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MAS AND DOR NMR STUDY OF Al–Si ORDER IN THE ANALCIME–POLLUCITE SERIES

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ABSTRACT

Al–Si order in the analcime – pollucite series (ideally $NaAlSi_2O_6 \cdot H_2O$ – $CsAlSi_2O_6$) was studied using magic angle spinning (MAS) and double rotation (DOR) nuclear magnetic resonance (NMR). The ^{27}Al, ^{29}Si, ^{23}Na and ^{133}Cs NMR spectra of natural and synthetic samples show signs of increasing disorder from analcime to pollucite, but the synthetic phases may contain up to about 50 mol.% pollucite without a significant increase in disorder compared to end-member analcime. Cubic pollucite is the most disordered; however, complete disorder is not observed, even in rapidly formed, synthetic end-member pollucite. In the cubic framework, cations are not randomly distributed among tetrahedrally coordinated sites, but follow an Al–O–Al avoidance rule and probably also the extended Loewenstein rule. Analcime and cesian analcime show an increased degree of order with symmetry less than cubic, but remain incompletely ordered. The influence of Si/Al ratio on degree of order was demonstrated; with increasing Si/Al, intensity shifts in the ^{29}Si spectra from the Si(3Al) and Si(2Al) peaks to the Si(1Al) peak.

Keywords: analcime, pollucite, leucite, cesium, nuclear magnetic resonance, Al–Si order, zeolites.

SOMMAIRE

Nous avons étudié le degré d'ordre des atomes Al et Si dans les compositions de la série analcime – pollucite (en théorie, $NaAlSi_2O_6 \cdot H_2O$ – $CsAlSi_2O_6$) en utilisant la résonance magnétique nucléaire avec spinning à l'angle magique et avec rotation double. Les spectres des atomes ^{27}Al, ^{29}Si, ^{23}Na et ^{133}Cs d'échantillons naturels et synthétiques témoignent d'une augmentation du désordre en allant du pôle analcime vers le pôle pollucite. Par contre, les préparations synthétiques peuvent contenir jusqu'à environ 50% (base molaire) de pollucite sans perte importante du degré d'ordre qui caractérise l'analcime pure. La pollucite cubique est la plus désordonnée, sans pour autant être complètement désordonnée, même dans des cas de croissance rapide de cristaux synthétiques ayant la composition idéale. Dans la trame cubique, les cations Al et Si ne sont pas distribués de façon aléatoire parmi les sites, mais seraient plutôt régis par la règle voulant que les liaisons Al–O–Al ne sont pas favorisées, et probablement aussi par la règle généralisée de Loewenstein. Analcime et analcime césique font preuve d'un degré d'ordre plus élevé, avec une symétrie inférieure à cubique, mais ceux-ci demeurent incomplètement ordonnées. Nous documentons aussi l'influence exercée par le rapport Si/Al sur le degré d'ordre; à mesure que Si/Al augmente, l'intensité des pics Si(3Al) et Si(2Al) du spectre de ^{29}Si diminue, tandis que l'intensité du pic Si(1Al) augmente.

(Traduit par la Rédaction)

Mots-clés: analcime, pollucite, leucite, césium, résonance magnétique nucléaire, degré d'ordre Al–Si, zéolites.

INTRODUCTION

Members of the analcime – pollucite series are of petrogenetic interest as indicators of advanced fractionation in rare-element granitic pegmatites (Černý 1974, 1992). They are important as natural analogues of synthetic phases involved in long-term containment of ^{135}Cs and ^{137}Cs nuclear waste (Černý 1979, Taylor *et al.* 1989, Teertstra & Černý 1992). The degree of Al–Si order in structurally related synthetic phases and isomorphous minerals (particularly leucite) has been a topic of recent NMR studies (Lippmaa *et al.* 1981, Murdoch *et al.* 1988, Phillips *et al.* 1989, Kohn *et al.* 1991). However, the Cs-enriched members have not been investigated, and are a part of the present study.

The MAS NMR spectrum of tetragonal leucite (Phillips *et al.* 1989, Palmer *et al.* 1989) suggests a lower degree of Al–Si order than in analcime, with tetragonal or higher symmetry (Murdoch *et al.* 1988, Yoder & Weir 1960). In contrast, X-ray single-crystal refinements of the structure of leucite have not indicated any long-range Al–Si order (Mazzi *et al.* 1976).

Complete disorder is expected in the isotropic phases (such as pollucite), as random occupancy of the 48*g* tetrahedral sites is a requirement of cubic (*Ia*3*d*) symmetry. The degree of Al–Si order in the analcime–wairakite series has not been studied by NMR, but X-ray structure refinements of monoclinic wairakite indicate complete order of Al and Si (Takéuchi *et al.* 1979). Here, we investigate the variable degree of Al–Si order in analcime and pollucite, and the influence of Na–Cs substitution in intermediate members.

Crystal chemistry and structure

The aluminosilicate framework of analcime ($NaAlSi_2O_6{\cdot}H_2O$) is shared by wairakite ($Ca_{0.5}AlSi_2O_6{\cdot}H_2O$), leucite ($KAlSi_2O_6$), ammonioleucite ($NH_4AlSi_2O_6$) and pollucite ($CsAlSi_2O_6$), and is similar to that in other, rarer minerals (Galli *et al.* 1978). Two cation sites are available in the anionic framework: a 6-coordinated cavity around the 24*c* equipoint contains small cations such as Na^+ or Ca^{2+}, and an irregular 12-coordinated cavity around the 16*b* equipoint contains larger cations such as K^+, Cs^+ or NH_4^+, as well as molecular H_2O (Beger 1969). Wide ranges of chemistry are found among synthetic phases that are isomorphous with analcime and leucite (Bayer 1973, Torres-Martinez & West 1989). Considering these minerals as a group, we may study the various influences, such as crystal chemistry or thermal history, on degree of Al–Si order and the relationships to variable crystal symmetry.

