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THE ALKALI-METAL POSITIONS IN Cs-Li BERYL

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ABSTRACT

The crystal structure of a Cs-rich beryl, *a* 9.212(2), *c* 9.236(3)Å, has been refined in the space group *P6/mcc* to an *R* index of 5.5% for 381 observed reflections. Mean tetrahedral and octahedral distances indicate that Li occurs in the Be site and not in the Al site. Difference Fourier maps show that the alkali cations are confined to the 2*a* and 2*b* sites in the channel, with Cs occurring at the 2*a* site. Stereochemical and bond-strength arguments suggest that all Na is in 2*b* and all water is in 2*a*, and that Na is bonded to at least one and possibly two water molecules in the channel. In most published analyses of beryl, the number of H_2O units exceeds twice that of Na atoms. Crystallochemical arguments provide maximum limits on the possible alkali-metal substitutions in beryl; approximately 100 published beryl analyses show that these limits are approached, but not exceeded.

SOMMAIRE

La structure cristalline du béryl riche en césium, *a* 9.212(2), *c* 9.236(3)Å, a été affinée dans le groupe spatial *P6/mcc* jusqu'au résidu $R=5.5\%$ pour les 381 réflexions observées. Les distances interatomiques moyennes dans les tétraèdres et les octaèdres indiquent que le lithium remplace le béryllium et non l'aluminium. Les séries différence de Fourier placent les cations alcalins aux sites 2*a* et 2*b*, dans le tunnel, et le césium en 2*a*. Par considérations stéréochimiques et analyse des valences de liaison, on situe tout le sodium en 2*b* et toute l'eau en 2*a*, et l'on conclut que le sodium devrait être lié à une ou deux molécules d'eau dans le tunnel. La plupart des analyses de béryl publiées indiquent un nombre de molécules d'eau au moins deux fois plus grand que celui des atomes de sodium. Par raisonnements cristallochimiques, on établit des limites maximales aux substitutions des métaux alcalins dans le béryl. Dans une centaine d'analyses publiées, on vérifie que ces limites sont frisées, mais non dépassées.

(Traduit par la Rédaction)

INTRODUCTION

In its ideal form, the chemical formula of beryl may be written as $Be_3Al_2Si_6O_{18}$. The crystal structure of beryl was determined by Bragg & West (1926), who showed that it consisted of six-membered rings of Si tetrahedra perpendicular to the *c* axis, linked laterally and vertically to adjacent rings by Be tetrahedra, thus forming four-membered Be-Si rings parallel to *c* (Gibbs *et al.* 1968); the Al occurs between the six-membered rings in a distorted octahedron, sharing oxygens with both Si and Be. This structure was confirmed by Belov & Matveeva (1951) and Bergerhoff & Nowacki (1955), and accurate refinements have been reported by Gibbs *et al.* (1968) and Morosin (1972). Beryl was originally classified as a ring silicate (Deer *et al.* 1963; Bragg & Claringbull 1965), but persuasive arguments have been advanced that beryl should be classified as a framework silicate (Zoltai 1960; Gibbs *et al.* 1968). Chemical analyses of natural beryls indicate the presence of significant amounts of additional components, particularly water and the alkali elements. These compositional variations in beryl correlate strongly with the geochemical and paragenetic characteristics of the pegmatites in which they occur. Although a comprehensive classification scheme for beryl must include the physical and morphological characteristics of the mineral (Feklitchev 1964), the alkali variation in most beryls from uncontaminated granitic pegmatites is a fairly adequate basis for classification. The following scheme is after Beus (1960) as modified by Černý (1975).

(1) *alkali-free beryl*: total alkalis <0.1 wt. %; occurs in vugs of predominantly graphic pegmatites, and schlieren- and pocket-type bodies in granites.

(2) *alkali-poor potassic and sodic-potassic beryl*: K predominant, ranging between 0.5-1.0 wt. %; occurs in schlieren- and pocket-type pegmatites in granites, and in quartz cores of simple blocky pegmatites.

(3) *sodic beryl*: Na predominant, ranges between 0.5-1.0 wt. %; occurs in pegmatites with albite-rich assemblages but very poor in rare alkalis.

