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INFRARED SPECTROSCOPY AND CRYSTAL CHEMISTRY OF THE BERYL GROUP

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ABSTRACT

The infrared spectra of 27 natural and two synthetic samples of powdered beryl were measured at room (25°C) and liquid nitrogen (–180°C) temperatures. Water molecules occur in two different orientations (type I and type II), for which absorption bands are clearly visible at low temperatures. The ratio of the absorbances due to type-II and type-I O–H stretching modes at 3600/3698 and 3660/3698 cm^{-1} show a positive correlation with Na content, and show that high concentration of alkalis is responsible for the type-II configuration. The presence of hydroxyl groups, in a H_2O (type II) – Na – (OH) configuration, is proposed for alkali-rich beryl on the basis of the 3658 cm^{-1} absorbance. The absorption frequencies for different samples of beryl are correlated with structural and compositional parameters. Unsubstituted beryl, beryl with substitutions in the octahedral site, and beryl with substitutions in the tetrahedral site, are clearly discriminated using absorption bands in the range 1060–1020 cm^{-1}. The relationships help to reconcile controversies concerning the proper assignment of absorption frequencies to structural details.

Keywords: beryl, crystal chemistry, infrared spectrum, H_2O orientation.

SOMMAIRE

Le spectre infrarouge de vingt-sept échantillons naturels et de deux échantillons synthétiques de béryl ont été mesurés à température ambiante (25°C) ainsi qu'à la température de l'azote liquide (–180°C). Les molécules d'eau se trouvent dans une de deux orientations différentes (dites de type I et de type II); leurs bandes d'absorption sont rendues très évidentes dans les spectres obtenus à basse température. Le rapport des absorptions dues au mode d'étirement de la liaison O–H de type I et de type II, 3600/3698 et 3660/3698 cm^{-1}, montrent une corrélation positive avec la teneur en Na, et démontrent que la teneur élevée en alcalins est responsable de la présence de molécules d'eau de type II. Des groupes d'hydroxyle dans une configuration H_2O (type II) – Na – (OH) seraient responsables de l'absorption à 3658 cm^{-1} dans le béryl enrichi en alcalins. Les fréquences d'absorption dans les différents échantillons de béryl sont analysées en fonction des paramètres structuraux et compositionnels. Nous pouvons distinguer facilement le béryl sans substitution, le béryl ayant une substitution impliquant le site à coordinence octaédrique, et le béryl ayant une substitution impliquant le site à coordinence tétraédrique, en utilisant les bandes d'absorption dans l'intervalle 1060–1020 cm^{-1}. Les relations que nous décrivons contribuent à éclaicir les aspects controversés de l'attribution des fréquences d'absorption aux caractères structuraux.

(Traduit par la Rédaction)

Mots-clés: béryl, chimie cristalline, spectre infrarouge, orientation des molécules d'eau.

INTRODUCTION

Substitutions involving tetrahedrally and octahedrally coordinated cations and the presence of channel constituents (*e.g.*, H_2O, Na, OH) influence the infrared (IR) absorption spectrum of beryl. In this paper, we explore the influence of the *c*/*a* ratio, bond distances, and site occupancies on the position of vibration bands. This type of analysis can help to characterize materials commonly found in very small amounts. We also propose a solution to discrepancies in the assignment of the IR bands to Be–O and ring Si–O–Si bonds.

The availability of a large number of beryl samples that cover the full range of chemical variation recognized to date invited a systematic study by infrared-absorption spectroscopy in order to characterize fully the broadly variable crystal chemistry of beryl. In a previous paper (Aurisicchio *et al.* 1988), we re-evaluated the complex crystal-chemistry of beryl on the basis of new chemical data and X-ray refinements of the structure of beryl samples of different compositions and from different sources. Our evaluation showed that the main substitutions involve divalent and trivalent ions (Fe^{2+}, Mn^{2+}, Mg^{2+}, Fe^{3+}, Cr^{3+}), as well as V^{5+} and Ti^{4+} for Al in the octahedrally coordinated site and Li for Be in the tetrahedrally coordinated (T') site. Substitutions giving rise to charge imbalance require the incorporation of alkali ions (Na) into the channel in the $2a$ position, between the stacked six-membered Si rings, whereas Cs, Rb, and K enter the $2b$ position, at the center of each ring. The H_2O molecules fit in the $2a$ sites only. The effects of these substitutions on the cell parameters led to the definition of two solid-solutions series on the basis of the c/a ratio: i) octahedrally substituted beryl, with c/a values from 0.991 to 0.996, with substitutions in the O site: $\mathrm{Me}^{3+}\mathrm{Al}_{-1}$ or $R_{f\,\mathrm{channel}}^{+}Me^{2+}\square_{-1}\mathrm{Al}_{-1}$, and (ii) tetrahedrally substituted beryl, with c/a values in the range from 0.999 to 1.003, with substitutions in the T' site: $R_{f\,\mathrm{channel}}^{+}\mathrm{Li}^{+}\square_{-1}\mathrm{Be}_{-1}$.

