

The Rietveld structure refinement of an exceptionally pure sample of clinoptilolite from Ecuador and its Na-, K-, and Ca-exchanged forms

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Keywords: clinoptilolite, Ecuador, XRPD, synchrotron, Rietveld method

Abstract. The crystal structures of a highly pure, sedimentary clinoptilolite and the Na-, K-, and Ca-exchanged forms were refined by the Rietveld method using X-ray diffraction data collected with both conventional and synchrotron sources and different instrumental geometries. The refined structures showed that the clinoptilolite framework is not sensitive to cation exchange with Na⁺, K⁺ or Ca²⁺. The M1 extraframework cation site is occupied by Na, Ca, and Ba, M2 by Ca, M3 by K, and M4 by Mg. The M1 site occupancy significantly influences the configuration of extraframework water molecules.

Introduction

Clinoptilolite [HEU] is a monoclinic zeolite belonging to the group of tabular zeolites. The framework is built up out of (Si,Al)₁₀O₂₀ units arranged in sheets. The sheets are connected in the (010) plane to form a three-dimensional channel system consisting of A channels built up of flattened ten-membered rings and B channels formed by regular eight-membered rings running along the c-axis. The C channels are oriented along the a axis and consist of regular eight-membered rings [1-3]. Clinoptilolite is distinguished from heulandite by a framework Si/Al > 4.

Extraframework cation sites are situated on the (010) mirror plane (figure 1). Most sites can be occupied only partially, due to incompatibilities with other cation and water positions. The M1 site in cage II, formed by channel A and C, is preferentially occupied by Na and often also contains Ca. The M2 site in cage I, formed by channel B and C, usually contains Ca [1,4]. The M3 site near the centre of the eight-membered ring at the intersection of the A and C channel shows cation framework distances suitable for K. Mg is situated in the centre of the cage II (M4) coordinated only to H₂O molecules [5].

Few crystal structure refinements of very fine-grained (2-20 µm) natural sedimentary clinoptilolite are reported in the literature [6] due to the presence of inseparable sample impurities such as clay minerals and feldspars.

Here, a comparison is made between Rietveld crystal structures of natural, K-, Na-, and Ca-exchanged clinoptilolite refined from data collected at various conventional and synchrotron sources.

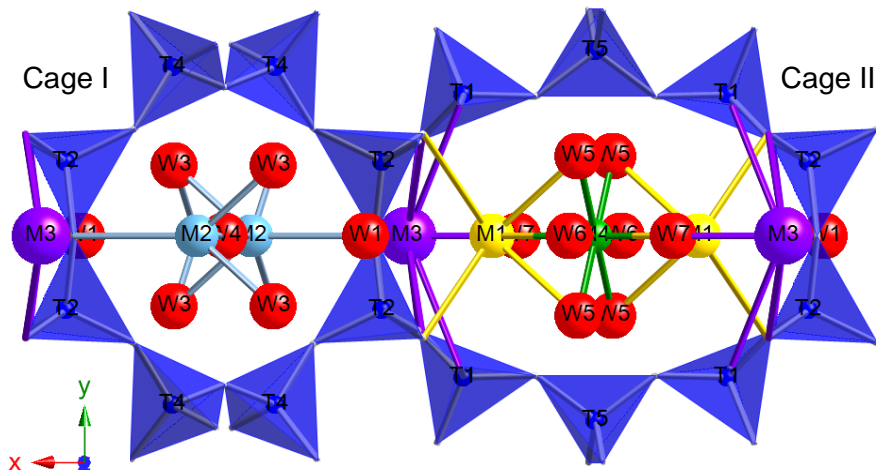


Figure 1. Overview of the clinoptilolite structure projected along the c^* -axis; extraframework cations and water molecules are shown in cage I, at the intersection of the B and C channel, and cage II, at the intersection of the A and C channel.

Experimental

The clinoptilolite studied here contains only ca. 1 wt% quartz as impurity. This specimen allowed for a direct structure refinement based on laboratory and synchrotron diffraction data. The sample was taken along the Rio Ayampe in the vicinity of the village of Guale and occurred as a series of white to greenish tuff layers situated within the volcanoclastic Cayo Formation (Ecuador) [7]. The clinoptilolite sample was exchanged to Na, Ca, and K by immersion in regularly renewed nearly saturated solutions of the corresponding acetates for 20 days at 333 K. The crystal chemistry was determined by X-ray Fluorescence (XRF) spectroscopy and thermal analysis (TG) on bulk samples. X-ray powder diffraction data were collected at lab sources for all samples, and at the synchrotron Italian beamline BM08 at ESRF for the natural and Na-exchanged samples. The in-house data were collected with a Philips PW 1830, Bragg-Brentano geometry, Cu $K\alpha$ radiation, and with a Panalytical X'Pert Pro diffractometer with a θ/θ geometry, Cu $K\alpha$ radiation, and a Real Time Multiple Strip (RTMS) detector.