(4) *sodic-lithian beryl*: Na ranges between 0.0-2.0 wt. %; Li up to 0.6 wt. %, Cs low; occurs in Li-bearing pegmatites.

(5) *lithian-cesian beryl*: high Na and Li with Cs >0.5 wt. %; occurs in extremely differentiated

Li-rich pegmatites with metasomatic lepidolite units, frequently pollucite-bearing; also as late hydrothermal crystals in vugs in these pegmatites.

Recent work (Černý 1975) has indicated that the alkali content of beryl may be used quantitatively to further delineate the geochemical characterization of pegmatites and to identify petrogenetically related pegmatite groups. On a smaller scale, this may also be used to indicate differences within apparently homogeneous groups of cogenetic pegmatites (Černý & Turnock 1975).

Although the geochemical behavior of beryl seems fairly well-characterized, the crystallographic aspects of the alkali substitution in the structure are not clear. Thus the degree to which any crystal-chemical limitations impose constraints on the alkali variation is to a large extent obscure. Two models have been proposed for the alkali variation in beryls. Beus (1960) proposed a coupled substitution of the form $Li^+ \rightleftharpoons Al^{3+}$, $Al^{3+} \rightleftharpoons Be^{2+}$ with additional alkalis entering the channel to maintain overall charge neutrality. This was supported by Evans & Mrose (1966) on the basis of preliminary refinements of pure synthetic beryl and a Cs-rich beryl. Conversely, Belov (1958) proposed the substitution $Li^+ \rightleftharpoons Be^{2+}$ and this was supported by the results of a partial refinement of a Cs-Li beryl (Bakakin *et al.* 1969). Thus both mechanisms are supported by preliminary structure-refinement results and the problem is still unresolved. The configuration of the channel alkalis is also not well-characterized. Bakakin & Belov (1962), in an extensive study of the crystal chemistry of beryl, proposed that Na, Ca and excess Li occupy the 2*a* site (in the plane of the Si_6O_{18} rings) and Cs, Rb and sometimes K occur in the channels between the 2*a* and 2*b* positions. Conversely, Feklitchev (1963) proposed that the alkalis occupy the 2*b* position with channel H_2O in the 2*a* position. On the basis of the ratio of the intensities of the $21\bar{3}1$ and $11\bar{2}2$ reflections for a series of alkali-rich beryls, Vorma *et al.* (1965) proposed that the channel alkalis and H_2O occupy the 2*a* position. The preliminary results of Evans & Mrose (1966) indicated that Cs occupies the 2*a* position, but no information was provided on the site-occupancy of Na and H_2O. The position of the water molecules in synthetic non-alkaline beryl has been established as 2*a* by Gibbs *et al.* (1968) and Morosin (1972). However, the role of water in the channel seems to vary, depending on the presence or absence of channel alkalis. In an exhaustive study on the polarized infrared spectra of both natural and synthetic beryls (Wood & Nassau 1968), it was shown that the H-H vector of the water molecules in alkali-free beryl is parallel to the *c* axis, whereas for alkali beryls, some of the water molecules have their H-H vector perpendicular to the *c* axis. Wood & Nassau suggested that this difference was due to the presence of neighboring alkali cations, but the exact nature of the interaction was not clear. The crystal-structure refinement of a Cs-rich beryl was undertaken in order to clarify the role of the alkalis in the structure as they seem to have important petrogenetic implications.

TABLE 1. MISCELLANEOUS DATA

Analysis**		Unit cell content*			
SiO_2	62.00%	Si	11.91	a	9.212(2)Å
Al_2O_3	17.71	Al	4.01	c	9.236(3)Å
Fe_2O_3	0.018	Fe	.003	V	678.25Å^3
BeO	11.32	Mg	.005	Sp. Gr.	P6/mcc
MgO	0.017	Mn	.001	D_{obs}	2.781g/cm^3
CaO	0.030	Be	5.225	D_{calc}	2.785
MnO	0.004	Li	.873	ϵ	-
Li_2O	1.13	Ca	.006	ω	1.594
Na_2O	1.68	Na	.626	$\mu(cm^{-1})$	12.64
K_2O	0.266	K	.065	crystal dimensions	.18 x .07 x .05 (mm)
Rb_2O	0.109	Rb	.013		
Cs_2O	3.27	Cs	.268	no. of $\lvert F_{obs}\rvert > 4\sigma$	381
H_2O^+	2.06	H_2O	1.32		
H_2O^-	0.07			R(obs.)	5.5%
	99.68			R(all data)	6.2%
				R_w(obs.)	6.0%
				R_w(all data)	6.2%