The framework undergoes reversible, purely displacive phase-transformations with decreased temperature or increased pressure to better fit the site of the available cation [Roth *et al.* (1991); this is the "untwisting of collapsed frameworks" of Taylor & Henderson (1968), the "tetrahedral rotation" of Hirao *et al.* (1976) and the "polyhedral tilting" of Hazen & Finger (1979)]. These transformations result in decreased symmetry from cubic (*Ia*3*d*), to tetragonal ($I4_1/acd$ with both $a < c$ and $a > c$, to $I4_1/a$), orthorhombic (*Ibca*), monoclinic (*I*2/*a*) and triclinic (*I*1). However, the transformations are influenced by degree of Al–Si order (Peacor 1968, Palmer *et al.* 1989).

Lower symmetries than cubic also are favored by an increased strength of cation bonding with the framework. This promotes ordering of the extra-framework cation sites with the next-nearest-neighbor [AlO_4], as in wairakite (Takéuchi *et al.* 1979) or even analcime (Mazzi & Galli 1978).

Analcime is typically disordered and cubic (Gottardi & Alberti 1985) or partially ordered, with lower symmetry (Akizuki 1981, Murdoch *et al.* 1988), but has the potential to be highly ordered, as suggested by symmetries as low as triclinic (Hazen & Finger 1979). Mazzi & Galli (1978) showed that the symmetries of tetragonal and orthorhombic analcime arise from variable ordering of Al into crystallographically distinct tetrahedral sites, and from the related occupancies of the nearest Na site. However, in an X-ray-diffraction and neutron-diffraction structure refinement of monoclinic analcime, Pechar (1988) claimed a disordered (Al,Si) distribution.

An additional influence on degree of order may be variability in the Si/Al ratio, more typical of analcime (Edgar 1984), pollucite (Černý 1974) and ammonioleucite (Hori *et al.* 1986) than leucite or wairakite. One reason that Si/Al ratios are variable is because the tetrahedral 48*g* sites are topologically equivalent. Si/Al ratios near 2.0 are probably thermodynamically the most stable (Khundadze *et al.* 1970, Senderov & Khitarov 1971). $(Cs,Na)_{1.5}Al_{1.5}Si_{1.5}O_6$ was recently synthesized with a Si/Al ratio of 1.0 and a fully ordered analcime-type framework (Dimitrijevic *et al.* 1991). Si/Al ratios of synthetic analcime vary from 1.5 to 10 or more depending on the Si/Al ratio of the material from which it crystallized (Saha 1961, Haaker *et al.* 1985). If Si/Al is equal to 2.0, Al fills 16 out of the 48*g* sites in a unit cell based on 96 atoms of oxygen. In analcime, the 16 charge-balancing Na^+ atoms may be distributed among 24*c* sites. If Si/Al exceeds 2.0, Al fills less than 16 of the 48*g* sites. In this case, in pollucite the charge-balancing Cs^+ atoms have some choice among the 16*b* sites, which leads to a potential for ordering.

EXPERIMENTAL

Mineral samples

Mineral grains were hand-picked under a binocular microscope, and verified to be single-phase by X-ray powder diffraction. The homogeneity of the samples was established by electron microprobe (EMP) analysis; previous studies have indicated a widespread heterogeneity of sodian pollucite (Teertstra *et al.* 1992). Index of refraction (*n*) was determined in Cargille oils calibrated using a Spencer refractometer. Absolute quantities of H_2O were determined at 900°C in a Karl Fischer titration using a Mitsubishi moisture meter.

Analcime (sample PA–150) from the Sherritt Gordon Ni–Cu–Zn mine, Lynn Lake, northwestern Manitoba, consists of birefringent single crystals up to 5 mm across, with a trapezohedral morphology. The crystals selected are clear, colorless and homogeneous.

Cesian analcime (sample PA–122) from the Tanco pegmatite, southeastern Manitoba, consists of single crystals up to 1.5 cm across, with trapezohedral morphology. Associated minerals are described in Černý (1972). The crystals are birefringent, biaxial negative with a 2*V* of 85°, and twinned in radial sectors, possibly octants. The single crystal used in this study is clear, colourless and homogeneous.

Pollucite from near Norway, Maine (sample PA–031; University of Manitoba M–47) is gemmy, clear and colourless, and isotropic. The material used in this study is almost completely homogeneous, with the exception of rare thin (< 10 μm) veinlets of Cs-rich pollucite ± quartz. The veinlets comprise less than 1% of the material used and should not influence the NMR results.

Synthetic samples

Synthetic samples were crystallized hydrothermally from aluminosilicate gel in Teflon-lined Parr bombs at 200°C with autogenous pressure for 100 hours. Known amounts of anhydrous sodium metasilicate and aluminum trichloride hexahydrate were dissolved separately in the minimum required quantities of distilled water at room temperature. The aluminum-bearing solution was rinsed into the sodium metasilicate solution with rapid stirring. The pH was lowered with 1.0 N HCl to a pH between 7 to 8 to allow the aluminosilicate solution to gel. The gel was then rinsed to remove excess sodium chloride and filtered to remove excess water. CsCl was added to obtain a specific Na/Cs ratio in the gel, and 1.0 N NaOH or CsOH was added to raise the pH to 12. The pH was also measured after crystallization, again at room temperature. The resultant subspherical crystals are optically isotropic, clear and colourless, and up to 30 μm in diameter. The yields are greater than 95%. The products were verified to be single-phase by optical microscopy, X-ray powder diffraction and EMP analysis.

Analysis of samples

Polished thin sections of the samples were analyzed with a CAMEBAX SX–50 electron microprobe, using the "PAP" data-reduction procedure of Pouchou & Pichoir (1985). Back-scattered electron imaging was used to investigate the homogeneity of all the samples.

