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Characterization of synthetic Cs-Li cancrinite grown in a butanediol-water system: An NMR spectroscopic and Rietveld refinement study

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ABSTRACT

A Cs-Li-analogue of cancrinite has been synthesized from tetraethoxysilane and Al sec-butoxide in a mixture of 1,3-butanediol and water. Cs and Li were introduced as hydroxides. Synthesis was done at autogeneous pressure and T = 473 K for 100 h. The synthesis product was characterized by powder X-ray diffraction, IR-spectroscopy, thermogravimetry, ^{1}H, ^{6}Li, ^{7}Li, ^{133}Cs, ^{27}Al, ^{29}Si MAS, and {^{1}H} ^{13}C CPMAS NMR and Rietveld structure refinement. ^{29}Si MAS NMR and ^{27}Al MAS NMR spectroscopy show a framework with strong alternating order of the SiO_4 and AlO_4 tetrahedra and an Si/Al ratio of one. ^{6}Li MAS NMR suggests the existence of two different signals that cannot be resolved in the ^{7}Li MAS NMR spectrum. ^{133}Cs MAS NMR shows only a single resonance. The thermogravimetric analysis reveals a continuous weight loss in several steps, indicating the evaporation of water of hydration. IR spectroscopy shows evidence for hydroxyl anions and water included in the cancrinite framework. The Rietveld structure refinement is consistent with a completely ordered alumosilicate framework with an Si/Al ratio of one and the presence of both molecular water and hydroxyl groups in the hexagonal channel, a result different from the previously published structure. Cs is exclusively located in the ε-cages; Li ions are located in the channels and are coordinated by water molecules.

INTRODUCTION

Cancrinite has the chemical formula $Na_6Ca[AlSiO_4]_6(CO_3)\cdot 2H_2O$ and a structure composed of layers of six-membered rings called the secondary building units (Meier and Olson 1992). Its structure in the hexagonal space group $P6_3$ is characterized by the periodic arrangement of the ε-cages forming an infinite one-dimensional twelve-membered ring channel with a diameter of 5.9 Å along the crystallographic c-axis (Meier and Olson 1992).

Synthetic analogues of cancrinite-group minerals have been prepared not only with carbonate (Barrer and White 1952) but also with other anions [e.g., selenate (Lindner et al. 1996) and nitrate (Barrer et al. 1970)]. An interesting fact is that the synthesis succeeds only in the presence of specific anions, preferably those with threefold symmetry. However, another approach is the use of a carefully selected combination of cations in which a large cation is combined with a small cation in the synthesis.

A well-studied combination of ions in synthesis is that of the large Cs cation with the small Li cation. Syntheses in aqueous solution at temperatures between 373 and 473 K were first done by Barrer and Sieber (1977) and later by Collela and de'Gennaro (1989). Reactants were pure Si and Al oxides, and Li and Cs hydroxides. The structure was characterized by Rietveld refinement using powder X-ray diffraction (XRD) data and chemical analysis (Norby et al. 1991), which showed that the Cs cations are located exclusively in the e-cages but the Li cations are in the channel. From the refined Si-O and Al-O distances (average 1.69 Å), they proposed that Al and Si were randomly distributed among the framework tetrahedra, although the ^{29}Si MAS NMR spectra showed only a single line. In addition, the refinement had unusually high displacement factors for the framework atoms, especially Si and Al, and the residuals $R(F^2)$, R_p, and R_{wp} were above or equal to 0.1.

We have synthesized the Cs-Li-analogue of cancrinite with another approach using a mixture of 1,3-butanediol with 50% by volume of water as a solvent. Tetraethoxysilane and Al sec-butoxide were used as silica and alumina sources, and Cs and Li hydroxides were used to introduce the cations. The synthesis product was extensively characterized by solid-state NMR spectroscopy and Rietveld refinement. We show from NMR spectroscopy that the aluminosilicate framework displays strong alternating Si/Al order, a pattern that is consistent with the structure refinement, which also suggests the presence of both molecular water and hydroxyl groups. The results differ from those of Norby et al. (1991) in these conclusions, but it should be noted that they followed a different synthetic approach starting from Al and Si oxide.

EXPERIMENTAL METHODS

Tetraethoxysilane (3.22 g, $C_8H_{20}O_4Si$, TEOS; FLUKA 86578) and Al sec-butoxide (3.82 g, $C_{12}H_{27}AlO_3$, FLUKA 06190) were stirred together with 10 mL deionized water and

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10 mL 1,3-butanediol [$C_4H_8(OH)_2$; FLUKA 18940]. Then 1.2 g Li hydroxide ($LiOH \cdot H_2O$, FLUKA 62531) and 3.5 g Cs hydroxide (CsOH, FLUKA 21000) were added. Hydrothermal synthesis of the Li-Cs cancrinite was done at a temperature of 473 K at autogeneous pressure in 50 mL Teflon-coated steel autoclaves under static conditions for 100 h. The product was washed with acetone to remove organic residues, rinsed with 500 mL deionized water, and dried overnight at 353 K. Figure 1 shows typical needle-like cancrinite crystals in bundles with grain sizes between 2 and 5 μm. Note also the presence of some amorphous material.