$R = \sum(\lvert F_{obs}\rvert - \lvert F_{calc}\rvert) / \sum \lvert F_{obs}\rvert$

$R_w = (\sum w(\lvert F_{obs}\rvert - \lvert F_{calc}\rvert)^2 / \sum w F_{obs}^2)^{1/2}$, $w=1$

Temperature factor form used: $\exp(-\sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j \beta_{ij})$

*Calculated on the basis of 36 oxygens/unit cell, excluding H_2O.

**Analysts: K. Ramlal and R.M. Hill, 1974.

EXPERIMENTAL

The crystals used in this study were from the Tanco deposit, Manitoba. The chemical analysis (see Černý & Simpson in prep. for analytical methods) is presented in Table 1, together with the chemical formula calculated on the basis of 18 anions, excluding water. Single-crystal precession photographs exhibited hexagonal symmetry with systematic absences *hhl*, $l=2n+1$ and *h0l*, $l=2n+1$, consistent with the space group *P6/mcc* as established by earlier studies (Bragg & West 1926; Belov & Matveeva 1951; Gibbs *et al.* 1968; Morosin 1972). Least-squares refinement of 15 reflections aligned automatically on a four-circle diffractometer gave the following cell dimensions: *a* 9.212(2), *c* 9.236(3)Å. These values are statistically identical with those obtained by refinement of the powder-diffraction record: *a* 9.211(1), *c* 9.231(4)Å.

A prismatic crystal of dimensions 0.18×0.07

×0.05 mm was used to collect the intensity data; the experimental details are given in Hawthorne & Ferguson (1975). A total of 2171 reflections was measured over 4 asymmetric units out to 65°2θ ($\sin\theta/\lambda=0.758$, $\lambda=0.71069$Å). The data were corrected for Lorentz, polarization and background effects, and then averaged to produce an asymmetric set. No absorption corrections were performed as they were negligible for this crystal (for a cylinder, $\mu r=0.04$). A reflection was considered as observed if its magnitude exceeded that of four standard deviations based on counting statistics; of the 436 unique reflections, 381 were classed as observed.

REFINEMENT

Scattering curves for neutral atoms were taken from Cromer & Mann (1968) and anomalous dispersion corrections from Cromer & Liberman (1970). The atomic coordinates and equivalent isotropic temperature factors of synthetic alkali-free beryl (Morosin 1972) were used as initial input to the least-squares program RFINE (Finger 1969); initially the alkalis in the formula were not considered in the refinement. Several cycles of full-matrix least-squares refinement, gradually increasing the number of variables, resulted in convergence at an *R* index (see Table 1) of 18.4% for isotropic temperature factors. At this stage, only the mean bond length of the Be site was significantly different from those reported by Gibbs *et al.* (1968) and Morosin (1972), and thus the Li in the formula unit was assigned to this site. In order to assign the channel alkalis and water molecules to specific positions, a difference Fourier map was calculated at this stage. Figure 1 shows a difference map in the 01.0 plane in the vicinity of the *c* axis. The only significant density observed in the map lies at the special positions 2*a*(00¼) and 2*b*(000), indicating that the channel atoms are confined to the special positions at $z=0$ and ¼. The problem of three cation species distributed over two sites in a crystal structure does not have a unique solution in the refinement of single-crystal X-ray data. Thus the channel alkali distribution cannot be elucidated purely from the X-ray data. However, limits can be put on the possible variations of site-chemistry and this, together with crystal-chemical arguments, should be sufficient to give the actual distribution. It is apparent from Figure 1 that there is far greater scattering power at 2*a* than at 2*b;* a total electron count at each site gives the following approximate values: $2b=3.4$ electrons, $2a=15.5$ electrons. This total of 18.9 electrons compares favorably with the total of 18.45 electrons available from the channel cations. Small amounts of Rb, K and Li occur in the channel sites (Table 1); for the purposes of the refinement, Li was combined with Na and the other alkalis were combined with Cs, with the amounts of Cs and Na suitably modified for the differences in scattering factors. The numbers of electrons available from each of the three species considered are as follows: Cs 8.25, Na 3.60, H_2O 6.60. From the electron counts at the 2*a* and 2*b* sites given above, the following observations may be made:

(i) as the total density observed at 2*b* is far less than the amount of Cs in the channel, most of the Cs must reside at 2*a*. In addition, if the observed density at 2*b* is considered as due to Cs occupying that site, the number of atoms occupying the 2*a* site exceeds 1.0. This suggests that all Cs resides at 2*a*.

(ii) as the density observed at 2*b* is approximately half that contributed by the H_2O in the channel, at least half of the water resides at 2*a*.

It is notable that the electron count at 2*b* is approximately equal to the amount of Na available in the channel. As the scattering powers of Na and H_2O are approximately the same, it is not possible to identify the species at 2*b* from the X-ray data. As the data do not define whether or not Na or H_2O occupies the 2*b* site, the choice of either alternative does not affect the refinement to any great extent. Thus Na was assigned to the 2*b* site, and Cs and H_2O to the 2*a* site. The isotropic temperature factors at these sites

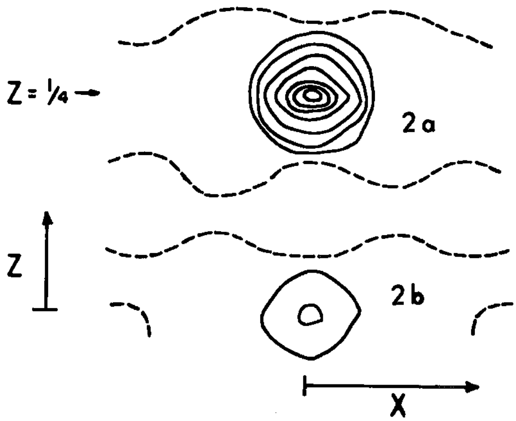

FIG. 1. Difference Fourier map in the (01.0) plane in the vicinity of the *c* axis; the contour interval is arbitrary.

were initially set at 1.5Å^2, and least-squares refinement of all variables for an isotropic thermal model resulted in convergence at an R index of 6.4%. Temperature factors were converted to anisotropic of the form given in Table 1, and full-matrix refinement of all variables resulted in convergence at R and R_w indices of 5.5 and 6.0% (observed reflections) and 6.2% and 6.2% (all reflections) respectively. These values are slightly higher than are generally encountered in well-refined mineral structures. This may be the result of slight positional disorder or anisotropic thermal vibrations of the channel cations, as difference Fourier maps calculated after the final cycle showed some evidence of this. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 2 and the anisotropic temperature factor coefficients are given in Table 3. Interatomic distances and angles and the magnitudes and orientations of the principal axes of the thermal ellipsoids were calculated with the program ERRORS (L. W. Finger, pers. comm.) and are given in Tables 4 and 5, respectively. Structure factor tables are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

TABLE 2. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS

	Site	x	y	z	B_{equiv} (Å^2)
Si	12ℓ	0.3892(2)	0.1189(2)	0	0.60(3)
Be	6f	1/2	0	1/4	0.77(12)
Al	4c	2/3	1/3	1/4	0.64(4)
0(1)	12ℓ	0.3048(5)	0.2352(6)	0	1.17(7)
0(2)	24m	0.4983(4)	0.1473(4)	0.1445(3)	1.09(5)
Na	2b	0	0	0	2.3(3)*
Cs	2a	0	0	1/4	2.5(1)*
H_2O	2a	0	0	1/4	2.5(1)*

*Isotropic temperature factors refined only

TABLE 3. ANISOTROPIC TEMPERATURE COEFFICIENTS (β_{ij} x 10^4)

