basis of several industrial applications, including nuclear waste remediation, water softening, and the preparation of protonated forms that are solid acid catalysts. The nanoporosity and typically relatively weak bonding of the charge-balancing cations to the aluminosilicate framework oxygen atoms are both important in facilitating ion exchange.[2] Ion exchange is normally carried out at ambient pressure by contacting the solid zeolite with an aqueous solution or molten salt of the cation to be introduced. If the cation is too large to enter the pores of the zeolite or the energy of binding is unfavorable, the process fails; in some cases, the exchange is readily reversed, and back-exchange occurs. This is a common problem for large Cs^+ ions that must be removed from high-level radioactive waste; few zeolites have been found to exchange Cs^+ selectively and then retain it. Recent work has demonstrated that at high pressure, some zeolites can enter a "superhydrated" state wherein the lattice and pore windows expand because of the additional water molecules that have been forced into the pores.[3−5] Here we develop this approach to show for the first time that the application of pressure can enable the direct ion exchange of Cs^+ for Na^+ in aluminosilicate and gallosilicate zeolites, which does not occur at ambient pressure. Because the exchange can occur only under high-pressure conditions, the large Cs^+ cations remain trapped when the pressure is released, and they are not back-exchanged with Na^+ under reflux conditions in concentrated solutions. This is therefore a way to produce new zeolites containing large cations that could provide a method for making systems containing trapped radionuclides less likely to leach back into the environment.

Natrolite is a naturally occurring small-pore zeolite. It is composed of pentameric 4−1 T_5O_{10} units connected along the *c* axis to form infinite chains (Figure 1a) that link to form a two-dimensional eight-membered-ring pore system along the *a* and *b* axes connected by further eight-membered-ring pores along the *c* axis. Natrolite normally has poor ion-exchange properties because of strong bonding of the Na^+ ions within the pores and low water mobility.[6] Multiple 7 day aqueous exchanges at 60 °C provide only partial (<50%) replacement of Na^+ with monovalent ions (Li^+, K^+, Ag^+, Tl^+, NH_4^+), and <20% incorporation of Hg^{2+}, Cd^{2+}, Zn^{2+}, Ba^{2+}, Ni^{2+}, or Co^{2+} occurs.[6] Extended (50−60 day) aqueous exchanges at 60 °C have been reported to produce the K^+ and Cd^{2+} forms,[7,8] although our attempts to repeat the Cd experiment failed. Through the use of high-temperature melts, the Li^+ (7 days, 280 °C),[9] K^+ (6 days, 190 °C),[9] and NH_4^+ (16 days, 190 °C)[10] forms have been made. Recently, the K^+ form was produced via a series of extended high-temperature aqueous exchanges and then the Rb^+- and Cs^+-substituted forms were produced from it; this stepwise process was needed to achieve incorporation of the large alkali-metal ions.[11] To our knowledge, large cations such as Cs^+ have never been directly introduced into the Na^+ form.

The behavior of natrolite under pressure in water-containing fluids is particularly interesting in that an unusual cell volume expansion occurs as a result of pressurization in the region 0.8−1.5 GPa. As speculated in the original work,[12] this anomalous pressure-induced expansion phenomenon has been shown to be due to forcing additional water molecules into the crystalline structure, resulting in expansion of the pores.[3−5] The resulting transition from $Na_{16}Al_{16}Si_{24}O_{80}\cdot 16H_2O$ to $Na_{16}Al_{16}Si_{24}O_{80}\cdot 32H_2O$ is described as the formation of a "superhydrated" phase. The structural changes that lead to expansion can be described by rotation of the fibrous chains along the *c* axis to produce a net anisotropic volume increase by expansion along the *a* and *b* axes and pore diameters in the (001) plane. The gallosilicate forms of natrolite also display the same pressure-induced expansion and superhydration phenomena,[13,14] but at lower pressures. NMR measurements indicate that in addition to these structural changes, the water mobility increases with pressure.[15]

In this work, bulk ion-exchange experiments were performed[16] on both the alumino- and gallosilicate forms of natrolite at 1 GPa, the pressure where maximum pore expansion is known to occur in the aluminosilicate system.[4] The experiments were carried out in a piston-cylinder device using specially designed Teflon capsules. The zeolite samples were placed in the capsules with saturated CsCl solutions and initially heated to 60, 100, or 150 °C for 1 h.

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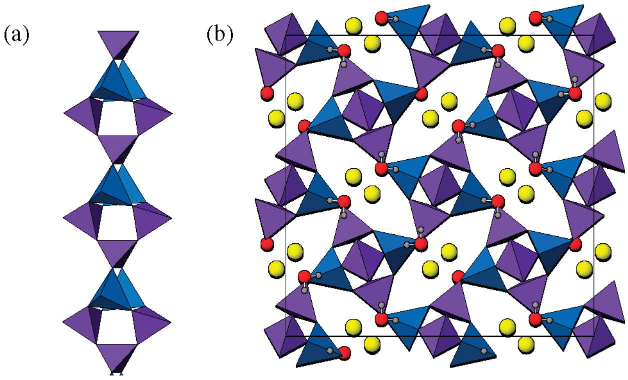

Figure 1. (a) Natrolite chains running along the *c* axis. (b) View of the overall structure down the *c* axis, showing the pore structure. Al/Ga and Si tetrahedra are shown in purple and blue, respectively, Na^+ cations in yellow, and O atoms of water molecules in red.