Addition of NIST SRM 640 Si standard allowed the refinement of absolute lattice parameters. Structure models were taken from the literature [5,6]; atomic coordinates and population parameters were refined in the first stages, only Si was used as zeolite framework cation, finally thermal parameters were refined. Site occupancies were cross-checked with crystal chemistry. The Rietveld refinements were conducted with both EXPGUI-GSAS [8,9] and Topas Academic® [10] packages.

Table 1. Clinoptilolite crystal chemistry of natural and exchanged samples are reported and compared to the chemistry obtained from Rietveld structure refinements on X-ray diffraction patterns collected at different equipment and source types.

Sample Equipment	Extraframework cation and water content from XRF and TG based on Al _{7.10} Si _{28.90} O ₇₂ framework	Extraframework cation and water content from the Rietveld refinement based on Si ₃₆ O ₇₂ framework
Natural X'Pert		Na _{0.92} K _{1.28} Ca _{1.91} Ba _{0.04} Mg _{0.67} ·23.53H ₂ O
Natural PW1830	Na _{0.92} K _{1.31} Ca _{1.95} Ba _{0.05} Mg _{0.63} ·22.15H ₂ O	Na _{0.92} K _{1.25} Ca _{2.16} Ba _{0.07} Mg _{0.65} ·24.04H ₂ O
Natural ESRF BM08		Na _{0.92} K _{1.31} Ca _{1.97} Ba _{0.05} Mg _{0.61} ·23.25H ₂ O
Na exchanged X'Pert	Na _{3.97} K _{0.98} Ca _{0.91} Ba _{0.03} Mg _{0.41} ·23.29H ₂ O	Na _{3.11} K _{1.26} Ca _{1.51} Mg _{0.72} ·23.16H ₂ O
Na exchanged Ca exchanged X'Pert	Na _{0.60} K _{1.22} Ca _{2.00} Ba _{0.04} Mg _{0.61} ·23.13H ₂ O	Na _{0.64} K _{1.31} Ca _{2.36} Ba _{0.08} Mg _{0.67} ·24.23H ₂ O
K exchanged X'Pert	Na _{0.45} K _{4.39} Ca _{1.02} Ba _{0.02} Mg _{0.42} ·21.64H ₂ O	K _{4.38} Ca _{1.48} Mg _{0.58} ·20.48H ₂ O

Results

XRF results indicated that the cation exchange was not complete (table 1). Exchange of K and Mg cations was reported least successful [6], respectively owing to the high density of framework bonds (7) of K in M3, and to the large effective diameter of the water solvation sphere of Mg (M4) in clinoptilolite. The final residuals of the Rietveld refinements were situated between 0.01 and 0.07 for R_p, 0.02 and 0.10 for R_{wp}, and 0.04 and 0.08 for R(F²). Refined cell parameters, refinement statistics, framework and extraframework atomic coordinates, population and thermal parameters, bond distances, and T-O-T and O-T-O angles can be obtained from the authors upon request. In general, differences between refined models are modest compared to variability in structure models proposed in the literature.

The overall crystal chemistry determined from XRD showed very good agreement with XRF and TG bulk chemistry when a mixed occupancy of M1 by Na, Ca, and Ba was assumed (table 1). In the Na and K exchanged forms, incorporation of Na in M2 is suggested from comparison of crystal chemistry with population parameters. Diffraction experiments cannot differentiate between statistical and dynamical disorder in extraframework cation positions [11]. This resulted in relatively large thermal parameters, and in some cases, in a significantly wider spread of extraframework site fractional coordinates than expected from esd. (table 2).

Table 2. Space group, cell parameters, extraframework cation site coordinates, population and thermal parameters. The estimated standard deviation values are reported between parentheses.