Infrared spectroscopy was done on a Bruker IFS66v/s FT IR spectrometer in order to obtain data about included anions, water molecules, and impurities such as carbon dioxide or adsorbed organic solvents. Two milligrams of the cancrinite were distributed in 200 mg of dry unground KBr (stored at 393 K in an oven). The mixture was transferred into a pellet press and after 5 minutes of evacuation, the pellet was pressed at 2 kbar for 5 minutes. The accumulation time of the IR spectrum was 60 seconds.

The NMR spectra were recorded on a Bruker AVANCE DSX 400 NMR spectrometer. ^{29}Si MAS NMR measurements were done using a self-built standard 14 mm MAS probe with a Chemagnetics stator at 79.49 MHz with a single pulse duration of 9 μs (90° pulse time was 18 μs) and a 120 s recycle delay. Tetramethylsilane was used as a reference standard and 1300 scans were accumulated at a spinning rate of 3 kHz. {^{1}H} ^{13}C CPMAS NMR experiments were carried out at a transmitter frequency of 100.63 MHz with a ^{1}H 90° pulse length of 6.5 μs, a contact time of 5.0 ms, and a recycle delay of 5 s using a standard Bruker 7 mm MAS probe at a rotation frequency of 3.5 kHz. Tetramethylsilane was used as a reference standard and 10000 scans were acquired. The ^{1}H and ^{27}Al MAS NMR spectra were obtained at 400.13 MHz and 104.26 MHz, respectively, using a standard 4 mm Bruker MAS probe. Typical conditions were pulse lengths of 0.6 μs [90° pulse time for aqueous $Al(NO_3)_3$ solution was 6.5 μs] and recycle delays of 5 s for ^{27}Al, and a 1.0 μs pulse length (90° pulse time was 5.3 μs) and a recycle delay of 5 s for ^{1}H. A total of 600 scans were accumulated at a MAS rotation frequency of 12 kHz for the ^{27}Al MAS NMR spectra and 120 scans for the ^{1}H MAS NMR spectra. A 1.0 *M* aqueous Al nitrate solution and tetramethylsilane were used as reference standards for ^{27}Al and ^{1}H, respectively. ^{6}Li and ^{7}Li MAS NMR spectra were recorded at transmitter frequencies of 58.88 and 155.50 MHz, respectively, using the same standard 4 mm Bruker MAS probe. The spectra were accumulated at a rotation frequency of 12 kHz with a pulse length of 0.6 μs (90° pulse time for aqueous LiCl solution was 4.3 μs for ^{7}Li and 11.7 μs for ^{6}Li) and recycle delays of 300 ms and 1 s, respectively. The total number of scans were 113 000 and 4700 scans, respectively. The reference standard for both nuclei was a 1 *M* LiCl solution. The ^{133}Cs MAS NMR spectrum was recorded at a transmitter frequency of 52.48 MHz with a pulselength of 1.0 μs (90° pulse time for aqueous CsCl solution was 13.2 μs), a rotation frequency of 12 kHz and a recycle delay of 500 ms. A total of 30 000 scans were accumulated, and a 1 *M* CsCl solution was used as reference standard.

Thermogravimetric analyses were performed between room temperature and 1273 K on a TA Instruments Inc., TA2000 thermal-analysis system equipped with a TG51 thermogravimetric analyzer. The heating rate was 10 K per minute. Coulometric titration of carbon was performed on a Deltronik DELTROMAT 500 electronic titrator with an integrated oxidation furnace.

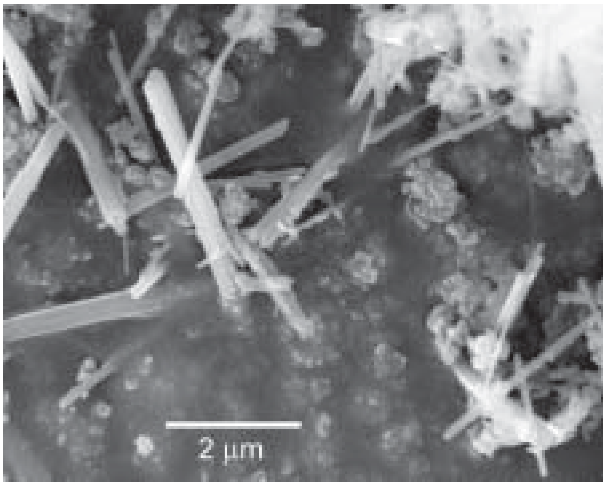

FIGURE 1. Scanning electron micrograph of synthetic Cs-Li cancrinite.

The powder XRD was recorded over the range of 5 to 90° 2θ with Cu*K*α radiation on a Siemens D5000 diffractometer equipped with a graphite-crystal monochromator in the diffracted beam, Soller slits in the incident and diffracted beam, 1.0 mm divergence and antiscatter slits, and a 0.2 mm receiving slit. A step interval of 0.02° 2θ and a counting time of 20 s/step was used. Samples were lightly pressed from the bottom of an Al sample holder against a ground glass slide; the cavity in the holder measured 43 × 24 × 1.5 mm. The textured surface of the glass minimized preferred orientation of anisotropic grains in the part of the powder that is in contact with the glass. In addition, the fine grain size (<2 μm) was helpful in minimizing preferred orientation. With a sample holder of 43 mm length and a 1.0 mm slit (0.5°), all of the sample is illuminated. In fact, the beam would not leave the sample until about 4.7° 2θ. Rietveld structure refinement was carried out with the PC-program GSAS, written by Larson and von Dreele (1985).

