Chabazite Structures with Li^+ , Na^+ , Ag^+ , K^+ , NH_4^+ , Rb^+ and Cs^+ as Extra-framework Cations

Mihye Kong,¹ Zhenxian Liu,² Thomas Vogt,^{3,4} Yongjae Lee^{1, *}

¹Department of Earth System Sciences, Yonsei University, Seoul 120-749, Korea

²Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington DC 20015, U.S.A

³Department of Chemistry and Biochemistry & NanoCenter, University of South Carolina, Columbia, SC 29208, U.S.A

⁴Bragg Institute, Australian Science and Technology Organization, PMB 1, Menai, NSW 2234, Australia

ABSTRACT

Chabazites with Li^+ , Na^+ , Ag^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ as monovalent extra-framework cations have been prepared from natural chabazite (ORI-CHA, $\text{Ca}_{1.6}\text{Na}_{0.5}\text{Si}_{8.4}\text{Al}_{3.6}\text{O}_{24}\cdot 14.3\text{H}_2\text{O}$) and characterized using a combination of Rietveld analyses of high-resolution synchrotron X-ray powder diffraction data and synchrotron infrared (IR) spectroscopy. All monovalent cation-exchanged chabazites crystallize in the rhombohedral space group $\text{R}\bar{3}\text{m}$; Li-CHA ($\text{Li}_{2.9}\text{Si}_{8.6}\text{Al}_{3.4}\text{O}_{24}\cdot 13.2\text{H}_2\text{O}$), $a=9.4068(6)$, $\alpha=94.9156(9)$; Na-CHA ($\text{Na}_{3.4}\text{Si}_{8.6}\text{Al}_{3.4}\text{O}_{24}\cdot 11.4\text{H}_2\text{O}$), $a=9.4216(3)$, $\alpha=94.0773(6)$; Ag-CHA ($\text{Ag}_{3.5}\text{Si}_{8.5}\text{Al}_{3.5}\text{O}_{24}\cdot 15.9\text{H}_2\text{O}$), $a=9.4402(4)$, $\alpha=94.1354(9)$; K-CHA ($\text{K}_{3.2}\text{Si}_{8.7}\text{Al}_{3.3}\text{O}_{24}\cdot 10.7\text{H}_2\text{O}$), $a=9.4420(1)$, $\alpha=94.2540(3)$; NH_4 -CHA ($(\text{NH}_4)_{2.1}\text{Si}_{8.4}\text{Al}_{3.6}\text{O}_{24}\cdot 11.6\text{H}_2\text{O}$), $a=9.4378(9)$, $\alpha=94.6101(1)$; Rb-CHA ($\text{Rb}_{4.1}\text{Si}_{7.9}\text{Al}_{4.1}\text{O}_{24}\cdot 6.5\text{H}_2\text{O}$), $a=9.4318(4)$, $\alpha=94.533(1)$; Cs-CHA ($\text{Cs}_{3.4}\text{Si}_{8.6}\text{Al}_{3.4}\text{O}_{24}\cdot 6.4\text{H}_2\text{O}$), $a=9.4447(4)$, $\alpha=94.2604(8)$. We establish correlations between the unit-cell volume, extra-framework cation distribution, and cation selectivity in chabazites. We establish that the unit cell volume of monovalent-cation exchanged chabazites decreases

30 in the order of decreasing ion selectivity, based on the standard free hydration energies of
31 exchange i.e., $\text{Cs}^+ > \text{K}^+ > \text{Ag}^+ > \text{Rb}^+ > \text{Na}^+ > \text{Li}^+$ and not the cation size.

32

33 **Keywords:** Chabazite, monovalent cation exchange, Rietveld refinement

Introduction

Chabazite is one of the most ubiquitous natural zeolites and has excellent ion-exchange properties and a wide range of industrial and technological applications [1, 2, 3]. Natural chabazite is a mineral with variable composition (i.e. $\text{Ca}_{1.6}\text{Na}_{0.5}\text{Si}_{8.4}\text{Al}_{3.6}\text{O}_{24} \cdot 14.3\text{H}_2\text{O}$) and occurs predominantly in cavities of basaltic rocks [4, 5]. Its framework is built up of double six-membered rings (D6R) stacked in an ABC sequence and linked by tilted four-membered rings [6, 7]. The six-membered rings form the top and bottom of the D6R secondary building unit, whose geometry is approximately that of a hexagonal prism [8]. The framework contains large ellipsoidal cavities with approximate apertures of $6.7 \times 10 \text{ \AA}$ which are accessible through eight-membered rings [9]. The largest opening of the eight-membered ring has a dimension of $3.8 \times 3.8 \text{ \AA}$ and is located in the direction normal to the (001) crystal plane [3, 11]. Chabazites have rhombohedral symmetry (space group $R\bar{3}m$) with only one tetrahedral framework site; the Al/Si distribution in this site is disordered [12]. Exchangeable cations and water molecules in chabazite are located in various sites whose location and occupation depends on the cation [13]. Extra-framework cation and H_2O molecule positions in natural and cation-exchanged hydrated chabazites were proposed first by Alberti et al. [14] and Calligaris et al. [15] and more recently by Nakatsuka et al. [16] and Zema et al. [7] and are of interest for rationalizing their ion-exchange behavior [17] as well as molecular diffusion and associated sieving properties [18]. Chabazite has an ion-exchanged capacity (CEC) of approx. 3.81 meq/g [9, 19] and its cation selectivity sequence, based on the standard free energies of exchange, is $\text{Ti}^+ > \text{Cs}^+ > \text{K}^+ > \text{Ag}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{Pb}^{2+} > \text{Na}^+ = \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Li}^+$ [9, 10, 20].