Site	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si	25(2)	25(2)	14(1)	13(2)	0	0
Be	42(9)	20(11)	16(7)	1/2 $_{22}$	0	0
Al	29(2)	$_{11}$	14(2)	1/2 $_{11}$	0	0
0(1)	53(7)	43(6)	39(4)	32(6)	0	0
0(2)	48(4)	54(4)	24(2)	30(3)	-16(3)	-13(3)

TABLE 4. SELECTED INTERATOMIC DISTANCES AND ANGLES

Si-0(1)		1.608(4)Å	Be-0(2)	x 4	1.677(3)Å
Si-0(1)a		1.601(4)			
Si-0(2)	x 2	1.612(3)	Al-0(2)	x 4	1.906(3)
⟨Si-0⟩		1.608			
			Cs-0(2)	x 12	3.439(3)
Na-0(1)	x 6	2.548(5)			
Na-H_2O	x 2	2.310(1)	H_2O-0(2)	x 12	3.439(5)
0(1)-0(1)a		2.548(5)	0(1)-Si-0(1)a		105.2(3)°
0(2)-0(1)a	x 2	2.608(5)	0(2)-Si-0(1)a	x 2	108.6(2)
0(2)-0(1)	x 2	2.657(5)	0(2)-Si-0(I)	x 2	111.2(1)
0(2)-0(2)b		2.670(5)	0(2)-Si-0(2)b		111.8(2)
⟨0-0⟩		2.625	⟨0-Si-0⟩		109.4
0(2)-0(2)c	x 2	2.730(6)	0(2)-Be-0(2)c	x 2	108.9(2)
0(2)-0(2)d	x 2	2.393(5)	0(2)-Be-0(2)d	x 2	91.0(2)
0(2)-0(2)e	x 2	3.053(6)	0(2)-Be-0(2)e	x 2	131.1(2)
⟨0-0⟩		2.725	⟨0-Be-0⟩		110.3
0(2)-0(2)g	x 3	2.706(5)	0(2)-Al-0(2)g	x 3	90.4(2)
0(2)-0(2)d	x 3	2.393(5)	0(2)-Al-0(2)d	x 3	77.8(2)
0(2)-0(2)f	x 6	2.838(5)	0(2)-Al-0(2)f	x 6	96.2(1)
⟨0-0⟩		2.694	⟨0-Al-0⟩		90.2

Equivalent positions: a=y, y-x, -z; b=x, y, -z; c=1-x, -y, -z; d=1+y-x, y, ½-z; e=x-y, -y, ½-z; f=1+y-x, 1-x, z; g=x, x-y, ½-z

DISCUSSION

Comparison of the mean polyhedral bond lengths in non-alkali and alkali beryl (Table 6) indicates that Li^+ substitutes directly for Be^{2+}.

TABLE 5. MAGNITUDE AND ORIENTATION* OF THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS.

	R.M.S. Displacement	Angle to a-axis	Angle to b-axis	Angle to c-axis
Si	0.079(4)Å	90°	90°	0°
	0.091(3)	161(169)	41(169)	90
	0.092(3)	70(171)	50(171)	90
Be	0.081(23)	90	30	90
	0.083(19)	90	90	0
	0.126(17)	0	120	90
Al	0.077(7)	90	90	0
	0.096(4)	90	150	90
	0.096(4)	90	30	90
0(1)	0.100(9)	126(11)	16(11)	90
	0.130(7)	90	90	0
	0.133(8)	46(11)	74(11)	90
0(2)	0.081(7)	63(7)	88(7)	34(5)
	0.117(6)	37(8)	151(8)	104(8)
	0.145(5)	67(7)	61(8)	120(4)

*Large standard deviations on the axis orientations indicate that the vibration directions are not well-defined.