RESULTS AND DISCUSSION

X-ray powder diffraction and infrared spectroscopy

The powder XRD pattern (Fig. 2) shows only reflections resulting from cancrinite and is consistent with space group *P*6$_3$. The intensity distribution of the reflections is very similar to that of the powder XRD pattern of Norby et al. (1991). There are no indications of the presence of extraneous phases or amorphous materials.

The IR spectrum (Fig. 3) shows both asymmetric and symmetric T-O-T bending modes of the cancrinite framework (T = Si, Al) in the mid-infrared with three characteristic vibrations in the range between 500–800 cm^{-1} (Flanigen et al. 1971). The absorption band at 1680 cm^{-1} can be assigned to the bending mode of water molecules that are adsorbed in the cancrinite channel (Hackbarth et al. 1999). The band at 1410 cm^{-1} indi-

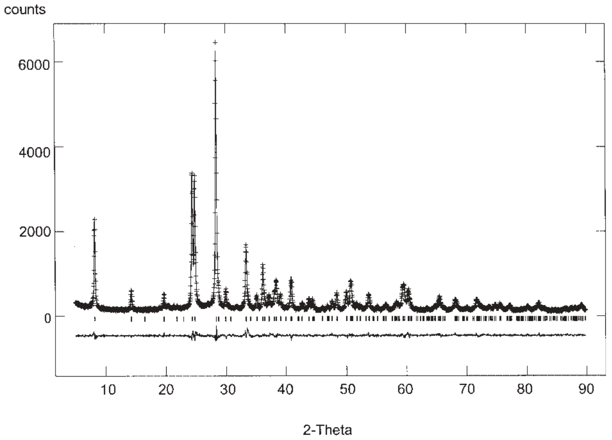

FIGURE 2. Powder XRD pattern of Cs-Li cancrinite at $T = 296$ K. The difference pattern of the Rietveld refinement and the Bragg reflection positions are also shown.

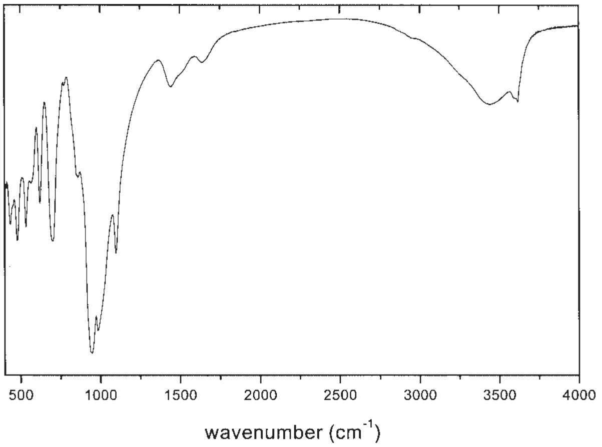

FIGURE 3. Infrared spectrum of the Cs-Li cancrinite.

cates enclathrated carbonate impurities. The C-content has been additionally checked by coulometric titration and equals 0.3 wt% C for the calcined sample (annealing of the cancrinite at 773 K for 5 days in a heated air-stream; normal content of a fully occupied carbonate cancrinite is 1.2 wt% C) and 1.3 wt% C for the “as-synthesized” sample. The higher content of the “as-synthesized” sample is due to the organic residuals from the reactants and the solvents, which is supported by ^{1}H and {^{1}H} ^{13}C CP MAS NMR spectroscopy as discussed below. Moreover, water shows resonances in the range of 2800–3800 cm^{-1}. Hydroxyl anions are thought to be the source of the observed stretching vibration at 3618 cm^{-1}. Surface-adsorbed residuals of the organic solvent and/or small amounts of amorphous material cause C-H valence vibrations at 2950–2850 cm^{-1} (Hesse et al. 1987) and the symmetric and asymmetric bending modes at 1300–1500 cm^{-1}.

Thermogravimetry

Thermogravimetric analysis of the Cs-Li cancrinite show a decreasing total weight loss with increasing reaction time as depicted in Figure 4. A three-stage loss in weight can be detected. The behavior is very similar to that of basic hydrosodalite studied by Felsche and Luger (1987). The first step, between 350 and 900 K, can be interpreted as the loss of water molecules located in the channel and the combustion of organic residuals. In contrast, carbonate cancrinite is already dehydrated at temperatures up to 700 K (Buhl 1991). The second step, between 973 and 1173 K, can be assigned to the decomposition and reaction of the hydroxyl anion, which produces half a water molecule and Cs-Li oxide. Above 973 K, the cancrinite decomposes to a nepheline-like phase. The weight loss of water is 8.04 wt% and the total weight loss is 9.04 wt%.