In the present study, we report the structures of Li-, Na-, Ag-, K-, NH_4 -, Rb-, and Cs-chabazites as well as the natural form at ambient conditions and investigate the extra-framework cation occupancies in order to assess the role of the cation radius, ion-exchange selectivity and H_2O content.

Experimental Methods

A sample of a natural chabazite from Rubendorf, Bohemia was used in this work. The synthesis of Li-, Na-, Ag-, K-, NH₄-, Rb-, and Cs-exchanged chabazite followed the ion-exchange procedure described in detail by Lee et al. [21]. The structural water contents were derived from Rietveld refinements as outlined below.

Structural characterizations of the as-prepared cation-forms of chabazites at ambient conditions were performed at the wiggler beamline 5A at Pohang Accelerator Laboratory (PAL), Korea. The incident beam was monochromatized using a Si (111) double crystal monochromator and detuned by 30% to minimize the contamination by higher harmonics, in particular, the third-order reflection of silicon. An image plate detector (Mar345, Mar Research GmbH Co., Germany) was used in the transmission mode to collect data. The sample to detector distance was ca. 287 mm which gave us scattering angle coverage in 2θ up to ca. 40°. We measured with about 10 second exposure times. Powdered chabazite samples were packed into 0.30 mm quartz capillaries. The wavelength ($\lambda=0.6927(5)$ Å) and 2-dimensional position of the incident beam, sample to detector distance and detector tilt were determined using a LaB₆ standard (SRM 660).

The structural models were derived from a series of profile fitting procedures using the GSAS suite of programs [22]. The background was fitted with a Chebyshev polynomial with ≤ 24 coefficients, and the pseudo-Voigt profile function of Thompson et al. was used to model the observed Bragg peaks [23]. In order to reduce the number of parameters, isotropic displacement factors were refined by grouping the framework tetrahedral atoms, the framework oxygen atoms, and the extra-framework cations and water oxygen atoms, respectively. The Al/Si ratio in the TO₄ tetrahedra (T=Si, Al) was fixed according to the elemental analysis, which are in the range between 1.93 and 2.64 (Table 1). Geometrical soft-restraints on the T-O and O-O bond distances in the tetrahedra were applied: the distances between Si-O and Al-O were restrained to target values of 1.660 ± 0.001 Å, and the O-O distances to 2.710 ± 0.005 Å for the Si- and Al-tetrahedra. Extra-framework cations and H₂O molecules were located from difference Fourier maps. To model the H₂O molecule,

only the oxygen scattering factor was used. In the final stages of the refinements, the weights of the soft-restraints were reduced. This did not lead to any significant changes of the interatomic distances, and the convergence was achieved by refining simultaneously all background and profile parameters, scale factor, lattice constants, 2 θ -zero shift, the atomic positional and displacement parameters, the occupancy factors for the extra-framework cations and water oxygen atoms. The final refined parameters are summarized in Table 1, and selected bond distances and angles are listed in Table 2.

Synchrotron IR experiments were carried out at U2A beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The far-IR spectra were collected with a Bruker IFS 66v/S Fourier transform infrared (FTIR) spectrometer in combination with a custom-made vacuum microscope system equipped with a helium cooled Si bolometer detector (Infrared Laboratories) and a 3.5 μm thick Mylar beamsplitter. The mid-IR spectra were then collected in transmission mode with a Bruker Vertex 80v FTIR spectrometer and a Hyperion 2000 IR microscope with a nitrogen-cooled MCT detector at the U2A side station. The spectra were collected in the range of 100–700 cm^{-1} for the far-IR and 650–5000 cm^{-1} for the mid-IR. A spectral resolution of 4 cm^{-1} was applied to all measurements. In order to avoid saturated absorption of phonon vibrational bands, cation-exchanged chabazite samples were placed between the anvils of a diamond anvil cell and compressed to a few micrometers thickness.

Results and Discussion

Synchrotron X-ray powder diffraction data of Li-, Na-, Ag-, K-, NH_4 -, Rb-, Cs-exchanged chabazites (Li-CHA, Na-CHA, Ag-CHA, K-CHA, NH_4 -CHA, Rb-CHA and Cs-CHA, respectively) all have reflections which can be indexed by the rhombohedral space group $R\bar{3}m$ as observed in the natural form (Ca, Na-CHA, Figure 1). The seven different structural models of the ion-exchanged chabazites were derived using Rietveld refinements (Tables 1-2) and are depicted in Figure 4 and 5. The T-O mean distances vary between

1.647(3)-1.660(4) Å for seven different models, due to the site preference for Al³⁺ in the tetrahedral sites.

Infrared spectroscopy is a complementary tool for investigating chemical bonds in materials; in particular, it is extremely sensitive to hydrogen bonds. The infrared absorption spectra were acquired in the region of 100-4000 cm⁻¹. The strong infrared absorption bands between 820 and 1080 cm⁻¹ can be assigned to the antisymmetric stretching vibrations of the tetrahedral Si(Al)-O bonds while the symmetric stretching vibrations of the Si(Al)-O bonds fall in the range of 710-790 cm⁻¹ (Table 3). The libration bands of the water molecule around the *a*-axis lie at 620 cm⁻¹ and the bonds due to bending vibrations of the tetrahedral bonds are found in the range of 400-420 cm⁻¹ (Table 3 and Figure 3a). Bands of very strong antisymmetric and symmetric stretching vibrations of hydroxyl groups lie in the region between 3420 and 3700 cm⁻¹. The medium intensity H-O-H bending vibrations are found near 1610 cm⁻¹ in the infrared absorption spectrum and provide direct evidence that H₂O molecules exists in the crystal structure. In order to determine the number of possible hydrogen sites in the structures, peak-fitting was performed in the O-H stretching vibration region from 2000 to 5000 cm⁻¹ after baseline correction. All spectra can be fit well by five bands with two dominant bands between 3100 and 3600 cm⁻¹ indicating the number of possible hydrogen sites (Figure 3b).