TABLE 6. COMPARISON OF THE BOND LENGTHS IN REFINED BERYL STRUCTURES

		Synthetic beryl	Hydrous beryl	Synthetic beryl	n beryl	Li-Cs beryl	Li-Cs beryl
Si-01		1.594(5)	1.597(5)	1.592(1)	1.598(12)	1.618(12)	1.608(4)
Si-01		1.595(5)	1.592(3)	1.594(1)	1.594(12)	1.599(12)	1.601(4)
Si-02	x 2	1.620(3)	1.628(3)	1.620(1)	1.614(12)	1.617(12)	1.612(3)
⟨Si-0⟩		1.607	1.611	1.607	1.605	1.613	1.608
Al-0	x 6	1.903(3)	1.903(3)	1.904(1)	1.917(8)	1.907(8)	1.906(3)
Be-0	x 4	1.660(3)	1.654(3)	1.653(1)	1.656(12)	1.672(12)	1.677(3)
Reference*		1	1	2	3	4	5

*References: 1 - Gibbs et al. (1968); 2 - Morosin (1972); 3 - Solov'yeva et al. (1966); 4 - Bakakin et al. (1969); 5 - this study

The mean bond lengths for the Si tetrahedron and Al octahedron in Cs beryl are identical with those observed in pure synthetic beryl, whereas the mean bond length for the Be tetrahedron is 0.02Å greater in the Cs beryl; this can only be explained by direct substitution of Li (tetrahedral ionic radius = 0.590Å) for Be (r=0.27Å). Substitution of Li (octahedral ionic radius = 0.76Å) for Al (r=0.535Å) would increase the size of the Al octahedron; this increase was not observed. Thus the present study confirms the model advanced by Bakakin *et al.* (1969) that Li substitutes directly into the Be tetrahedron, and does not occupy the Al octahedron as suggested by Beus (1960) and Mrose & Evans (1966).

Substitution of Li into the Be tetrahedron produces a bond-strength deficiency to the O(2) anion. However, the O(2) anion is remote from the channel in the structure and cannot bond to the channel alkalis. The bond-strength sum around O(2) can be increased by a shortening of the Si-O(2) bond with a concomitant lengthening of the Si-O(1) bonds; inspection of Table 6 shows this to be the case. This leaves a bond-strength deficiency on the O(1) anion that may be compensated by bonding directly to the channel alkalis. The 2*b* site lies in the plane of the hexagonal Si_6O_{18} ring and is surrounded by six oxygen atoms at a distance of 2.55Å, arranged in a planar hexagonal ring. The 2*a* site is halfway between two Si_6O_{18} rings and is surrounded by twelve oxygen atoms arranged in a slightly distorted hexagonal antiprism at a distance of 3.44Å. Examination of inorganic structures containing Na shows that 2.55Å is a typical Na-O bonding distance, whereas 3.44Å is too large to be considered as a bonding contact for Na-O. Using the bond-strength curves of Brown & Shannon (1973), an Na-O distance of 2.55Å would have a bond strength of 0.132, whereas a distance of 3.44Å would have a bond strength of 0.024. If Na occupies the 2*a* position, it must be bonded to two channel waters to have a reasonable bond-strength sum; in this case, the sum would be $(0.024\times12) + 0.23\times2 = 0.71$. However, this requires that the amount of water at the 2*b* position be twice the amount of Na at the 2*a* position. This is incompatible with the observed density at 2*b* and thus Na must occur in the 2*b* site at (000). A similar argument may be applied to the Cs occupancy of the 2*a* site. A distance of 2.55Å is much shorter than any Cs-O bond normally encountered in inorganic crystal structures, whereas 3.44Å lies within the range normally observed. Bond-strength parameters are not currently available for Cs, and thus the arguments used above for Na cannot be directly applied to Cs. However, examination of the bond lengths and bond strengths in a series of alkali-metal metavanadates (Hawthorne & Calvo, in prep.) suggests a bond strength of 0.08 for a Cs-O bond length of 3.44Å. From the observed coordination number of [12], this leads to a bond-strength sum of 0.96 around the Cs, which is in good agreement with the expected value of 1.0. This reinforces our conclusion concerning the distribution of the channel species. The bond-strength sum around Cs approximates its ideal value and hence Cs has no need to bond to the channel water, in agreement with our contention that the observed electron density at the 2*b* site is due solely to Na.