Nuclear magnetic resonance spectroscopy

The ^{29}Si MAS NMR spectrum shows mainly one narrow signal at –81.6 ppm (Fig. 5a) indicating that the framework consists of completely ordered SiO_4 and AlO_4 tetrahedra with an Si/Al ratio of one. Additionally, a broad background signal can be observed between –67 ppm and –92 ppm, which is thought to be due to amorphous material. Its relative signal intensity of ≈20% is overestimated due to the much shorter ^{29}Si relaxation time of the amorphous material in comparison to that of the crystalline compound. The small sharp signal at –40 ppm is due to a spinning sideband.

The ^{27}Al MAS NMR spectrum shows a signal at 62.8 ppm, which can be assigned to the tetrahedral framework Al atoms (Fig. 5b). Amorphous material is thought to contribute to a broadening of the base of the tetrahedral signal. The octahedral signal at 15.5 ppm is too sharp and symmetrical to be due to an amorphous phase and must result from an alumina phase or extra-framework Al. However, additional reflections are not present in the powder XRD pattern. The relative signal area is ≈8%, which is considerably lower than the signal intensity in the ^{29}Si MAS NMR spectrum.

The ^{1}H MAS NMR spectrum (Fig. 5c) shows a complex pattern of resonances with maxima at 5.3 ppm, 3.5 ppm, and 1.5 ppm. A signal shoulder can be observed at about 4.5 ppm. Organic residuals from incomplete hydrolysis of the reactants and the solvent are thought to be the source of the several resonances at 3.5 ppm and 1.5 ppm (methine, methylene, and methyl protons) (Hesse et al. 1987), and mask the signals of water and hydroxyl groups. After removal of the organic residuals by calcination, only two resonances remain in the ^{1}H MAS NMR

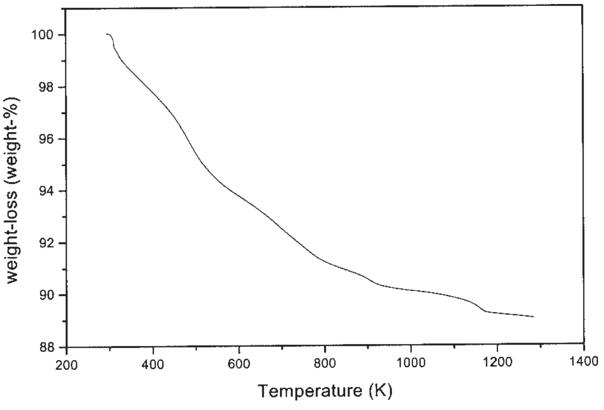

FIGURE 4. Thermogravimetric analysis of the Cs-Li cancrinite.