The structural model of natural chabazite (Ca, Na-CHA) has a composition of Ca_{1.6}Na_{0.5}Si_{8.4}Al_{3.6}O₂₄·14.3H₂O and is described in a rhombohedral unit cell with *a*=9.4194(2) Å (Table 1). The cation sites found are the same as established by Alberti et al., Calligaris et al. and Nakatsuka et al (Figure 4). The C1 site is in the center of the D6R cage and has an octahedral coordination to six framework oxygen atoms [C1-O4=2.994(5) Å] and the lowest occupancy of 0.05(2) which corresponds 0.05(2) atoms per unit cell. The C2 site is located along the [111] axis in the large cage near a six-membered ring of the D6R cage. It is closely coordinated by three oxygens of the six-membered ring at 2.526(4) Å and loosely to the other three oxygens at distances of 3.07(1) Å. The C3 site is located along the [111] axis near the center of the large cage and has the highest occupancy of 0.29(3) which corresponds

0.58(6) atoms per unit cell amongst all cation sites. The C3 site is coordinated by 6 water molecules at short distances between 2.35(1) and 2.607(9) Å. The C4 site is near the eight-ring window and has distances of 3.02(2) Å to O2 and 3.02(3) Å to O3 (Figure 5). The H₂O molecules are located in the large cage (OW2, OW3, OW4, and OW5 site) and at the center of the eight-ring window (OW1 site).

In Li-CHA, our structural model results in a composition of Li_{2.9}Si_{8.6}Al_{3.4}O₂₄·13.2H₂O and a rhombohedral unit cell with $a=9.4068(5)$ Å (Table 1). This corresponds to a 0.7% smaller unit cell volume compared to natural Ca, Na-chabazite [i.e., 822.64(4) Å³ vs. 828.61(5) Å³] (Figure 2). Li cations are found in the C1, C2, C3, and C5a sites, at the center of the eight-ring window (Figure 4). The Li cations in the C2 site have the highest occupancy of 0.41(8) which corresponds 0.82(16) atoms per unit cell. The C5a site is located at the side of center of eight-ring window. The distance of the Li cations in the C1 site to the framework oxygens is 3.075(4) Å [Li1-O4], whereas from the C2 site Li has distances of 2.64(3) Å [Li2-O4] and 3.10(2) Å [Li2-O3] (Figure 5). The H₂O molecules are found in the same sites as in natural chabazite.

The structural refinement of Na-CHA converges to a composition of Na_{3.4}Si_{8.6}Al_{3.4}O₂₄·11.4H₂O and a rhombohedral unit cell with $a=9.4216(3)$ Å (Table 1). Na-CHA has a 0.1% larger unit cell volume compared to the natural Ca, Na-chabazite [i.e., 829.65(6) Å³ vs. 828.61(5) Å³] (Figure 2). As found by Alberti et al, four cation sites (C2, C3, C4, and C4a) and seven H₂O sites are occupied (Figure 4). The C1 site is empty in Na-CHA. It can only be occupied by small ions like Ca²⁺ and its occupancy is limited by electrostatic factors as pointed out in the literature (Calligaris et al., 1982). In natural chabazite, the Ca²⁺ ions are located in the C1 (occupancy of 0.05(2)), C2 (occupancy of 0.13(2)), C3 (occupancy of 0.29(3)) and C4 (occupancy of 0.11(1)) sites. Exchange of divalent calcium ions by monovalent sodium ions nearly quintuples the amount of cations found in the C2 site resulting in occupancy of 0.63(3) which corresponds 1.26(6) atoms per unit cell. This is most likely the result of reduced electrostatic repulsion. The disordered C4a site is about 1 Å away from the C4 site which has a low occupancy of 0.06(7) which

corresponds 0.72(9) atoms per unit cell. The H₂O site, OW7, is found only in Na-CHA and located along the [111] axis near the C2 site. The distance of the oxygen of OW7 to the C3 site is 2.393(6) Å (Figure 5).

In silver exchanged chabazite a 0.7% larger unit cell volume compared to the natural Ca, Na-chabazite is observed [i.e., 834.39(2) Å³ vs. 828.61(5) Å³] (Figure 2). The composition refined is Ag_{3.5}Si_{8.5}Al₃₅O₂₄·15.9H₂O and the material crystallizes in a rhombohedral unit cell with $a=9.4402(4)$ Å (Table 1). Ag-CHA differs from natural chabazite by the presence of both C2 and C4 sites and H₂O molecules in OW1a and OW2 (Figure 4). Ag⁺ cations are located along the ternary [111] axis in the large cage near a six-membered ring of the hexagonal prism. The distance to the nearest oxygen (Ag2-O4) is 2.610(6) Å. While the C3 site is empty in Ag-CHA, migration of Ag⁺ cations to the C3 site seems to be permitted via the six-membered ring after the loss of H₂O molecules (Figure 5).

In potassium exchanged chabazite a composition of K_{3.2}Si_{8.7}Al_{3.3}O₂₄·10.7H₂O is found and a rhombohedral unit cell with $a=9.4420(1)$ Å (Table 1), which represents a 0.7% unit cell volume expansion compared to natural Ca, Na-chabazite [i.e., 834.43(5) Å³ vs. 828.61(5) Å³] (Figure 2). The cations in K-CHA are all located in the C2 site (Figure 4). It is closely coordinated by three oxygens [K2-O4=2.795(5) Å] of the six-membered ring and to three further oxygens at larger distances [K2-O3=3.291(7) Å]. H₂O molecules (OW2) are found at a distance of 2.827(4) Å from the C2 site. The C3 site is too far away for any bonding interactions (Figure 5).