For pollucite, concentrations of major elements were measured using 15 kV, 20 nA, a beam size of 5 μm, and count times of 20 s. The standards used were pollucite (Al*K*α, Si*K*α, Cs*L*α) and albite (Na*K*α). Minor elements were determined using 15 kV, 40 nA, a beam size of 5 μm and count times of 50 s. The standards used were rubidian microcline (Rb*L*α), orthoclase (Fe*K*α, K*K*α), anorthite (Ca*K*α), hornblende (Mg*K*α) and vanadium diphosphate (P*K*α).

For analcime, concentrations of major elements were measured using 15 kV, 10 nA, a beam size of 20 μm, and count times of 20 s. Analcime interacts with the electron beam more strongly than pollucite; thus a larger beam-size and lower currents were necessary to prevent loss of counts due to sample volatilization. The standards used were albite (Na*K*α, Al*K*α, Si*K*α) and pollucite (Cs*L*α). Minor elements were determined using 15 kV, 10 nA, a beam size of 20 μm and count times of 50 s. Standards were the same as those for the determination of minor elements in pollucite.

Results of the analyses were recalculated to atomic contents on the basis of six atoms of oxygen per anhydrous formula unit (atoms p.f.u.). The CRK index was calculated as 100(Cs + Rb + K)/Σ cations (Černý 1974), where Σ cations represents the sum of concentrations of Na + Ca + Mg + Cs + Rb + K. The CRK index is based on assignment of Cs, Rb and K to the larger 16*b* site, and Na, Ca and Mg to the smaller 24*c* site in Beger's (1969) model of the crystal structure of pollucite.

NMR measurements

Magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra were obtained using a Doty high-speed MAS probe with a Bruker AMX–500 multinuclear Fourier Transform spectrometer console, with two magnets operating at 8.4 and 11.7 Tesla. The samples were spun at approximately 8 kHz at an angle of 54.7° to the magnetic field. ^{29}Si MAS NMR spectra were recorded at a frequency of 99.3 MHz with 8190 data points, a spectral width of 50 kHz, 30° pulses and delay of 5 to 30 s between pulses. ^{27}Al and ^{23}Na spectra were recorded at frequencies of 130.3 and 132.3 MHz at 11.7 T, and 93.8 and 95.2 MHz at 8.4 T, respectively, with a spectral width of 50 kHz, 10° pulses and a delay of 0.1 s between pulses. ^{133}Cs MAS NMR spectra were recorded at a frequency of 65.6 MHz at 11.7 T with 2000 data points, 1.0 μs pulses and a delay of 0.5 s between pulses. Peak positions were measured with reference to tetramethylsilane (TMS) for ^{29}Si, a 1 M aqueous solution of aluminum chloride for ^{27}Al, 0.1 M aqueous solution of NaCl for ^{23}Na, and 1 M aqueous solution of CsCl for ^{133}Cs.

The ^{29}Si signal-to-noise ratios of both the natural and synthetic samples are low owing to relatively long T_1 relaxation times. The relative areas of the ^{29}Si peaks were found by cutting out and weighing the peaks; this has previously been found to give as accurate values for these broad lines as least-squares-fitting techniques (Sherriff *et al.* 1987).

Quadrupolar interactions of nuclei with spin greater than ½, such as ^{27}Al and ^{23}Na, cause line broadening and peak shifts in solid-state NMR spectra. These can be reduced by double-angle rotation (DOR) NMR experiment in which an inner rotor spins at an angle of 30.2° to the magnetic field while an outer rotor spins at the magic angle of 54.7° (Wu *et al.* 1990). The inner rotor averages out second-order quadrupolar interactions, whereas the outer rotor reduces broadening due to dipole–dipole interactions and anisotropy in chemical shifts.

Double-rotation NMR spectra were obtained for ^{23}Na and ^{27}Al using a Bruker DOR probe with the 8.4 T magnet. For both nuclei, a spectral width of 25 kHz, pulse lengths of 2 μs and a delay between pulses of 1 s was used to record the spectra. Reference standards were the same as for the MAS experiments. Spectra were observed at different speeds of spinning in order to distinguish peaks from spinning sidebands (Xu & Sherriff 1993). A method of synchronization was used to eliminate odd-numbered spinning sidebands and increase signal-to-noise ratio (Wu *et al.* 1990).

RESULTS

Analytical results

Compositions of the natural and synthetic samples are given in Table 1. The synthetic crystals of end-member analcime were found to be homogeneous, as was the synthetic end-member pollucite. Unfortunately, only atomic ratios could be determined for the synthetic pollucite (SYNAN–09) because of a grain size too small for quantitative EMP analysis: Si/Al = 2.3 ± 0.1; CRK = 97 ± 3. In the bulk sample of SYNAN–09, isotropic crystals have a *n* of 1.522 and contain 0.96 wt.% H_2O.

Intermediate members of the analcime – pollucite solid solution (SYNAN–06) were found to be heterogeneous and growth-zoned in Na and Cs (Fig. 1A). The crystals are described here because they are probably analogous to synthetic phases that contain ^{135}Cs and ^{137}Cs nuclear wastes. Composition varies between crystals over the interval from CRK 36 to 76. Some variation in Si/Al ratio with CRK is evident (Fig. 1B), and is reflected in a plot of Al (atoms p.f.u.) *versus* CRK (Fig. 1C). This plot also gives the sum of cation charges (atoms p.f.u.) *versus* CRK to indicate the charge balance in the analytical results.