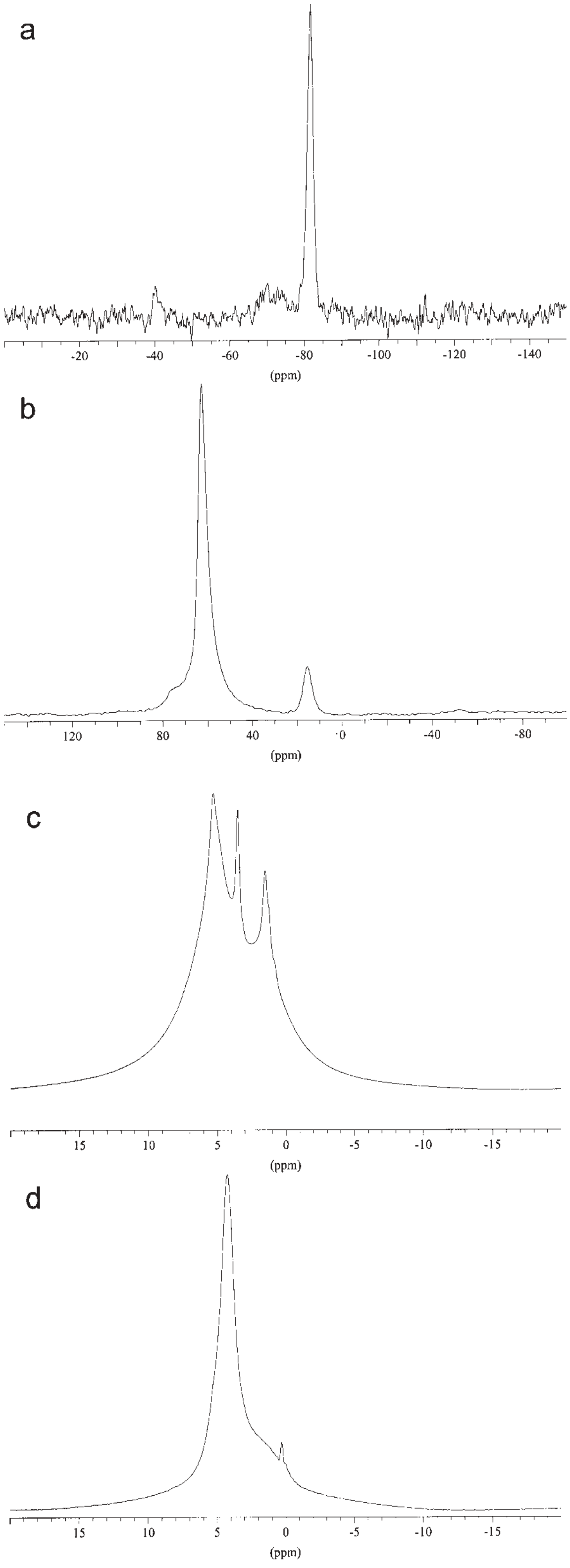

FIGURE 5. (**a**) ^{29}Si MAS NMR spectrum, (**b**) ^{27}Al MAS NMR spectrum, and (**c**) ^{1}H MAS NMR spectrum of the "as synthesized." (**d**) ^{1}H MAS NMR spectrum of the calcined Cs-Li cancrinite. The narrow signal contribution at 0 ppm is due to a transmitter breakthrough.

spectrum, as shown in Figure 5d. The narrow signal at 4.3 ppm can be attributed to hydroxyl groups whereas the water molecules localized in the channel cause the broad base in the signal with center of gravity at 3.4 ppm (Yesinowski et al. 1988).

The existence of residuals from incomplete hydrolysis of the reactant and the solvent is additionally supported by {^{1}H} ^{13}C CP MAS NMR spectroscopy. Figure 6a shows the spectrum of the "as-synthesized" cancrinite sample. The three resonances at 170 ppm, 62 ppm, and 29 ppm can be assigned to carbonate, methylene, and methyl-group carbon atoms, respectively. Only the carbonate signal remains in the spectrum of the calcined sample (Fig. 6b). The low intensity suggests that carbonate is present only as an impurity.

The ^{7}Li MAS NMR spectrum contains a single line at 0.0 ppm and the sideband intensity is strong (Fig. 7a). Sidebands from the outer spectral region are partially "folded back" and, characteristically, have wrong phasing. However, although different Li coordinations by water and hydroxyl anions in the channel are possible, there is no indication of any distinction between different crystallographic positions in the ^{7}Li MAS NMR spectrum. This is because the chemical shift ranges of both Li isotopes are very narrow and ^{7}Li ($I = 3/2$) suffers strong broadening from its strong quadrupolar interaction and the strong homonuclear dipolar coupling. The ^{6}Li isotope has a much lower natural abundance and a lower gyromagnetic ratio, but is much less affected by residual quadrupolar broadening. ^{6}Li is an $I = 1$ nucleus and shows lower quadrupolar interaction, and with magic angle spinning it is almost completely removed. The linewidth is much smaller and the separation of different Li signals from different sites is possible (Lee et al. 1998). The ^{6}Li MAS NMR spectrum shown in Figure 7b is a good example of the differences between the two isotopes. The spectrum appears to contain contributions from two similar, but distinct signals at 1.0 and 0.7 ppm, corresponding to different Li environments in the channel. The chemical shift indicates tetrahedral coordination by oxygen (Xu and Stebbins 1995).

The ^{133}Cs MAS NMR spectrum in Figure 8 shows a single line at 25.8 ppm. As with ^{6}Li, the $I = 7/2$ ^{133}Cs nucleus experiences little quadrupolar interaction. The small nuclear quadrupole moment, and the large chemical shift scale of ^{133}Cs make it possible that different sites could be well distinguished (Koller

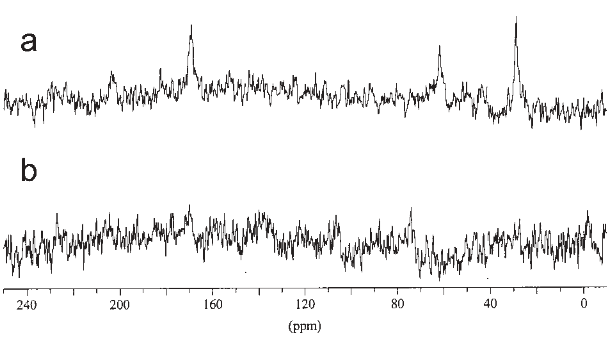

FIGURE 6. (**a**) {^{1}H} ^{13}C CP MAS NMR spectrum of the "as synthesized" and (**b**) of the calcined Cs-Li cancrinite.