The ammonium exchanged chabazite has a composition of (NH₄)_{2.1}Si_{8.4}Al_{3.6}O₂₄·11.6H₂O and crystallizes in a rhombohedral unit cell with $a=9.4378(9)$ Å (Table 1) corresponding to a 0.4% larger unit cell volume compared to the natural Ca, Na-chabazite [i.e., 832.01(5) Å³ vs. 828.61(5) Å³] (Figure 2). The NH₄⁺ cation was found in the C2a site with occupancy of 0.99(7) which corresponds 1.98(14) atoms per unit cell (Figure 4) and only the nitrogen atom was refined. C2a shifted along the 3-fold axis with respect to C2 site as described by Alberti et al (1982). We note a lower NH₄⁺ content of ca. 2.1 compared to a theoretically possible NH₄⁺ content of 3.6. Additional ammonium ions are disordered

within the zeolite cavities at lower occupancies preventing their detection in difference Fourier maps. The H₂O molecules are located in the OW1, OW1a, OW3, OW4, and OW5a sites. These sites differ from the ones proposed by [24].

The refinement of rubidium exchanged chabazite results in a composition of Rb_{4.1}Si_{7.9}Al_{4.1}O₂₄ 6.5H₂O and a rhombohedral unit cell with $a = 9.4318(4)$ Å (Table 1) which amounts to a 0.3% larger unit cell volume compared to the natural Ca, Na-chabazite [i.e., 830.73(1) Å³ vs. 828.61(5) Å³] (Figure 2). Most of the Rb⁺ cations are located in the C5 site, at the center of the eight-ring window (0, 1/2, 1/2), which is almost fully occupied (Figure 4) and coordinated by framework oxygens of the eight-ring window [Rb5-O1=3.43(1) Å and Rb5-O3=3.121(9) Å]. The other Rb⁺ ions are found to be in the same C2a site as occupied in NH₄-CHA with a distance to O3 of 3.41(1) Å (Figure 5). The H₂O molecules are located in OW2 and OW5 sites.

Sedimentary chabazite is very selective for Cs⁺ exchange and the location of Cs⁺ cations and H₂O molecules is important for modeling studies addressing the long-term stability of radioactive waste [25]. The cesium exchanged chabazite has a composition of Cs_{3.4}Si_{8.6}Al_{3.4}O₂₄ 6.4H₂O and a rhombohedral unit cell with $a = 9.4447(4)$ Å (Table 1) which corresponds to a 0.8% larger unit cell volume compared to the natural Ca, Na-chabazite [i.e., 835.15(6) Å³ vs. 828.61(5) Å³] (Figure 2). Cs-CHA has two cation and two H₂O sites. Cs⁺ cations are located primarily in the C5 site, at the center of the eight-ring window which is almost fully occupied. The remaining Cs⁺ cations are located in the C2a site along the [111] direction (Figure 4). The C1, C3, and C4 sites are empty. The Cs⁺ ions at site C5 are coordinated by four oxygen atoms O1, O1', O3, O3' of the eight-ring window [Cs5-O1=3.22(1) Å and Cs5-O3=3.29(1) Å] and two H₂O molecules OW2 and OW5a [Cs5-OW2=3.480(2) Å and Cs5-OW5a=3.18(3) Å]. Cs⁺ cations at the C2a site are 2.80(1) and 3.35(2) Å away from the O4 and O3 oxygen atoms of the six-membered ring, respectively (Figure 5).

Unit cell volumes of chabazites with different extra-framework cation vary by less than 1 % (Figure 1) and all Cs⁺, Rb⁺, K⁺ and Ag⁺ ions are located in the chabazite cage

because the double six-membered ring of chabazite are empty after replacing Ca^{2+} and Na^{+} ion in natural chabazite with larger ions (Figure 6). Unit cell volumes decrease as follows: $\text{Cs}^{+} > \text{K}^{+} > \text{Ag}^{+} > \text{Rb}^{+} > \text{Na}^{+} > \text{Li}^{+}$. This matches the cation selectivity originally established by Barrer et al (Figure 2) and points to the importance of the cation hydration energies (Sherry, 1979). Ab initio studies on the cation selectivity in alkali-exchanged chabazites confirm $\text{K} > \text{Na} > \text{Li}$ and the site preferences we observed [26].

Conclusion

We have demonstrated that the crystal chemistry of chabazite can be extended to larger monovalent cations and the occupancy of extra-framework cation sites varies depending on the cation. The extent of the volume expansion or reduction observed as the cation varies reveals lower values than those reported for natrolites. The chabazite framework is a rigid aluminosilicate structure with 3-dimensional channels and its medium Si/Al ratio favors cation exchange by monovalent cations or divalent ones with low hydration energies. The variation of the unit cell volume in monovalent-cation exchanged chabazites and the cation selectivity sequence allows for tailored molecular absorption and sieving as well as the immobilization of toxic and environmentally undesirable metals and complexes (i.e. NH_4^{+}) or radionuclides (i.e. $^{137}\text{Cs}^{+}$).

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Figure Captions

Figure 1. Synchrotron X-ray powder diffraction patterns of Li-CHA, Na-CHA, Ag-CHA, K-CHA, NH₄-CHA, Rb-CHA, and Cs-CHA. Miller indices are shown for selected Bragg peaks. The wavelength used was 0.6927(5) Å.

Figure 2. (a) Unit cell volumes of natural chabazite and Li-, Na-, Ag-, K-, NH₄-, Rb-, and Cs-exchanged chabazites at ambient conditions. Estimated standard deviations (e. s. d.) are smaller than symbols. (b) Correlation between the unit cell volume of exchanged chabazites and the cation selectivity established by Barrer [20].