Silicon NMR

In analcime, the ^{29}Si chemical shifts of individual peaks depend mainly on the number of Al atoms in the second coordination sphere of tetrahedrally coordinated Si atoms (Murdoch *et al.* 1988). Each additional Al next-nearest neighbor gives a shift of approximately 5 ppm to low field (Lippmaa *et al.* 1981). The number of Al atoms is designated using the nomenclature Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si(0Al) for the five possible next-nearest neighbor environments of the tetrahedra. Assignment of the peaks to specific environments of the tetrahedra was based on calculation of chemical shift using theoretical models

TABLE 1. CHEMICAL COMPOSITION OF THE SAMPLES USED

	Natural samples			Homogeneous synthetic analcime		
Oxide	PA-150	PA-122	PA-031	SYNAN-03	SYNAN-04	SYNAN-23
SiO_2 wt.%	52.89 (.14)	57.05 (.11)	47.77 (.14)	57.58 (.15)	55.36 (.12)	58.34 (.14)
Al_2O_3	24.63 (.05)	20.56 (.10)	16.02 (.05)	20.96 (.50)	22.26 (.05)	20.53 (.15)
Fe_2O_3	0.00	0.00	0.00	0.02	0.03 (.01)	0.05
P_2O_5	0.00	0.00	0.33 (.01)	0.00	0.00	0.00
Na_2O	13.31 (.11)	11.99 (.11)	1.67 (.01)	12.36 (.70)	13.08 (.06)	11.58 (.58)
K_2O	0.73 (.01)	0.02	0.02	0.02	0.02	0.11
Rb_2O	0.00	0.00	0.29 (.01)	0.00	0.00	0.00
Cs_2O	0.00	1.29 (.05)	32.52 (.20)	0.00	0.00	0.00
CaO	0.02	0.00	0.02	0.01	0.02	0.03
H_2O	7.67	7.37	1.70	7.54	7.85	7.54
sum	99.25	98.28	100.34	98.51	98.63	98.32
Si	2.06	2.11	2.14	2.10	2.04	2.13
Al	0.99	0.90	0.86	0.90	0.97	0.88
Na	0.98	0.86	0.15	0.88	0.94	0.82
Cs	0.00	0.02	0.63	0.00	0.00	0.00
Σ charges	1.00	0.88	0.81	0.88	0.94	0.83
Si/Al	2.03	2.36	2.44	2.33	2.11	2.41
CRK	0.6	2.4	81.2	0.01	0.01	0.08
n	1.488	1.486	1.519	1.489	1.484	1.484

Notes: 1) CRK = 100(Cs + Rb + K)/Σ cations.
2) Atomic contents on the basis of 6 atoms of oxygen per anhydrous formula unit.
3) n = index of refraction.
4) ( ) = one standard deviation based on 6-10 analyses.
5) See text (analytical results) for details of synthetic pollucite (SYNAN-09) and cesian analcime (SYNAN-06).

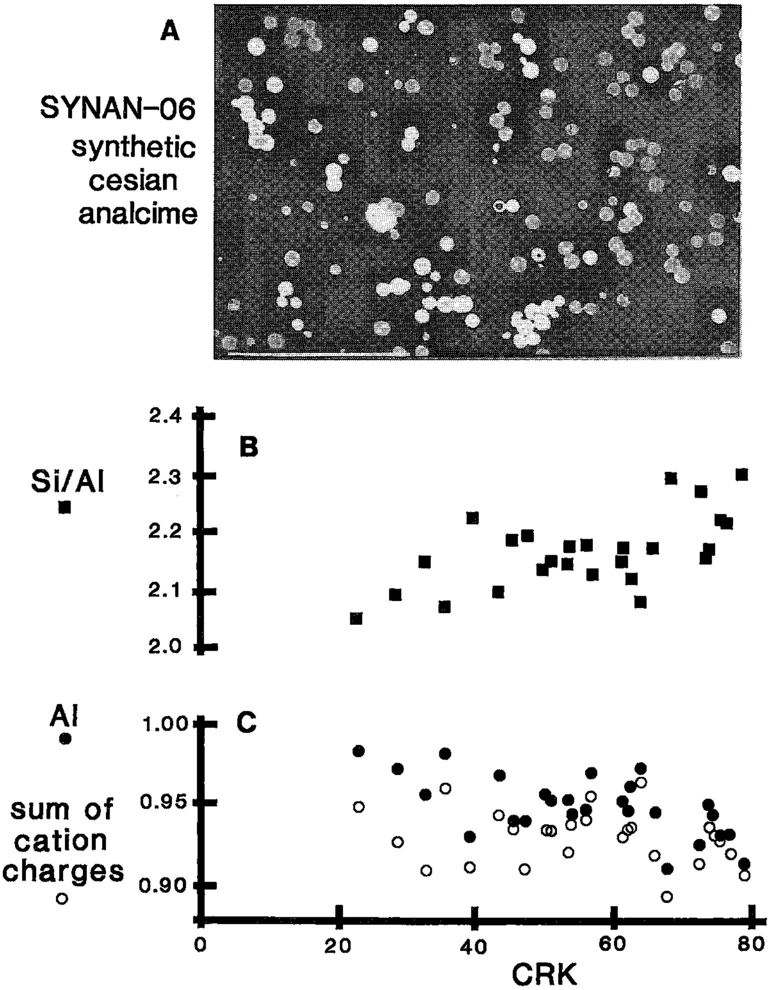

FIG. 1. a) Back-scattered electron image of synthetic cesian analcime (SYNAN–06). Brighter areas indicate higher Cs contents. Some grains have a Na-rich core, and a Cs-rich rim. Scale bar: 100 μm. b) Si/Al *versus* CRK [= 100*(Cs + Rb + K)/cation sum]. c) Al and sum of cation charges (atoms per formula unit) *versus* CRK. The analytical precision is ±0.02 (Si/Al), ±0.01 (Al, and sum of cation charges) and ±0.1 (CRK).

for local environments of silicon in tectosilicates (Sherriff *et al.* 1991).