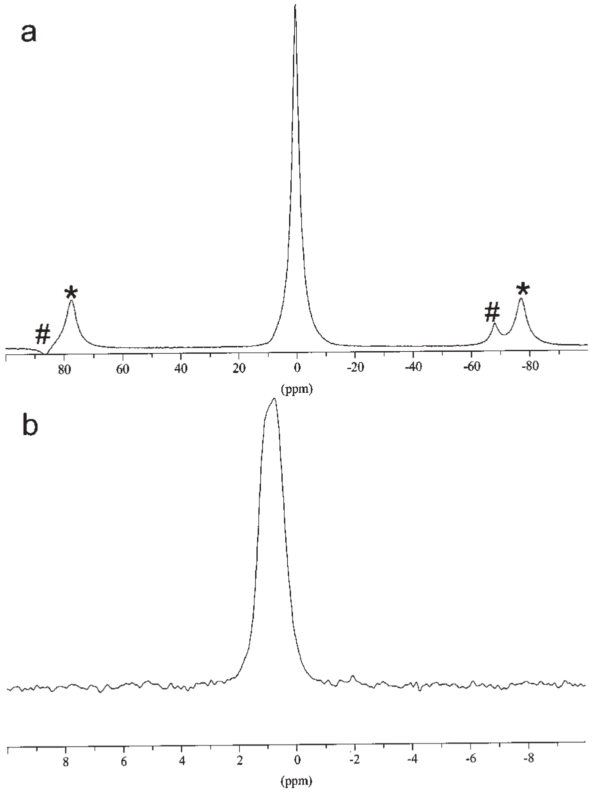

FIGURE 7. (**a**) ^{7}Li and (**b**) ^{6}Li MAS NMR spectrum of the Cs-Li cancrinite. Asterisks mark spinning sidebands. Number signs mark "folded back" spinning sidebands.

et al. 1995), if they were present. The observation of only a single resonance suggests the existence of a single crystallographic site.

Rietveld structure refinement

Because the ^{29}Si MAS NMR spectrum clearly indicates a strongly ordered alternating framework, a Rietveld refinement was carried out in order to compare the refined structure with that previously published (Norby et al. 1991). The GSAS program package of Larson and von Dreele (1985) was used.

Structure refinements for the cancrinite were performed in the hexagonal space group $P6_3$. As profile function, a Pseudovoigt function according to Howard (1982) and Thompson et al. (1987) was used. For the background, 57 fixed background points were used and, in addition, a linear interpolation function with 36 variable parameters was used in the Le Bail extraction mode. The Cs-Li cancrinite structure model of Norby et al. (1991) served as the starting model for the refinement with the difference that the two tetrahedral positions were occupied with Si and Al exclusively. The Si and Al positions were taken from the refinement of a basic cancrinite from Hassan and Grundy (1991). Restraints were set for the Si-O bond lengths (1.61 ± 0.05 Å), the Al-O bond lengths (1.72 ± 0.05 Å) and the O-T-O angles (T = Si, Al; 109.5 ± 1.0°). The restraint factor was decreased to 100 in the final cycles.

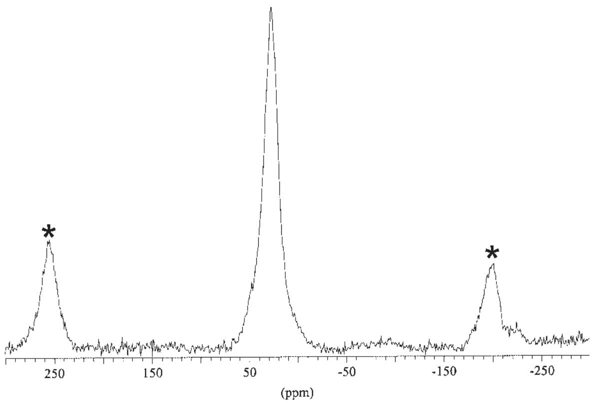

FIGURE 8. ^{133}Cs MAS NMR spectrum of the Cs-Li cancrinite. Asterisks mark spinning sidebands.

In the first few cycles, the framework atom positions were refined. The z-coordinate of Si1 was kept fixed. Subsequently the atomic positions of Cs, Li, and the water oxygen positions were refined. After several cycles, it turned out the algorithm shifted the Li ions toward the channel center, which makes little chemical and physical sense. Therefore the Li position and the water position were fixed on the previously determined positions (Norby et al. 1991). In the difference Fourier map, strong residual electron density could be observed on the 2a position at 0, 0, 0, and on a 6c position at 0.10, 0.18, 0.00. The implied presence of carbonate can be excluded by the distance of 1.94 Å between these positions (C-O distance in carbonate is 1.27–1.30 Å), which is too large to accommodate the covalent bonding that would be involved. The residual electron density suggests the existence of a hydroxyl anion oxygen atom position and a second water oxygen position as in the case of basic cancrinite described by Hassan and Grundy (1991). This finding is also in agreement with the results of IR spectroscopy (OH^- vibration at 3618 cm^{-1}, H_2O vibration at 1650 cm^{-1}, and 2800–3800 cm^{-1}), ^{1}H MAS NMR spectroscopy (narrow OH signal at 4.3 ppm, broad H_2O resonance at 3.4 ppm), and the thermogravimetric results. From this evidence for anions in the channel, the cation occupancies were first fixed to 1.0 and all atomic positions were refined. After that the occupancies of the water and hydroxyl oxygen positions were refined. The cancrinite structure cannot contain more than two hydroxyl anions per unit cell. Comparing the occupancies of the three oxygen sites in the channel it seems most likely that the 2a position can be assigned to the hydroxyl anion (OH1) and both other positions to water molecules [OH2(1) and OH2(2)]. The occupancy of the OH1 position was less than 1.0. From this result it can be concluded that the cation positions are also not fully occupied. Refinement of the Cs occupancy factor showed no deviation from 1.0. Because a separate refinement of the Li occupancy is not possible due to the low electron density of Li (2e$^-$ per cation) the occupancy was chemically restrained to be the same as the hydroxyl oxygen occupancy. Finally, the displacement factors were refined in separate cycles. The displacement factor of Li1 was fixed to $U_{\text{iso}} = 0.02$ for the same reasons that the occupancy factor was restrained. The refinement converged with $R_{wp} = 0.0729$, $R_p = 0.0561$ and $R(F^2) = 0.0359$. All crystal and experimental data are given in Table 1. The powder pattern, the Bragg positions, and the difference pattern are depicted in Figure 2. Atomic parameters are given in Table 2 and selected atomic distances and angles in Table 3[1]. Bond-valence summations around the framework Si and Al atoms, as well as the framework O atoms give values that are in good agreement with the theoretical values (Brown and Altermatt 1985; Brese and O'Keefe 1991). The bond-valence value of 1.22 v.u. for Li deviates from the theoretical value but this difference can be attributed to the difficulty of an exact determination of the Li atom parameters due to the very low electron density of the Li cation.