Figure 3. (a) Far-infrared absorption spectra from 100 to 500 cm⁻¹ and 500 to 4000 cm⁻¹ for Li-, Na-, K-, NH₄-, Rb-, Cs-exchanged chabazites. Bending O-Si(Al)-O (a), Libration of H₂O (b), Symmetric stretching Si(Al)-O (c), Antisymmetric stretching Si(Al)-O (d), Stretching TO₄ (e), Vibration NH₄⁺ (f), Bending H-O-H (g), Vibration NH₄⁺ (h), Antisymmetric and symmetric stretching vibration O-H (i). (b) IR spectra (2500 to 4000 cm⁻¹) peak fitting of Li-, Na-, K-, NH₄-, Rb-, Cs-exchanged chabazites.

Figure 4. Structural models of the hydrates phases at ambient conditions of (a) Li-CHA, (b) Na-CHA, (c) Ag-CHA, (d) K-CHA, (e) NH₄-CHA, (f) Rb-CHA, and (g) Cs-CHA, (h) Ca, Na-CHA, depicted along the ternary axis [111]. Opened circles represent known extra-framework cation sites, filled ones indicate newly established ones. Grey small ones are oxygen atoms of H₂O molecules. Grey stick bond, tetrahedron, illustrate a disordered distribution of Si (Al) atoms in the framework.

Figure 5. Cation positions along [100] in the hydrated phases at ambient conditions of (a) Li-CHA, (b) Na-CHA, (c) Ag-CHA, (d) K-CHA, (e) NH₄-CHA, (f) Rb-CHA, and (g) Cs-

320 CHA, (h) Ca, Na-CHA. Opened circles represent known extra-framework cation sites;
321 filled ones indicate newly established ones. Grey stick bond, tetrahedron, illustrate a
322 disordered distribution of Si (Al) atoms in the framework.

323

324 Figure 6. Cation selectivity and occupancy in secondary building units of monovalent
325 cation-exchanged chabazites. The first bar (yellow) represents the ionic radius and second
326 bar (red), third bar (blue) and forth bar (cyan) indicates the cation site occupancy per unit cell
327 in the secondary building units in chabazite, respectively.

Fig. 1

Fig. 2

Fig. 3

(a) Li-CHA

(b) Na-CHA

(c) Ag-CHA

(d) K-CHA

(e) NH₄-CHA

(f) Rb-CHA

(g) Cs-CHA

(h) ORI-CHA

Fig. 4

Fig. 5

Fig. 6

1 **Table 1.** Final refined atomic coordinates for the natural and Li-, Na-, Ag-, K-, NH₄-, Rb-, Cs-
 2 exchanged chabazites at ambient conditions.*

		Ca, Na-CHA	Li-CHA	Na-CHA	Ag-CHA	K-CHA	NH ₄ -CHA	Rb-CHA	Cs-CHA
Space group		R $\bar{3}$ m	R $\bar{3}$ m	R $\bar{3}$ m	R $\bar{3}$ m	R $\bar{3}$ m	R $\bar{3}$ m	R $\bar{3}$ m	R $\bar{3}$ m
R _{wp} (%), χ^2		3.92, 4.06	4.57, 3.73	5.91, 5.82	5.65, 7.45	4.92, 4.02	4.69, 3.75	2.34, 3.23	8.54, 15.97
Unit-cell composition		Ca _{1.6} Na _{0.5} Si _{8.4} Al _{3.6} O ₂₄	Li _{2.9} Si _{8.6} Al _{3.4} O ₂₄	Na _{3.4} Si _{8.6} Al _{3.4} O ₂₄	Ag _{3.5} Si _{8.5} Al _{3.5} O ₂₄	K _{3.2} Si _{8.7} Al _{3.3} O ₂₄	(NH ₄) _{2.1} Si _{8.4} Al _{3.6} O ₂₄	Rb _{4.1} Si _{7.9} Al _{4.1} O ₂₄	Cs _{3.4} Si _{8.6} Al _{3.4} O ₂₄
†		×14.3H ₂ O	×13.2H ₂ O	×11.4H ₂ O	×15.9H ₂ O	×10.7H ₂ O	×11.6H ₂ O	×6.5H ₂ O	×6.4H ₂ O
Cell parameters (Å)	a	9.419(1)	9.4068(6)	9.4216(3)	9.4402(4)	9.4420(1)	9.4378(9)	9.4318(4)	9.4447(4)
Cell volume (Å ³)	α (°)	94.2104(2)	94.9156(9)	94.0773(6)	94.1354(9)	94.2540(3)	94.6101(1)	94.533(1)	94.2604(8)
	V	828.61(5)	822.64(4)	829.65(6)	834.39(2)	834.43(5)	832.01(5)	830.73(1)	835.2(1)
T	x	0.1037(6)	0.1072(5)	0.1031(2)	0.1047(7)	0.1036(1)	0.1054(6)	0.1065(3)	0.1007(1)
12i	y	0.3368(9)	0.3341(6)	0.3320(3)	0.3359(3)	0.3348(1)	0.3355(7)	0.3336(7)	0.3329(4)
	z	0.8776(8)	0.8800(6)	0.8772(2)	0.8789(4)	0.8767(1)	0.8783(7)	0.8824(7)	0.8756(3)
	U _{iso}	0.014(1)	0.010(1)	0.0042(9)	0.0009(2)	0.0105(8)	0.0081(6)	0.008(1)	0.008(1)
O1	x	0.2584(4)	0.2570(4)	0.2642(5)	0.2548(8)	0.2617(4)	0.2597(4)	0.2523(8)	0.2710(8)
6f	y	-0.2584(4)	-0.2570(4)	-0.2642(5)	-0.2548(8)	-0.2617(4)	-0.2597(4)	-0.2523(8)	-0.2710(8)
	z	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	U _{iso}	0.019(1)	0.023(1)	0.0240(1)	0.0850(4)	0.0183(4)	0.0234(2)	0.013(1)	0.0045(5)
O2	x	0.1588(4)	0.1535(1)	0.1504(5)	0.1574(7)	0.1552(4)	0.1568(2)	0.1515(6)	0.1512(7)
6g	y	-0.1588(4)	-0.1535(1)	-0.1504(5)	-0.1574(7)	-0.1552(4)	-0.1568(2)	-0.1515(6)	-0.1512(7)
	z	0.5(1)	0.5(1)	0.5(1)	0.5(1)	0.5(1)	0.5(1)	0.5(1)	0.5(1)
O3	x	0.2507(4)	0.2592(5)	0.2569(5)	0.2558(7)	0.2527(4)	0.2553(4)	0.2611(6)	0.2485(9)
6h	y	0.2507(4)	0.2592(5)	0.2569(5)	0.2558(7)	0.2527(4)	0.2553(4)	0.2611(6)	0.2485(9)
	z	0.8867(7)	0.8940(6)	0.8798(9)	0.8898(4)	0.8846(7)	0.8916(6)	0.8861(1)	0.8808(3)
O4	x	0.0307(4)	0.0317(4)	0.0317(5)	0.0357(6)	0.0281(5)	0.0312(4)	0.0358(5)	0.0285(8)
6h	y	0.0307(4)	0.0317(4)	0.0317(5)	0.0357(6)	0.0281(5)	0.0312(4)	0.0358(5)	0.0285(8)
	z	0.3196(6)	0.3295(5)	0.3149(7)	0.3338(0)	0.3191(6)	0.3271(5)	0.3150(8)	0.312(1)
C1	x	0.0000	0.0000				0.0000		
1a	y	0.0000	0.0000				0.0000		
	z	0.0000	0.0000				0.0000		
	f	0.052(1)	0.045(1)				0.149(1)		
	U _{iso}	0.014(1)	0.004(1)				0.0170(6)		
C2	x	0.1961(2)	0.2070(4)	0.2118(1)	0.2060(3)	0.2279(4)			
2c	y	0.1961(2)	0.2070(4)	0.2118(1)	0.2060(3)	0.2279(4)			
	z	0.1961(2)	0.2070(4)	0.2118(1)	0.2060(3)	0.2279(4)			
	f	0.132(1)	0.418(1)	0.633(1)	0.752(1)	0.925(1)			
	U _{iso}			0.0020(4)	0.080(1)	0.0331(1)			
C2a	x						0.2429(9)	0.2439(7)	0.2321(3)
2c	y						0.2429(9)	0.2439(7)	0.2321(3)
	z						0.2429(9)	0.2439(7)	0.2321(3)
	f						0.997(1)	0.575(1)	0.214(1)
	U _{iso}							0.075(1)	0.0932(7)