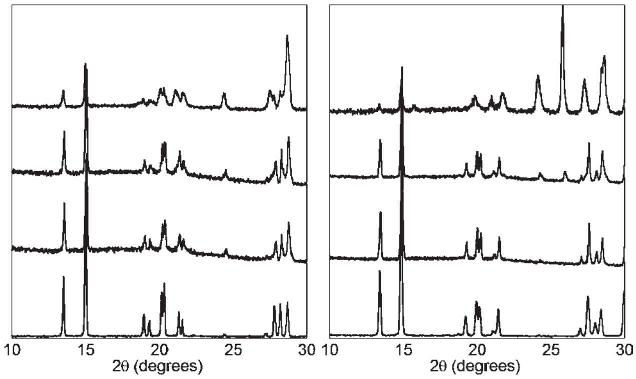

Figure 2. PXRD patterns (Cu Kα_1) for the (left) aluminosilicate and (right) gallosilicate systems (from bottom to top) before exchange and after 1 h exchanges at 60, 100, and 150 °C at 1 GPa.

Powder X-ray diffraction (PXRD) was used to determine that the framework remained intact in the recovered samples (Figure 2). There was no evidence of sample degradation up to 100 °C; however, some asymmetric peak broadening on the low-angle side occurred when the exchange was done at 150 °C, and there was evidence for an impurity phase at higher temperatures for the gallosilicate form.

The level of Cs/Na exchange was measured using scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) analysis (Table 1) Each derived composition shown in the table is an average from several grains. Ion exchange clearly occurred, and the proportion of Cs^+ versus Na^+ ions introduced into the structure increased with run temperature. To test whether back-exchange occurred in the absence of pressure, samples that had been treated at 100 °C were then refluxed in a concentrated NaCl solution for 24 h at ambient pressure. For the aluminosilicate system, the cesium content dropped from 18 to 12%, but for the gallosilicate system, it was reduced from 28 to 5%. This indicates that the majority of the large Cs^+ cations remain trapped in the aluminosilicate material but that back-exchange reactions can occur at ambient pressure for the more flexible gallosilicate material with slightly larger pores. We carried out Rietveld refinements of the PXRD data in an attempt to gain further information about the Cs^+ cation locations within the pores for comparison with the fully exchanged Cs^+ form.[11] The results were inconclusive; for the aluminosilicate with a significant Cs content, this was due in large part to a peak asymmetry that could not be satisfactorily modeled. The change in unit cell volume for the aluminosilicate (Table 1) is again consistent with Cs^+ exchange at 150 °C, where there is a 1% increase from the starting material. Although smaller than expected relative to the fully exchanged system,[11] the change is significant, and there are several plausible explanations for the small volume, including more efficient siting of Cs inside the pores or different water content; both could occur from the pressure treatment. In order to confirm that Cs was indeed located within the natrolite grains and not present as an amorphous or unidentified phase, transmission electron microscopy (TEM), electron diffraction, and EDX analysis studies were performed on the sample treated at 150 °C (Figure 3). The electron diffraction patterns presented sharp reflections that could be fully indexed assuming the *Fdd*2 space group of the precursor material, proving that the natrolite framework remained intact. EDX analysis of single grains unambiguously demonstrated the partial exchange of Cs^+ for Na^+.

Table 1. Analytical SEM/EDX Results and Unit Cell Volumes for the Samples after Exchange for 1 h at 1 GPa at Three Different Temperatures[a]

T (°C)	unit cell composition	% Cs^+	Cs/Na	*V* ($Å^3$)
60	$Na_{12.0}Cs_{1.6}Si_{24}Al_{14.0}O_{80}$	12.0	0.14	2244(1)
100	$Na_{11.4}Cs_{2.5}Si_{24}Al_{14.4}O_{80}$	17.9	0.22	2239(1)
150	$Na_{8.3}Cs_{9.0}Si_{24}Al_{14.9}O_{80}$	52.2	1.12	2263(2)
60	$Na_{10.4}Cs_{0.6}Si_{24}Ga_{19.4}O_{80}$	5.4	0.06	2304(1)
100	$Na_{9.2}Cs_{3.5}Si_{24}Ga_{19.2}O_{80}$	27.6	0.38	2303(1)
150	$Na_{0.1}Cs_{15.1}Si_{24}Ga_{18.3}O_{80}$	99.3	137	–

[a] Estimated errors are ±2 atom %. The volume for the last gallosilicate sample could not be determined because of interference from the impurity peaks.