Our structure differs from that published by Norby et al. (1991), as shown in Figure 9, most importantly in the strong ordering of the tetrahedral framework atoms. The mean Si-O distance is 1.65 Å and the Al-O distance is 1.74 Å. The average tetrahedral O-T-O angle lies close to the ideal value of 109.5°. However, some of the angles are as low as 98° and others as high as 122°. There could be different reasons for this variation. First, the Cs cation that occupies the ε-cages has a large ionic radius and therefore the ε-cage is maximally expanded. This could also be the reason why water molecules, normally present in the ε-cage of cancrinite, are absent. Secondly, the large electron density difference between Li and Cs makes it difficult to refine the exact Li1 positions from the powder XRD data. It also influences the exact determination of the framework electron densities. Because of the possible tolerance between the calculated Li positions and the correct Li positions the algorithm tries to shift the framework O3 and O4 atoms toward the channel to fit the electron density defi-

TABLE 1. Crystal data and details of experimental powder X-ray diffraction and structure refinement

	Cs-Li cancrinite $Cs_2Li_{5.46}[AlSiO_4]_6(OH)_{1.48}\ (H_2O)_{7.8}$
Crystal data	
Crystal system	Hexagonal
Spacegroup	$P6_3$
Z	1
a_0	12.41595(24) Å
c_0	4.97019(14) Å
M	1170.33 g/mol
V	663.535(26) Å^3
T	296 K
ρ	2.929 g/cm^3
X-ray data collection	
2-Theta range:	$5° < 2θ < 90.0°$
Step width:	0.02
Rietveld refinement	
Contributing reflections	466
Parameters varied in final cycle	36
Δ/σ	<0.01
R_{wp}	0.0729
R_{exp}	0.0594
R_p	0.0561
$R(F^2)$	0.0359
DWd	1.340
χ^2	1.536
$\Delta\rho_{max}$	+0.44 e/Å^3
$\Delta\rho_{min}$	–0.60 e/Å^3

TABLE 3. Selected interatomic distances (Å) and angles (deg) for the Cs-Li cancrinite at T = 296 K

Atoms		Distance/Å	Atoms	Angle/deg
Si1-O1		1.64(1)	O1-Si1-O2	110(1)
Si1-O2		1.62(1)	O1-Si1-O3	104(1)
Si1-O3		1.66(2)	O1-Si1-O4	103(1)
Si1-O4		1.69(1)	O2-Si1-O3	120(1)
Average:		1.65	O2-Si1-O4	101(1)
			O3-Si1-O4	117(1)
			Average:	109
Al1-O1		1.73(1)	O1-Al1-O2	112(1)
Al1-O2		1.73(1)	O1-Al1-O3	106(1)
Al1-O3		1.76(2)	O1-Al1-O4	122(1)
Al1-O4		1.75(1)	O2-Al1-O3	98(1)
Average:		1.74	O2-Al1-O4	114(1)
			O3-Al1-O4	101(1)
			Average:	109
Cs1-O1	3×	3.646(9)		
Cs1-O2	3×	3.288(17)		
Cs1-O2	3×	3.316(15)		
Cs1-O3	3×	3.705(12)		
Cs1-O4	3×	3.482(12)		
Li1-O1		2.27(6)		
Li1-O3		2.14(6)		
Li1-O4		1.76(5)		
Li1-OH2(1)		2.03(4)		
Li1-OH2(2)		1.62(5)		
OH1-OH2(1)	3×	1.95(3)		
OH1-OH2(1)	3×	1.97(4)		
OH1-OH2(2)	3×	1.95(3)		

TABLE 2. Atomic parameters of Cs-Li cancrinite at T = 296 K

Atom	$P6_3$	Occupancy	x	y	z	U_{iso}
Cs1	2b	1.0	1/3	2/3	0.2723(22)	0.0316(9)
Li1	6c	0.91(2)	0.169(4)	0.3084(23)	0.246(14)	0.02*
Al1	6c	1.0	0.0812(10)	0.4090(9)	0.75†	0.002(1)‡
Si1	6c	1.0	0.3405(9)	0.4154(8)	0.7757(33)	0.002
O1	6c	1.0	0.2024(12)	0.3831(8)	0.6739(27)	0.007(1)‡
O2	6c	1.0	0.1311(7)	0.5663(14)	0.776(4)	0.007
O3	6c	1.0	0.0491(15)	0.3720(14)	0.0926(26)	0.007
O4	6c	1.0	0.3199(23)	0.3874(14)	0.1100(34)	0.007
OH2(1)	6c	0.81(1)	0.8909(18)	0.0229(18)	0.758(9)	0.045(6)‡
OH2(2)	6c	0.49(1)	0.0728(53)	0.1734(28)	0.118(5)	0.045
OH1	2a	0.74(2)	0	0	0.006(10)	0.018(7)