The ^{29}Si spectrum of natural analcime (PA–150; Fig. 2A) has a major peak at a chemical shift of –96 ppm, and minor peaks with chemical shifts of –91 and –101 ppm. The major peak is assigned to Si(2Al), and the minor peaks to Si(3Al) and Si(1Al), respectively.

The spectra of synthetic analcime (SYNAN–03, 04 and 23; Figs. 2B, C), natural cesian analcime (PA–122), and synthetic cesian analcime (SYNAN–06) are similar to that of natural analcime. Peak assignments and chemical shifts are given in Table 2, together with the relative areas under the peaks. Differences in the spectra lie mainly in the relative intensity of the peaks. The greater intensity of the minor peaks of synthetic analcime compared to the case for natural analcime is due to a greater proportion of Si in the Si(3Al) and Si(1Al) environments.

The ^{29}Si spectrum of natural pollucite (PA–031; Fig. 3A) has two major peaks with chemical shifts (Table 2) of –96 and –101 ppm, assigned to Si(2Al) and Si(1Al), respectively. The spectrum of

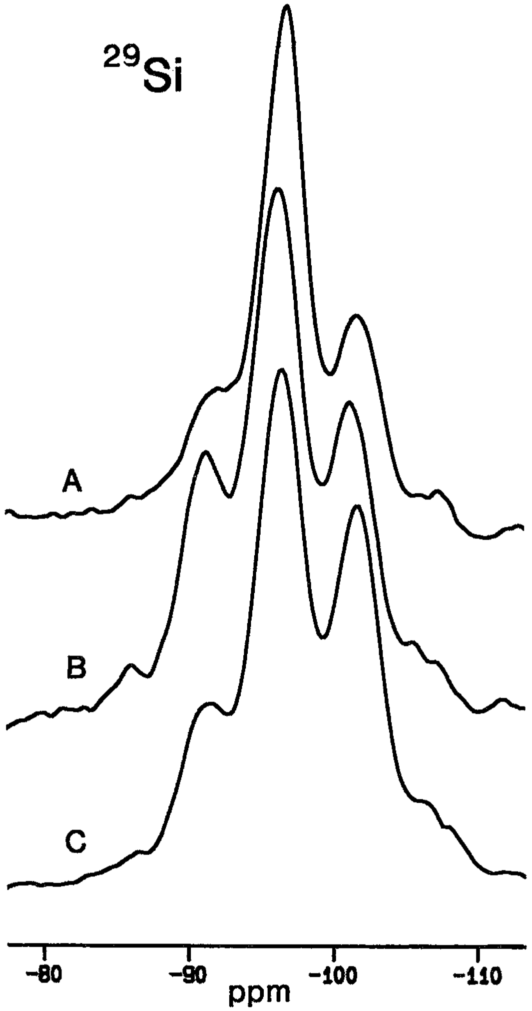

FIG. 2. ^{29}Si MAS NMR spectra of A) birefringent natural analcime (PA–150), B) cubic synthetic analcime (SYNAN–03), and C) cubic synthetic analcime (PA–122) with a higher Si/Al ratio than SYNAN–03.

synthetic pollucite (SYNAN–09; Fig. 3B) is similar to that of natural pollucite, but the corresponding peaks are broader.

Aluminum NMR

The ^{27}Al spectra of all the natural and synthetic samples consist of one broad resonance. In the MAS spectrum of natural pollucite, this peak has a position near 59 ppm, and a peak width at half-height of 550 Hz at 11.7 T (Table 3). There is no significant

TABLE 2. ^{29}Si MAS NMR PARAMETERS

Sample	Peak position, ppm (relative area of peak) Si(3Al)	Si(2Al)	Si(1Al)
PA-150	-91.3	-96.3	-101.0
	(14)	(65)	(21)
PA-122		-96.9	-101.4
	(0)	(75)	(25)
PA-031		-96.4	-101.4
	(0)	(68)	(32)
SYNAN-03	-91.1	-96.2	-101.1
	(20)	(56)	(24)
SYNAN-04	-91.3	-96.5	-101.7
	(23)	(51)	(26)
SYNAN-23	-91.5	-96.4	-101.7
	(15)	(50)	(35)
SYNAN-06	-91.2	-96.5	-101.0
	(20)	(54)	(26)
SYNAN-09		-96.7	-100.6
	(0)	(77)	(23)

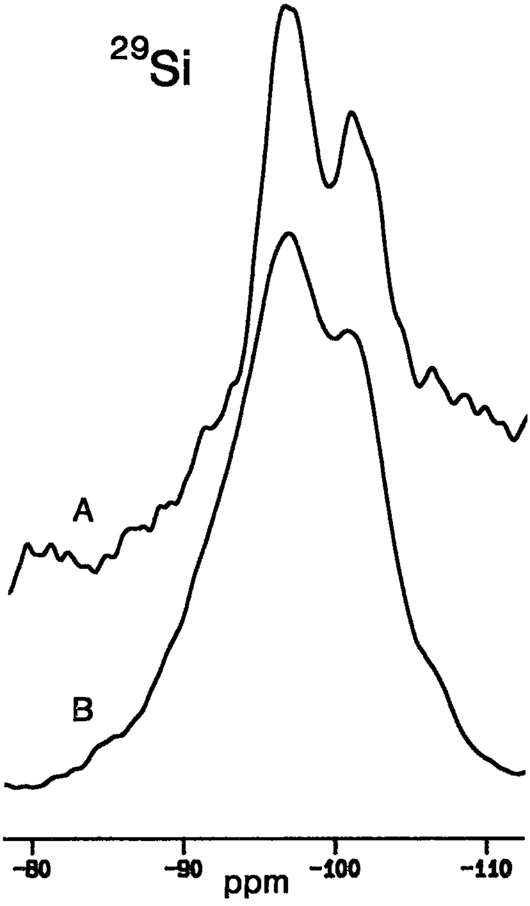

FIG. 3. ^{29}Si MAS NMR spectra of A) cubic natural pollucite (PA–031), and B) cubic synthetic pollucite (SYNAN–09).