The only problem remaining concerns the role of water in the channel. Examination of the cell contents (Table 1) indicates that there are 0.164 vacancies at the 2*a* site and 0.362 small alkali cations at the 2*b* site; these values provide certain restrictions on the possible local arrangements of channel species. In addition, each of the species substituting into the channel sites has an effect on the neighboring channel sites because of the short distance between the 2*a* and 2*b* sites. Thus the occurrence of Cs at 2*a* must be accompanied by vacancies at the two neighboring 2*b* sites; the occurrence of Na at one of these positions would lead to an incompatible cation-cation distance of 2.31Å as compared with their ionic radii sum of 3.06Å. With a local configuration ($\square_a$–Na–$\square_a$–Na–$\square_a$–Na), there can be a maximum of 0.164 Na per formula unit not bonded to H_2O; hence there is a *minimum* of 0.198 Na per formula unit that must be bonded to H_2O. Wood & Nassau (1968) showed that there are two types of water spectra observed in beryl, and suggested that the reorientation of the water molecule was due to the presence of a neighboring alkali-metal cation. It is clear from the present study that the reorientation of the water molecule is due specifically to a bonding interaction between the small alkali-metal cations (Na and Li) and H_2O.

The H-H vector of non-bonded water is oriented parallel to the *c* axis. In order to avoid a Na-H contact, non-bonded water at 2*a* must be accompanied by vacancies at the two neighboring 2*b* sites. If it is assumed that 0.164 Na per formula unit is not bonded to any water, then simple stoichiometric arguments, combined with the occurrence of vacancies surrounding both Cs and non-bonded H_2O, indicate that all remaining Na (0.198 atoms per formula unit) must be bonded to two H_2O molecules. Alternatively, if it is assumed that Na is always bonded to H_2O, then 0.328 Na per formula unit may be bonded only to one H_2O molecule, with the remaining 0.034 atoms bonded to two H_2O molecules; as this remaining amount of Na (small alkali cations) is approximately equal to the amount of Li occurring in the channel (0.049 atoms per formula unit), it is tempting to draw the conclusion that channel Na bonds to one H_2O molecule whereas channel Li bonds to two water molecules. However, there is no direct evidence of this.

A consideration of the bond strengths around the channel cations should give some further indication as to the local configuration around the small alkali cations in the channels. As indicated above, the observed 2*a*-O(1) distance of 2.548Å gives a bond-strength sum of 0.79 v.u. around the Na position; this is considerably lower than the ideal value of 1.0 v.u. However, the observed 2*a*-2*b* distance of 2.31Å indicates a bond strength of 0.23 v.u. for a Na-H_2O bond, bringing the bond-strength sum around the Na close to its ideal value. This suggests that Na will always bond to one H_2O molecule in order to satisfy its bond-strength requirements. If the 2*b* site is occupied by Li, the bond-strength sum around the Li is $0.082 \times 6 + 0.122 \times 2 = 0.738$ v.u., assuming that Li is bonded to two H_2O molecules. Although this is significantly less than the ideal value of 1.0 v.u., it is possible that the bond strength is satisfied by a contraction of the 2*b*-O(1) distance when 2*b* is occupied by Li (a factor that will not be apparent in the refinement due to the low occupancy of 2*b* by Li and the averaging effect of X-rays) and/or a slight positional disorder of H_2O at the 2*a* position.

Although the arguments given above suggest that Na need bond only to one H_2O molecule, the stoichiometry of some alkali-rich beryls (e.g. Feklitchev 1964, 6c and 7; Deer *et al.* 1962, 13; Beus 1960, 38; Bakakin *et al.* 1970, 25) indicate that some Na must be bonded to two H_2O molecules. Although this would tend to produce a bond-strength excess around the Na, this could be compensated by a slight positional disorder of the H_2O molecules off the 2*a* position and away from the Na atom. As Na is bonded to channel water molecules, the Na content of a beryl should impose a lower limt on possible water content, and may give some indication of whether Na is generally bonded to one or two H_2O molecules. Figure 2 shows the variation of H_2O with that of Na in a number of analyzed beryls taken from the literature. Approximately 85% of the analyses fall to the water-rich side of a line $Na=2H_2O$, indicating that there is more than sufficient water to satisfy the bonding requirements of Na in the channel. Of the remaining 15% of the analyses, most have a considerable number of vacancies at the tetrahedral and/or octahedral sites. It is unlikely that the framework structure of beryl can accommodate vacancies in the amounts suggested by these analyses. Conversely, it is unlikely on the basis of ionic size that Na would substitute into these sites. Although many of the analyses were not performed for minor components such as Mg, Fe^{2+}, Fe^{3+}, Cr or N, the total wt. % of the oxides is generally ~100%, apparently precluding the possibility of these minor components being present in amounts sufficient to fill the vacancies at the tetrahedral and/or octahedral sites. Partly in order to resolve this point, a statistical study of chemical variations in beryls is being undertaken. In spite of the conflicting analyses, Figure 2 does suggest that the Na content of alkali beryls may control the minimum possible amount of water present in the structure.