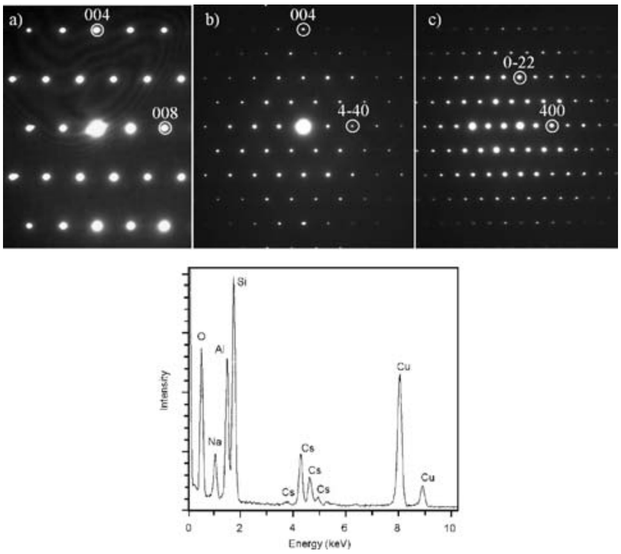

Figure 3. (top) Zone-axis electron diffraction patterns along the (a) ⟨100⟩, (b) ⟨110⟩, and (c) ⟨011⟩ directions of a crystal of natrolite treated for 1 h at 150 °C. (bottom) EDX spectrum from the same grain (Cu is from the grid).

A second series of exchange experiments was carried out at 100 °C for the aluminosilicate material for different lengths of time (Figure 4). It was not clear whether the level of exchange

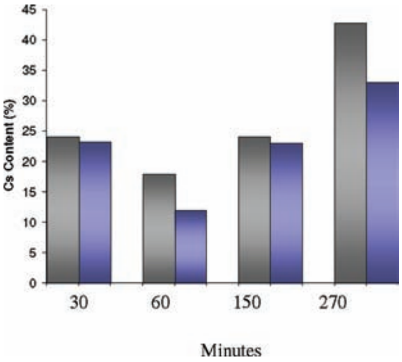

Figure 4. Levels of Cs$^+$ exchange for aluminosilicate natrolite as a function of time, as measured using SEM/EDX. The original level is shown in gray and that after attempted back-exchange with Na$^+$ in blue.

varied significantly between 30 and 150 min, but there is good evidence that it had increased after 270 min. PXRD was used to confirm the sample integrity. There were small changes in relative peak intensity and minor peak broadening that were more noticeable after the 270 min treatment, consistent with greater exchange. Investigation of back-exchange reactions confirmed that only minor amounts of Cs were lost after 24 h of reflux in a concentrated NaCl solution and that the unit cell volumes did not return to the starting values.

Our results constitute the first use of high pressure to effect an ion exchange process in a microporous material. We chose conditions for which the zeolite pores are in an expanded state because of the pressure-induced superhydration phenomenon. The large Cs$^+$ cations entered and were trapped inside the zeolite cages upon decompression, and any back-exchange reactions were greatly inhibited or even completely suppressed in the recovered materials at ambient pressure. Subsequent work will investigate means to optimize the process and determine whether the structures of the pressure-exchanged samples (particularly the cation siting) are the same as that found in Cs$^+$-substituted natrolite produced in stages via an intermediate K$^+$ form.[11] The unique high-pressure processing we demonstrate here could be applied to produce forms of zeolites containing unusual cations or systems that are more resistant to cation leaching and could be used, for example, to immobilize radionuclides. We believe that similar behavior should also occur for other small-pore systems that can be structurally modified by high-pressure treatment to increase pore sizes and/or water mobility.

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(16) Orthorhombic gallosilicate natrolite was synthesized as described by Hong et al.[17,18] The aluminosilicate natrolite came from natural sources as a finely powdered single crystal. A cylindrical Teflon capsule (6 × 10 mm) was loaded with 30−50 mg of natrolite and 3−4 drops of saturated CsCl solution. Care was taken to ensure that the capsules were completely filled with solution, as any air bubbles would have led to failure upon compression. The capsules were then placed in a non-end-loaded piston-cylinder press (Depths of the Earth Company, Cave Creek, AZ). Use of a NaCl pressure-transmitting medium gave actual sample pressures ~10% lower than nominally measured. The pressure was then increased to 1 GPa, and heat was applied using a graphite resistance furnace. Temperatures were measured to within ± 5 °C using a C-type thermocouple located ~1.5 mm from the sample. Runs were performed at 60, 100, and 150 °C for both natrolites. Capsules were held at temperature and pressure for 0.5−4.5 h and then quenched isobarically. The samples were retrieved from the Teflon capsules, washed thoroughly in deionized water, and dried in a desiccator for 48 h. Back-exchange of samples was performed by reflux in a NaCl solution (5 M, 250 mL) over 24 h. PXRD analysis was carried out using a Bruker D5000 diffractometer, and SEM/EDX was performed using a JEOL 6060 or Philips XL30 microscope. Unit cell compositions were calculated assuming 24 Si and 80 O atoms, and the amounts of Cs, Na, and Al were determined relative to the amount of Si.
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