TABLE 3. ^{27}Al MAS NMR PARAMETERS

Sample	Peak position, ppm		Peak width at half-height, Hz	
	AMX500	AMX360	AMX500	AMX360
PA-150	58.7	----	490	---
PA-122	58.9	57.3	490	620
PA-031	58.9	58.1	550	530
SYNAN-03	58.8	----	570	---
SYNAN-04	58.8	----	550	---
SYNAN-23	58.6	----	560	---
SYNAN-06	58.8	57.7	570	650
SYNAN-09	59.2	----	700	---

TABLE 4. ^{23}Na MAS NMR PARAMETERS

Sample	Peak position, ppm		Peak width at half-height, Hz	
	AMX500	AMX360	AMX500	AMX360
PA-150	-12.0	----	1420	----
PA-122	-12.1	-20.6	1220	1920
PA-031	-8.1	-12.7	1960	2430
SYNAN-03	-11.7	----	1640	----
SYNAN-04	-12.3	----	1380	----
SYNAN-23	-11.3	----	1590	----
SYNAN-06	-11.6	-20.0	1590	2340

shift in peak position from analcime to pollucite; however, the peak width at half-height increases from analcime to pollucite, with the synthetic samples having broader peaks.

^{27}Al DOR spectra show only one symmetrical peak (Fig. 4). In natural pollucite, at spinning rate speeds of the outer rotor of 800 Hz, the peak is at 51 ppm with a width at half-height of 410 Hz.

Sodium NMR

The ^{23}Na MAS peak for natural pollucite has a chemical shift of –8 ppm and a peak width at half-height of 2000 Hz (Table 4, Fig. 5A). The spectrum of natural cesian analcime consists of one broad, asymmetrical resonance with a peak position of –12 ppm and a width of 1200 Hz (Fig. 5B). A ^{23}Na spectrum could not be obtained from synthetic pollucite (SYNAN–09), as the content of Na was too low.

The ^{23}Na DOR spectrum of cesian analcime (PA–122; Fig. 6) consists of one peak at the same position as in the MAS spectra. The DOR peak, however, has an asymmetrical shoulder, which suggests that it is a combination of two or more peaks, resulting from different Na environments. This shoulder is larger in the ^{23}Na DOR spectrum of synthetic cesian analcime (SYNAN–06).

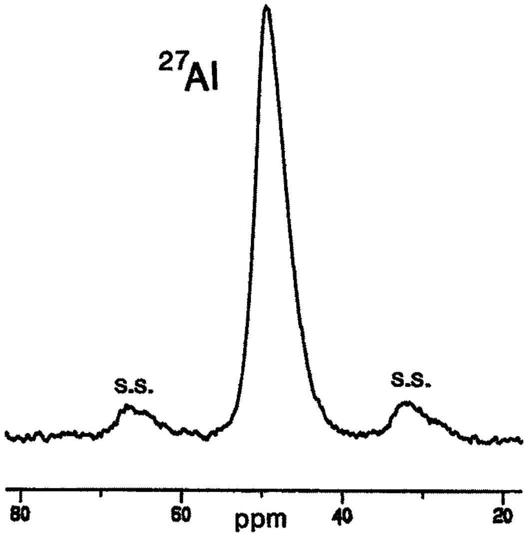

FIG. 4. ^{27}Al DOR NMR spectrum of natural pollucite (PA–031) showing a single, symmetrical peak. Spinning sidebands are marked (s.s.).

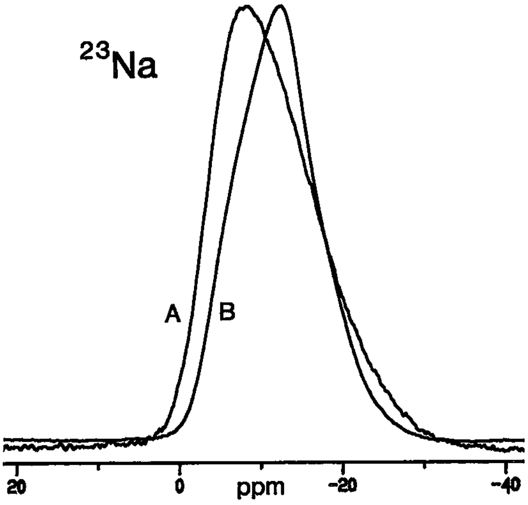

FIG. 5. ^{23}Na MAS NMR spectra of A) natural pollucite (PA–031), and B) natural cesian analcime (PA–122), showing asymmetrical peaks.

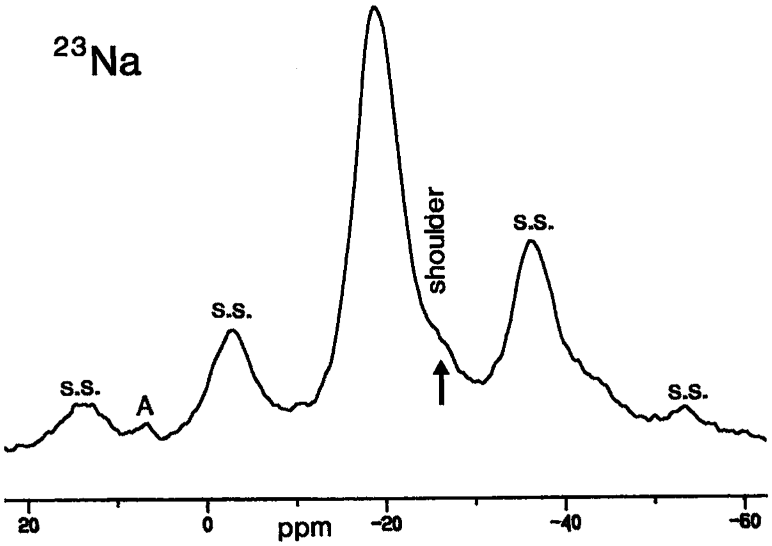

FIG. 6. ^{23}Na DOR NMR spectrum of natural cesian analcime (PA–122). Data were collected at a spinning speed of 800 Hz. The spinning sidebands (s.s.) were identified by their change in peak position at lower spinning speeds, whereas the main peak (with a width of 60 Hz) does not change in its position (19.3 ppm). The shoulder to the main peak is marked by the arrow. A small peak (A) was found in the same position as the reference standard, solid NaCl at 7.0 ppm, but this peak is not due to NaCl inclusions, as this gem-quality sample seems to be free of inclusions.