* Displacement parameter was kept fixed.
† Coordinate was kept fixed.
‡ Displacement parameters of Si1 and Al1, O1, O2, O3 and O4, OH2(1), and OH2(2) were restrained to be equal.

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[1] Further information of crystal structure refinement can be requested by Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen under CSD-No. 411487.

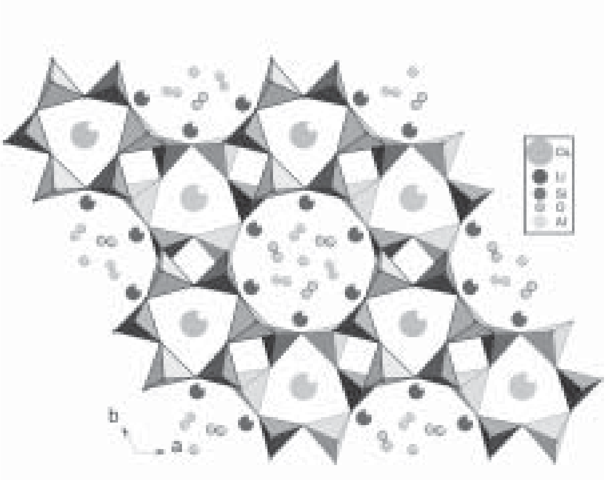

FIGURE 9. Hexagonal structure of the Cs-Li cancrinite as derived from the Rietveld refinement.

ciency. Nevertheless, the angles lie in the tolerance range to be a correct description of the structure. The low displacement factors of Si1, Al1, and O1-O4 are also a consequence of the large Cs cation radius, which induces absorption effects, and the correct determination of the framework atom electron densities of Si1 and Al1 and the O1-O4 atoms. Moreover, the presence of the large cation prevents the framework from executing large vibrations, because it is maximally expanded. A further substantial difference from the structure of Norby et al. (1991) is the presence of hydroxyl anions, which we assume to occupy the channel axis. On the other hand, the location of the hydroxyl anion deviates from the structural study of Hassan and Grundy (1991) who assigned one of the 6c positions in the channel to the hydroxyl anion. It should be noted that an exact assignment of the channel O positions to water or hydroxyl anions is not possible as the hydrogen positions cannot be determined. The total amount of water is 7.8 mol% H_2O, which is higher than the value of 5.58 mol% found by Norby et al. (1991). However, they also observed a second weight loss in the thermogravimetric analysis, which they assigned to the loss of additional cage water but was probably due to the decomposition of hydroxyl anions. Comparing the total calculated weight loss from our refined structure (12.3 wt% H_2O) with the result of the thermogravimetric analysis (9.04 wt% H_2O) indicates a higher value for the refined water molecule content. There may be several possible reasons for this difference: first, the channel positions are mainly occupied by water, but the hydrogen positions are not included in the refinement, which will yield too high an electron density for the remaining oxygen atoms and therefore overestimate the occupancies. Considering that the additional two electrons contribute to the O occupancy of the water molecules (OH2 positions), the correct occupancy factor can be calculated by multiplying the refined occupancy by 8/10. The calculated occupancy for OH2(1) is 0.65 for OH2(2) is 0.39, which yields a total occupancy of 1.04 for the OH2 positions. In this light, the two OH2 positions can be considered as partially occupied positions in the structure. In ≈60% of all cases OH2(2) is occupied and coordinates the Li cation, in the other 40%, the OH2(1) position is occupied. These results strongly correlate with the results from the ^{6}Li MAS NMR spectrum, which implies the contribution of two distinct, but similar signals for tetrahedrally coordinated Li. The Li cation is coordinated by three framework oxygen atoms (O1, O3, and O4) and by one water molecule [OH2(1) or OH2(2)]. Due to the two different bond distances [Li-OH2(1): 2.03 Å and Li-OH2(2): 1.62 Å], two signal contributions should originate. Calculating the water content with the corrected occupancies gives 9.8 wt%, which is in much better agreement with the TGA results (9.04 wt%). Moreover, the bond valence for Li (with the corrected occupancies) amounts 1.11 v.u. instead of 1.22 v.u. On the other hand, the high degree of motion of the water molecules induces a delocalization of O electron density in the channel. Thus, the refinement of the water positions and occupancies is difficult and probably overestimates occupancies. Finally, the IR spectroscopic results indicate the presence of carbonate impurities. The amount was too small to introduce these carbonate positions into the structure and to refine them. However, they contribute to the electron density and will also increase the calculated occupancies of the water O positions.

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