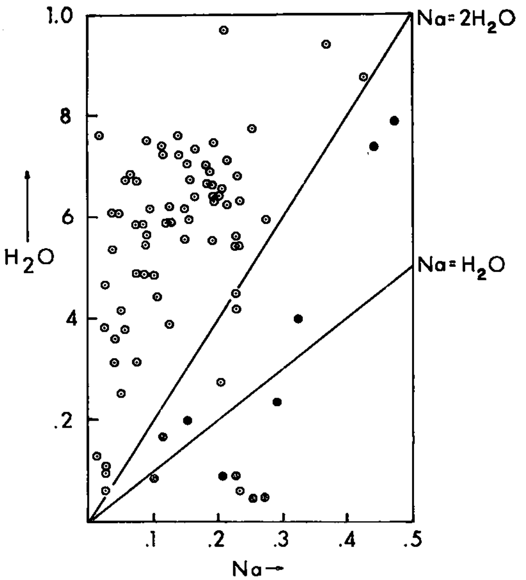

FIG. 2. The variation of Na and water in published beryl analyses. The full circles indicate analyses with vacancies at the octahedral and/or tetrahedral sites in the structure.

As indicated previously, each of the cation species substituting into the channel sites has an affect on the neighboring channel sites. Thus, limits will be imposed on the amount of each substitution that may occur in the beryl structure. From the arguments presented above, Na is bonded to one or two H_2O molecules at adjacent 2*a* sites; because these H_2O molecules are oriented so that the hydrogen atoms project up the channel, away from the Na atom, the surrounding 2*b* site(s) must be vacant in order to

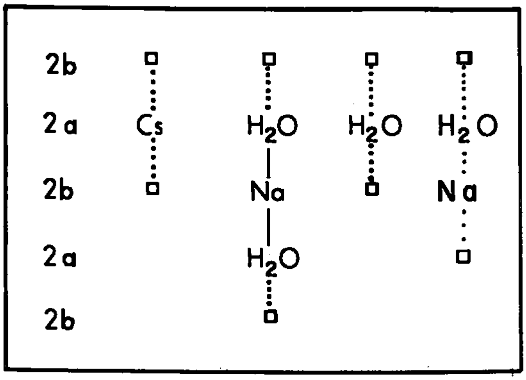

FIG. 3. The effect of channel species on adjacent channel sites in the beryl structure.

avoid a Na-H contact. All of the channel configurations are identified in Figure 3 and the maximum possible substitution of each is given in Table 7. Examination of approximately 100 published beryl analyses shows that these limits are not exceeded, although they are approached by extreme compositions.

TABLE 7. MAXIMUM LIMITS OF ALKALI SUBSTITUTION IN BERYL

Wyckoff symbol	a	b	c	f	l
Equipoint rank	2	2	4	6	12
1.	Cs_2	–	Al_4	Be_4Li_2	Si_{12}
2.*	$(H_2O)_2$	Na_1	Al_4	Be_5Li_1	Si_{12}
3.**	$(H_2O)_{1.33}$	$Na_{1.33}$	Al_4	$Be_{4.67}Li_{1.33}$	Si_{12}
4.	$(H_2O)_2$	–	Al_4	Be_6	Si_{12}

*$Li^+ + Na^+ + 2H_2O \rightleftharpoons Be^{2+} + \square_b + 2\square_a$

**$Li^+ + Na^+ + H_2O \rightleftharpoons Be^{2+} + \square_b + \square_a$

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