Cesium NMR

^{133}Cs spectra were obtained for synthetic cesian analcime (SYNAN–06) and natural pollucite (PA–031). The spectra both consist of one very broad, symmetrical resonance with a position near –49 ± 4 ppm.

DISCUSSION

Theoretically, the ^{29}Si spectrum of a completely ordered analcime with a Si/Al ratio of 2.0 should have only a single peak, due to the Si(2Al) environment. If the Si/Al ratio is greater than 2.0, and the structure is still ordered, an additional Si(1Al) peak should appear. With Si/Al ratios less than 2.0, the Si(3Al) peak should be present. Fully ordered sodian pollucite, with a Si/Al ratio of 1.0, has a single Si(4Al) peak at –89.6 ppm (Dimitrijevic *et al.* 1991).

Increasing disorder (at Si/Al = 2.0) is indicated by the appearance of Si(0Al), Si(3Al) and Si(4Al) peaks and a corresponding decrease in the intensity of the Si(2Al) peak. It may also be correlated with an increase in peak widths due to overlapping peaks from slightly differing ^{29}Si environments.

The ratio of the number of Si in the Si(2Al) environment to those in the Si(3Al) and Si(1Al) environments is greater in the spectrum of birefringent natural analcime (PA–150) than in that of cubic synthetic analcime (SYNAN–03). The difference in degree of order correlates in this case with the variation in symmetry. A ^{29}Si NMR spectrum for analcime from Golden, Colorado, reported by Murdoch *et al.* (1988), is very similar to our spectrum of cubic, synthetic analcime. They used peak simulations and computer calculations to propose (Al,Si) distributions among three different tetrahedrally coordinated sites in analcime. However, they did not state whether their crystal is birefringent: if cubic, it would have only one tetrahedral site, but if monoclinic, it must have six crystallographic sites. Analcime from the Golden, Colorado locality was described by Yoder & Weir (1960) as being isotropic to slightly birefringent, with a Si/Al ratio of 2.13.

The ^{29}Si spectrum of natural birefringent analcime (PA–150) is similar to the spectrum of natural birefringent cesian analcime (PA–122), except that the latter spectrum lacks the Si(3Al) and has a larger Si(1Al) peak. This cesian analcime is therefore more ordered than the end-member analcime, but the higher Si/Al ratio gives a larger Si(1Al) peak (Table 2). This is shown more clearly by the spectra of synthetic samples with differing Si/Al ratio. An increase in the relative intensity of the Si(1Al) peak is evident in a comparison of the spectrum of SYNAN–03, with a low Si/Al ratio (Fig. 2B), to that of SYNAN–23, with a higher Si/Al ratio (Fig. 2C).

The similarity of the spectrum of synthetic cesian analcime (SYNAN–06) to that of synthetic analcime (SYNAN–03 and SYNAN–04) shows that the framework of synthetic cesian analcime is not significantly more disordered than synthetic end-member analcime.

Both the natural and synthetic pollucite are cubic. Černý (1979) estimated the conditions of crystallization of natural pollucite to be in the range of 600 to 300°C at 4 to 2 kbar, but suggested that in natural B, F, Li, H_2O-rich pegmatite-forming granitic melts, the temperature is most likely 400 to 300°C. Despite this higher temperature of crystallization of natural pollucite, it is more ordered than the synthetic pollucite, which crystallized at 200°C (Figs. 3A, B). This could be due to a longer period of crystallization and cooling. The higher Cs content in the synthetic pollucite may make a significant contribution to disorder in the (Al,Si) framework; however, the pollucite could also have crystallized metastably at temperatures too low for ordering in the solid state.

The increase in ^{27}Al peak widths from analcime to pollucite indicates increasing disorder in the structure with increasing Cs content. As the number of Al–O–Al bonds is minimized (Loewenstein 1954), this must be due to disorder of Al and Si in the tetrahedrally coordinated sites four bonds away from the Al. Cesian analcime (PA–122) is optically biaxial and, therefore, has orthorhombic or lower symmetry, which requires at least three distinctive crystallographic sites. In the DOR spectrum of PA–122, the peak narrows to 410 Hz but does not separate into three peaks, probably because the three sites have similar environments or because disorder is causing sufficient broadening of each peak for them to not be resolvable. The resolution possible with the DOR technique is shown by the peak width of 43 Hz obtained for the ^{27}Al DOR spectrum of an extremely well-ordered sample of tugtupite (Xu & Sherriff 1994).

If there is more than one distinct Al environment in analcime, we would expect to observe the ±1/2 ↔ ±3/2 satellite transitions in the first spinning sidebands of the MAS spectra regardless of the strength of the magnetic field (Xu & Sherriff 1993), because the inner satellite transitions have small second moments and sufficient intensity to be observed (Samoson 1985). In two magnetic fields, the sidebands are broad but clearly without resolution into separate peaks.

These ^{27}Al results seem to conflict with those of Phillips *et al.* (1989), who reported the presence of three peaks in a MAS spectrum of leucite. Only one X-ray structure refinement of leucite has been published, as leucite is intensely twinned. This showed tetragonal symmetry and an (Al,Si) framework that is much more disordered than in analcime. Sample PA–122 has a symmetry lower than tetragonal, and should be more ordered than leucite, yet we see only one peak, even in DOR experiments.