C3	x	0.413(1)	0.4550(4)	0.4626(4)		0.4550(4)		
2c	y	0.413(1)	0.4550(4)	0.4626(4)		0.4550(4)		
	z	0.413(1)	0.4550(4)	0.4626(4)		0.4550(4)		
	f	0.293(1)	0.378(1)	0.237(1)		0.078(1)		
C4	x	0.5381(9)		0.5630(4)	0.5516(6)	0.5375(5)		
6h	y	0.5381(9)		0.5630(4)	0.5516(6)	0.5375(5)		
	z	0.2281(1)		0.2210(4)	0.223(1)	0.2068(7)		
	f	0.111(1)		0.138(1)	0.325(1)	0.200(1)		
C4a	x			0.5(1)				
12i	y			0.565(1)				
	z			0.197(1)				
	f			0.068(1)				
C5	x					0.500(1)	0.0000	
3e	y					0.500(1)	0.500(1)	
	z					0.0000	0.500(1)	
	f					0.979(1)	0.981(1)	
C5a	x		0.4750(7)					
6h	y		0.4750(7)					
	z		0.0610(9)					
	f		0.214(1)					
OW1	x	0.500(1)	0.5(1)	0.500(1)		0.500(1)	0.500(1)	
3e	y	0.500(1)	0.5(1)	0.500(1)		0.500(1)	0.500(1)	
	z	0.0000	0.0000	0.0000		0.0000	0.0000	
	f	0.870(1)	0.890(1)	0.777(8)		0.850(1)	0.585(1)	
	U _{iso}	0.064(1)	0.074(1)	0.0030(5)		0.0270(5)	0.1180(6)	
OW1a	x				0.0485(7)	0.4980(5)	0.4950(3)	
12i	y				0.448(1)	0.4980(5)	0.4950(3)	
	z				0.561(1)	0.1010(5)	0.1256(2)	
	f				0.864(1)	0.156(1)	0.379(1)	
	U _{iso}				0.1320(7)	0.0270(5)		
OW2	x	0.2370(5)	0.2427(3)	0.2790(4)	0.3058(6)	0.2706(8)	0.2846(4)	0.2783(7)
6h	y	0.2370(5)	0.2427(3)	0.2790(4)	0.3058(6)	0.2706(8)	0.2846(4)	0.2783(7)
	z	0.2460(9)	0.301(1)	0.5120(6)	0.5202(1)	0.5280(4)	0.5361(3)	0.5032(5)
	f	0.411(1)	0.323(1)	0.196(1)	0.927(1)	0.418(1)	0.726(1)	0.5032(5)
	U _{iso}						0.028(1)	0.002(1)
OW3	x	0.2042(2)	0.2309(2)	0.239(1)		0.2180(4)	0.2445(1)	
12i	y	0.3172(9)	0.3156(1)	0.314(1)		0.3150(4)	0.3035(8)	
	z	0.5042(1)	0.5208(3)	0.491(1)		0.5210(5)	0.5124(5)	
	f	0.484(1)	0.374(1)	0.191(1)		0.214(1)	0.349(1)	
OW4	x	0.3573(9)	0.3608(1)	0.3602(2)		0.3068(5)	0.3777(4)	
6f	y	-0.3573(9)	-0.3608(2)	-0.3602(2)		-0.4189(9)	-0.3777(4)	
	z	0.500(1)	0.500(1)	0.500(1)		0.5020(4)	0.500(1)	
	f	0.303(1)	0.364(1)	0.211(1)		0.179(1)	0.219(1)	
OW5	x	0.585(1)	0.5255(6)	0.5790(7)			0.5398(3)	
6h	y	0.585(1)	0.5255(6)	0.5790(7)			0.5398(3)	
	z	0.2670(5)	0.214(1)	0.3110(9)			0.2790(4)	