Site	Natural X'Pert	Natural PW1830	Natural ESRF	Na X'Pert	Na ESRF	Ca X'Pert	K X'Pert
Space	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>
<i>a</i> (Å)	17.684(2)	17.684(2)	17.684(2)	17.684(2)	17.684(2)	17.664(2)	17.6879(12)
<i>b</i> (Å)	17.965(2)	17.965(2)	17.965(2)	17.957(2)	17.957(2)	17.932(2)	17.9503(13)
<i>c</i> (Å)	7.4124(7)	7.4124(7)	7.4124(7)	7.4134(5)	7.4134(5)	7.4045(7)	7.4143(4)
β (°)	116.335(7)	116.335(7)	116.335(7)	116.332(5)	116.332(5)	116.333(6)	116.330(4)
M1 (<i>y</i> =0)							
<i>x</i>	0.139(2)	0.128(2)	0.134(2)	0.130(2)	0.128(2)	0.137(2)	0.129(2)
<i>z</i>	0.657(5)	0.654(5)	0.645(4)	0.676(3)	0.680(4)	0.668(6)	0.671(5)
Occ. (Na)	0.23	0.23	0.23	0.78(2)	0.77(2)	0.16	
Occ. (Ca)	0.135	0.135	0.135			0.195(14)	
Occ. (Ba)	0.010(4)	0.015(3)	0.012(4)			0.016	
Occ. (K)							0.458(11)
U _{iso}	0.045(11)	0.056(11)	0.054(11)	0.095(10)	0.11(1)	0.082(14)	0.095(10)
M2 (<i>y</i> =0.5)							
<i>x</i>	0.037(2)	0.0314(13)	0.0315(14)	0.039(2)	0.032(2)	0.0326(14)	0.037(2)
<i>z</i>	0.197(4)	0.202(3)	0.208(3)	0.243(3)	0.230(4)	0.209(3)	0.235(4)
Occ. (Ca)	0.342(9)	0.405(7)	0.356(9)	0.377(8)	0.396(10)	0.394(9)	0.369(9)
U _{iso}	0.092(11)	0.063(8)	0.038(9)	0.062(10)	0.070(9)	0.064(9)	0.079(11)
M3 (<i>y</i> =0.5)							
<i>x</i>	0.246(2)	0.247(2)	0.240(2)	0.242(2)	0.238(2)	0.240(2)	0.238(5)
<i>z</i>	0.041(6)	0.052(4)	0.012(7)	0.037(5)	0.058(4)	0.046(4)	0.030(10)
Occ. (K)	0.32(2)	0.313(11)	0.33(2)	0.31(2)	0.34(2)	0.33(2)	0.36(6)
U _{iso}	0.084(13)	0.050(11)	0.072(14)	0.068(14)	0.065(11)	0.051(11)	0.087(13)
M4 (<i>x</i> , <i>y</i> =0; <i>z</i> =0.5)							
Occ. (Mg)	0.33(4)	0.32(2)	0.31(2)	0.36(3)	0.34(4)	0.34(4)	0.29(5)
U _{iso}	0.10(3)	0.09(3)	0.17(4)	0.15(3)	0.13(3)	0.16(4)	0.15(4)
							M3' (<i>y</i> =0)
<i>x</i>							0.314(8)
<i>z</i>							0.067(14)
Occ. (K)							0.27(6)
U _{iso}							0.11(2)

Discussion and conclusions

T-O distances indicate that some (Si,Al) ordering is present in the clinoptilolite framework. As concluded by previous workers [4,5,10], the Al content seems largest in the T2 tetrahedron, which bridges the T₁₀O₂₀ layers and is closely associated with M3. Here, the clinoptilolite framework was not found very sensitive to cation exchange.

In all refinements, the coordination sphere of M1 (~2.8 Å) was significantly larger than for M2 (~2.55 Å), with Ca residing in the site with smaller coordination distances [5].

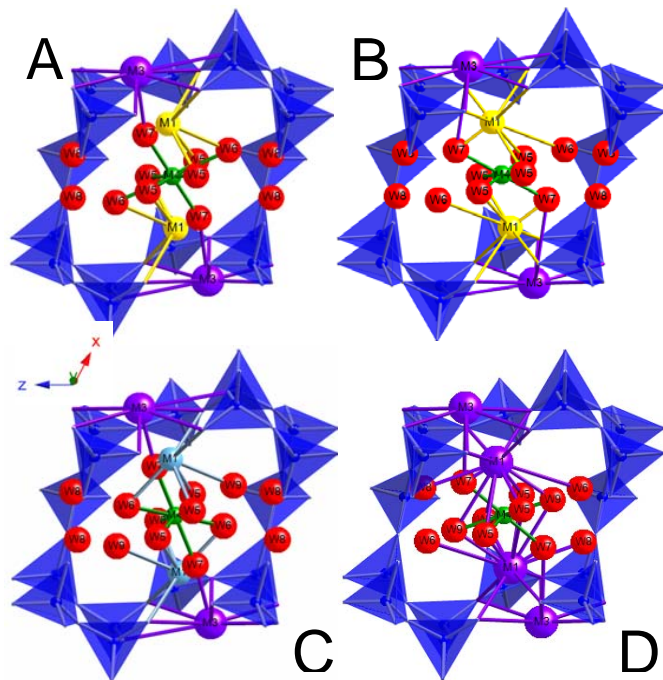


Figure 2. The influence of extraframework cation content on the extraframework configuration is shown. Different configurations of cage II extraframework cations (M1, M3, and M4) and water molecules (W5-W9) present in the natural clinoptilolite (A), Na-exchanged clinoptilolite (B), Ca-exchanged clinoptilolite (C), and K-exchanged clinoptilolite are depicted.

Higher occupancy of M1 in Na- and K-exchanged samples induced a positional shift towards the centre of cage I. Simultaneously, coordinating water molecules were situated at larger distances. The M3 site can be found at the intersection of the A and C channel (figure 2). This site is preferentially occupied by K, which fits into the rather large coordination sphere (3.1 Å). For K-exchanged clinoptilolite an additional M3' cation site, close to M3, was found and assigned to K. This M3' site was also previously reported for K-exchanged heulandite [12]. The Mg (M4) is six-fold coordinated by water molecules (W5, W6 or W9, and W7). Distortion of the ideal coordination is largest for Na- and K-exchanged samples.

All water molecule sites present, except W9, can be related to earlier studies, although a mixture of different published models fitted best the data. The W9 site has not been published elsewhere. This site can be seen as a split of the W6 site. W9 was introduced for the coordination of the larger extraframework cations in M1. It can also be coordinated to M4.

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