The ^{23}Na MAS spectra of synthetic samples tend to have broader peaks than the natural samples owing to the higher overall degree of disorder. However, the change in shape and position of the ^{23}Na MAS peak from analcime to pollucite indicates a change in the Na environment (Figs. 5A, B). The shift in ^{23}Na peak position with increasing Cs content was also visible in the DOR spectra. The shoulder to the main peak in the DOR spectrum, which indicates two Na environments, becomes more distinct with increasing Cs content. Variation in the local symmetry of the Na site does not seem to be the main factor, as there seems to be no strong variation between crystals of different symmetry. In single-crystal structure refinements (XRD), the electron distribution associated with the Na site is strongly anisotropic, in the direction of the H_2O molecules. A change in H_2O:Na ratio from 2:1 to 1:1 from analcime to pollucite may be the cause of the two ^{23}Na DOR peaks we observed, if it means that some Na atoms are flanked by one H_2O molecule rather than two.

Ordering, symmetry and composition

Analcime and pollucite belong to the Class 4 of zeolites (Gottardi & Alberti 1985); these are zeolites with Si in excess of Al, and a framework that favors disorder because the tetrahedrally coordinated sites are topologically identical. Order is defined crystallographically by a three-dimensional, patterned filling of cation sites. Disorder refers to a random distribution of cations, which in the tetrahedral sites favor variable Si/Al ratios. Si/Al ratios tend to be near 2.0 in most natural samples of analcime, although higher Si/Al ratios are typical of cesian analcime and pollucite.

In synthetic analcime, Khundadze *et al.* (1970), and Senderov & Khitarov (1971) showed that Si/Al ratios near 2.0 are thermodynamically the most stable and suggested that this constancy of composition is due to (Al,Si) order in the structure. However, order is not linked to Si/Al ratio, as crystals with Si/Al of 2.0 may be highly disordered. Based on results of chemical analyses, Pechar (1988) used an order–disorder parameter $Q = Si/(Si + Al + Fe^{3+})$ to describe the distribution of atoms in tetrahedrally coordinated sites and incorrectly concluded that his monoclinic analcime is disordered. This is a requirement of cubic symmetry. Our research indicates that variable degrees of order do not require changes in Si/Al ratio; therefore, this type of parameter cannot be used to quantify the degree of order.

The *Ia*3*d* space group requirement of "full disorder among 48*g* sites" should be interpreted liberally for long-range (X-ray and optical) observations. With random occupancy of Al among the 48*g* sites, we may expect Al–O–Al linkages, which must be avoided (Loewenstein 1954); however, in these Si-rich minerals, even Al–O–Si–O–Al linkages are likely to be avoided in line with the extended Loewenstein rule (Merlino 1984). This accounts for the partial order found even in rapidly formed synthetic pollucite. However, synthetic analcime has a greater degree of order. This situation may be explained by the proximity of Na to Al in analcime. The concept of local charge-balance in a small area (Pauling's second rule) is probably valid during crystal growth (Akizuki 1981).

Ordering in these minerals is known to be rather sluggish after crystallization (Khundadze *et al.* 1970). Only for synthetic wairakite has re-ordering been demonstrated on an experimental time-scale (Liou 1970). In natural analcime, ordering probably takes place mainly during crystal growth (Akizuki 1981, Papezik & Elias 1980). Akizuki (1981) related surface features of analcime crystals to optical symmetry (isotropic *versus* uniaxial), and suggested that the variable symmetry resulted from the degree of order produced during growth on a specific surface-topology. In this case, the cubic (*Ia*3*d*) phase is required to be more disordered; in general, we expect the highest degree of order in crystals with the lowest symmetry. However, lower symmetry could result from a slight, systematic rotation of the tetrahedra during growth, which does not involve ordering or even change during cooling from a higher-temperature, more symmetrical phase.

In natural pollucite, the presence of the large Cs atom may sterically hinder mechanisms of order; however, the relatively high temperature of crystallization can also be a factor. We have detected some degree of order in isotropic pollucite, suggesting that even a highly ordered framework can accommodate Cs as the dominant cation. In pollucite, symmetries lower than cubic may be due to ordering alone, as the framework requires little adjustment to fit the size of Cs^+ (Roth *et al.* 1991). A weak, local birefringence has been reported in natural pollucite but, to date, there are no published refinements of the noncubic structure.

CONCLUSIONS

We have observed only intermediate and variable degrees of order, in agreement with the findings of Gottardi & Alberti (1985); we have not found states of complete order or complete disorder, in agreement with the findings of Alberti (1991) in other zeolites. We conclude that there are no simple relationships between states of Al–Si order and symmetry in analcime and related ANA minerals, because of variable influences of composition, growth mechanisms, thermal history and displacive phase-transformations. The degree of order depends mainly on the type of interframework cation present, with a lesser influence of variable Si/Al ratios in the framework, mechanisms of crystal growth, phase transformations, pressure conditions and subsequent thermal history. In ANA crystals with symmetry lower than cubic, NMR cannot distinguish between crystallographically distinct sites because the sites have nearly equivalent environments of bonding.

The degree of disorder increases from analcime to pollucite, but complete disorder was not found. Even rapidly synthesized end-member pollucite is partially ordered as a result of Al–O–Al avoidance; the extended Loewenstein's rule probably also is applicable, as these minerals typically are Si-rich, with Si/Al greater than 2.0.

For containment of nuclear wastes in analcime-related phases, Si/Al ratios near 2.0 and low levels of ^{135}Cs and ^{137}Cs waste, with a Cs/Na ratio less than 1, are recommended on the basis of maximum potential degree of order and probable thermodynamic stability.

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