	f	0.268(1)	0.347(1)	0.131(1)		0.356(1)
OW5a **	x				0.4720(6)	0.4264(1)
12i	y				0.4720(6)	0.5430(4)
	z				0.7129(3)	0.6728(9)
	f				0.352(1)	0.250(1)
OW6	x			0.3040(4)		
2c	y			0.3040(4)		
	z			0.3040(4)		
	f			0.260(1)		
OW7	x			0.4010(4)		
6h	y			0.4010(4)		
	z			0.2140(5)		
	f			0.192(1)		

* The e.s.d values are in parentheses. C1, C2, C2a, C3, C4, C4a, C5, and C5a denote respective extra-framework cation sites. Isotropic displacement factors (U_{iso}) were refined by grouping the framework tetrahedral atoms, the framework oxygen atoms and the extra-framework cations and oxygen atoms for the water molecules, respectively.

† The unit-cell compositions are normalized based on 24 framework oxygen atoms.

** Number of positions and point symmetry for the $\text{NH}_4\text{-CHA}$ is 6.

4 **Table 2.** Selected interatomic distances (Å) less than 3.0 Å and angles (°) for the natural and Li-, Na-,
5 Ag-, K-, NH₄-, Rb-, Cs-exchanged chabazites at ambient conditions *

	Ca, Na-CHA	Li-CHA	Na-CHA	Ag-CHA	K-CHA	NH ₄ -CHA	Rb-CHA	Cs-CHA
T-O1	1.6472(2)	1.6416(9)	1.6535(3)	1.6510(4)	1.6485(6)	1.6504(2)	1.6530(4)	1.6620(5)
T-O2	1.6540(3)	1.6478(2)	1.6572(6)	1.6602(8)	1.6553(3)	1.6562(2)	1.6559(2)	1.6575(6)
T-O3	1.6550(3)	1.6473(2)	1.6567(6)	1.6619(8)	1.6564(3)	1.6579(3)	1.6584(2)	1.6575(5)
T-O4	1.6562(5)	1.6502(4)	1.6595(8)	1.6605(9)	1.6557(5)	1.6591(4)	1.6557(0)	1.6615(6)
mean	1.6531(3)	1.6467(4)	1.6567(6)	1.6584(7)	1.6540(4)	1.6559(3)	1.6558(3)	1.6596(6)
O1-T-O2	109.59(3)	107.87(9)	107.08(9)	110.60(4)	108.37(4)	107.96(1)	109.60(4)	105.00(4)
O1-T-O3	106.65(7)	111.12(5)	109.10(4)	108.30(5)	108.22(8)	109.72(6)	108.40(4)	108.10(5)
O1-T-O4	111.59(8)	111.87(3)	114.50(5)	114.10(5)	112.02(1)	112.69(5)	110.80(4)	115.80(5)
O2-T-O3	104.44(7)	104.65(4)	102.87(9)	103.14(7)	104.31(6)	104.35(5)	102.77(7)	105.57(1)
O2-T-O4	117.28(9)	111.41(3)	113.10(4)	111.80(5)	115.0(1)	113.74(6)	115.50(4)	114.80(6)
O3-T-O4	106.46(3)	109.7(1)	109.5(1)	108.20(5)	108.47(4)	108.02(1)	109.24(3)	106.90(4)
mean	109.00(6)	109.43(5)	109.36(6)	109.36(5)	109.40(5)	109.41(4)	109.39(4)	109.36(4)
T-O1-T	152.00(4)	150.73(5)	144.20(5)	154.60(8)	148.20(4)	149.70(4)	154.1(8)	110.60(4)
T-O2-T	135.12(4)	140.84(2)	143.70(5)	136.50(6)	139.10(4)	137.55(3)	141.4(5)	142.40(8)
T-O3-T	152.80(4)	145.26(4)	144.60(5)	148.00(7)	150.00(4)	148.60(4)	143.2(5)	151.80(8)
T-O4-T	140.84(9)	145.33(8)	139.60(4)	140.10(5)	142.99(2)	143.50(9)	139.2(4)	139.40(5)
mean	145.19(5)	145.54(5)	143.03(5)	144.80(7)	145.07(3)	144.84(5)	144.48(5)	136.05(6)
C1-O4	2.9940(5)							
C1-C2	2.9550(3)							
C2-O4	2.5260(4)	2.6380(6)	2.6000(9)	2.6100(6)		2.9130(8)		
C2-C2a	0.6700(4)	0.9400(5)	2.8700(5)		2.8300(4)			
C2-OW2			2.7270(3)		2.8400(5)	2.5600(6)		
C2-OW3			1.4000(6)					
C2-OW6			2.4200(5)					
C2-OW7								
							2.8210(8)	2.8010(3)
							2.7450(2)	2.5640(5)
C2a-OW2								
	2.6190(9)	1.3300(3)	1.1300(7)		1.3600(3)			
C3-C3	2.492(1)		2.7300(4)		2.6740(9)			
C3-C4			2.7820(8)					
C3-C4a	2.6070(9)	2.9000(7)	2.4500(5)		2.5400(5)			
C3-OW2	2.350(1)	2.5400(4)	2.4930(5)		2.6500(5)			
C3-OW3	2.3650(9)	2.041(2)	2.0100(4)		1.9580(1)			
C3-OW4					2.3100(4)			
	2.7200(5)	2.541(2)	2.1800(8)					
C3-OW5			2.2500(8)					
C3-OW6			2.3900(6)					
C3-OW7			2.3900(6)					
C4-O2			2.9210(7)	2.9250(9)				

C4-O3			2.5900(5)	2.7970(3)	2.919(1)	
C4-C4a			0.6200(4)			
C4-OW1	2.1520(8)		2.1500(4)		1.9600(6)	
C4-OW1a				1.8640(6)		
				2.7000(9)		
C4-OW2			2.7800(4)	2.507(1)	2.630(1)	
				2.882(1)		
C4-OW3	2.0750(9)		2.4100(4)		2.1050(4)	
C4-OW4	1.5870(1)		1.6210(4)		1.0870(8)	
C4-OW5	0.6600(5)		0.850(1)		1.0600(5)	
			2.6500(5)		2.9000(5)	
C4-OW7			2.0700(7)			
C4a-O3			2.9070(6)			
C4a-C4a			0.8960(2)			
C4a-OW1			1.9130(5)			
C4a-OW2			2.863(1)			
			2.3060(2)			
C4a-OW3			1.9170(4)			
			2.4230(6)			
			2.8310(6)			
C4a-OW4			2.1060(4)			
			1.6450(6)			
C4a-OW5			1.2600(9)			
			2.5200(5)			
C4a-OW7			1.7700(5)			
C5-OW5a					2.6200(4)	
C5a-C5a	2.980(1)					
C5a-OW1	1.3800(4)					
C5a-OW3	0.6900(7)					
C5a-OW5	2.3200(6)					
	1.5100(9)					
OW1-OW1a	2.5800(8)					
OW1-OW3					1.194(1)	
OW1-OW4	2.6740(1)	2.8980(2)	2.9500(6)		2.8010(6)	
OW1-OW5					2.9390(5)	
OW1-OW5a	2.6300(4)	2.0000(9)			0.9600(5)	
OW1-OW7					2.6910(1)	
			2.4900(4)			
OW1a-O1				2.6500(6)		
OW1a-OW1a				1.5570(4)	1.9200(0)	2.3900(4)
				1.8040(5)		
				0.9110(2)		
OW1a-OW2				2.8930(9)		
OW1a-OW3					2.2130(6)	
OW1a-OW4					2.5730(9)	
OW1a-OW5a					1.5330(5)	

OW2-O4	2.8100(9)	2.7320(8)			
	2.8900(5)				
OW2-OW2	0.1200(9)	0.8030(5)	2.9630(7)		
OW2-OW3	2.5400(8)	2.141(1)	0.5540(9)	0.6770(8)	
	2.6010(1)	2.6210(5)	2.8600(5)		
	2.6400(7)	2.7950(9)			
OW2-OW4			2.3800(5)	2.9600(4)	
				2.2000(5)	
				2.7800(5)	
OW2-OW5			2.850(1)	2.7900(4)	2.6800(5)
OW2-OW5a					2.4090(8)
					1.7800(4)
OW2-OW6					2.8640(2)
OW2-OW7			2.0200(5)		
			1.7240(4)		
OW3-OW3	1.5600(1)	2.8450(1)	1.0380(3)	1.3400(5)	0.8200(5)
	2.5810(7)		2.4490(5)	2.8500(8)	2.898(1)
OW3-OW4	2.9740(2)	2.6610(2)	2.7360(1)	2.6100(5)	2.567(1)
	2.403(1)	2.1940(1)	2.3420(4)	1.9300(5)	2.2800(3)
				2.7100(5)	
				2.8000(6)	
OW3-OW5	2.5870(2)	1.9910(6)	2.5400(9)	2.1300(5)	
	2.8800(4)		2.5400(9)		
OW3-OW5a					2.1160(4)
					2.6850(8)
					2.853(1)
OW3-OW6			1.9070(2)		
OW3-OW7			1.2460(9)		
			2.0560(3)		
OW4-O2	2.7390(7)	2.8730(7)			
OW4-OW4	1.9700(6)	1.9300(7)	1.9300(4)	2.7000(6)	2.9400(8)
				1.0900(7)	1.7000(5)
				2.2460(4)	
				1.4500(6)	
OW4-OW5	1.3250(4)	1.7180(6)	2.8800(5)	2.0300(5)	
			1.0820(5)		
OW4-OW5a					2.6860(8)
					1.2430(8)
OW4-OW7			2.6300(5)		
OW5-O2	2.8360(6)				
OW5-O3	2.6900(5)				
OW5-OW5	2.6100(5)		2.1600(8)		2.5200(5)
OW5-OW7			2.3800(9)		
OW5a-OW5a				2.4900(4)	2.9600(4)
					1.8000(7)

1.6200(7)

1.4400(6)

OW6-OW7

1.5700(5)

* The e.s.d values are in parentheses. Restraints on the T-O and O-O bond distances have been applied. Standard deviations for the mean values computed using

$$\sigma = 1/n \left[\sum_{i=1}^n \sigma_i^2 \right]^{1/2}$$

7 **Table 3.** Assignments of vibrational bands in the natural and Li-, Na-, K-, NH₄-, Rb-, Cs-exchanged
8 chabazites at ambient conditions.

Name	Measured frequencies (cm ⁻¹)	Bond
a	420(4)	O-Si(Al)-O (bending)
b	620(4)	H ₂ O (libration)
c	780(4)	Si(Al)-O (stretching)
d	990(4)-1080(4)	Si(Al)-O (stretching)
e	1110(4)	TO ₄ (stretching)
f	1406(4) 1465(4)	NH ₄ ⁺ (vibration)
g	1610(4)	H-O-H (bending)
h	3131(4)	NH ₄ ⁺ (stretching)
i	3650(4)	O-H (stretching)