The two series depart, with opposite slope, from "normal" (*i.e.*, unsubstituted) beryl (c/a in the range 0.997–0.998), which shows a composition close to the ideal stoichiometry, with a very low degree of substitution in both sites (*cf.* Figs. 5 and 6 in Aurisicchio *et al.* 1988). In the first series, a increases from 9.22 to 9.27 Å, and the c parameter remains approximately constant. In contrast, in the second series, the parameter a remains approximately constant, but c increases from 9.20 to 9.24 Å. Two end members can be derived from the above variations away from unsubstituted "normal" beryl $Al_2Be_3Si_6O_{18}\cdot zH_2O$:

[1] $R_f^{+}\mathrm{Al}Me^{2+}\mathrm{Be}_3\mathrm{Si}_6\mathrm{O}_{18}\cdot z\mathrm{H}_2\mathrm{O}$, octahedrally substituted beryl, and

[2] $R_f^{+}\mathrm{Al}_2\mathrm{Be}_2\mathrm{LiSi}_6\mathrm{O}_{18}\cdot z\mathrm{H}_2\mathrm{O}$, tetrahedrally substituted beryl,

where R_f^{+} = Na, Cs, Rb, K, in the sequence of decreasing average abundances, as proposed by Bakakin *et al.* (1970).

EXPERIMENTAL

IR spectra of two synthetic and 21 natural samples of beryl from different sources, chemically characterized by Aurisicchio *et al.* (1988), are the subject of this investigation. Beryl samples #31, #32 and #33 are new acquisitions since the 1988 paper appeared. The first (#31) is an emerald from the St. Teresiña mine, Brazil; #32 is a beryl transitional from "normal" to the tetrahedrally substituted variety from the

TABLE 1. CHEMICAL COMPOSITION OF BERYL SAMPLES

	31	32	33
SiO_2	64.36	63.65	64.78
Al_2O_3	13.99	17.54	14.84
Cr_2O_3	0.32	—	0.11
FeO	1.11	0.07	0.72
MgO	2.68	—	2.36
MnO	—	0.01	—
TiO_2	0.22	—	—
BeO	13.03	11.37	13.11
Li_2O	0.05	0.97	0.04
CaO	—	0.23	
Na_2O	2.03	1.60	1.64
K_2O	—	0.22	
Cs_2O	0.33	2.57	—
Rb_2O	—	—	0.06
L.O.I	2.00	1.97	2.01
Total	100.12	100.26	99.61
Numbers of ions on the basis of 18 atoms of oxygen			
Si	6.016	6.025	6.033
Al	1.541	1.957	1.628
Cr	0.024	—	0.008
Fe^{3+}	0.009	0.006	0.008
Fe^{2+}	0.077	—	0.048
Mg	0.373	—	0.328
Mn	—	0.006	—
Ti	0.015	—	—
Be	2.925	2.585	2.932
Li	0.019	0.369	0.015
Ca	—	0.023	—
Na	0.368	0.294	0.296
K	—	0.027	0.008
Cs	0.013	0.103	—
Rb	—	0.002	
c/a	0.9927	0.9986	0.9938

Samples 31 and 33 have been analyzed by the authors following the same techniques as described in Aurisicchio et al. (1988). Sample 32 was analyzed by the wet-chemical method in the Geochemistry Institute of the Academia Sinica, Guiyang, China. Dash: below limit of detection; Fe^{3+} by charge balance; L.O.I.: loss on ignition.

TABLE 2. DESCRIPTION AND LOCALITIES OF BERYL SPECIMENS

N°	SAMPLE	LOCALITY
1	Dark blue	Calcaferro Mine, Pietrasanta, Tuscany, Italy
2	Light blue	Calcaferro mine, Pietrasanta, Tuscany, Italy
3	Dark blue zoned	South Mount Cervandone, Piedmont, Italy
4	Dark green zoned	Mingora, Swat Valley, Pakistan
5	Light green	Val Vigezzo, Piedmont, Italy
6	Blue	Mohave Co., Arizona, n°117199 Smithsonian Institution
7	Pink-red zoned core	Wah Wah Mountains, Beaver Co., Utah
8	Pink-red zoned rim	Wah Wah Mountains, Beaver Co., Utah
10	Dark green	Muzo, Colombia
11	Pale green	Jos, Nigeria
12	Blue	Karoi, Zimbabwe
13	Light blue	Mursinka, Urals Mountains, Russia
15	Very pale blue	Cava Grignaschi, Val d'Ossola, Piedmont, Italy
16	Yellow	Fort Victoria Field, Zimbabwe
17	Very pale blue	S.Piero in Campo, Tuscany, Italy
18	Pale pink	Mt. Bity region, Madagascar
19	Light blue core of 20	Minas Gerais, Salinas Mine, Brazil
20	Pale pink rim of 19	Minas Gerais, Salinas Mine, Brazil
22	Pink	Nuristan region, Mawi Mine, Afgan
23	Green	Habachtal, Salzburg, Austria
24	Green	Morrua, Zambesia
26	Light green	Urals Mountains Russia
27	Pink	Mujane Mine, Zambesia
28	Pale pink	Pala Mine California
31	Dark green	Santa Teresiña, Brazil
32	White pinkish	Kokotohai, Xingian, China
33	Dark green	Djebel Zabarah, Egypt
S1	Colorless	Synthetic
S2	Dark green	Synthetic

Koktokay pegmatite, Xinjiang, China, and #33 is an emerald from Djebel Zabarah, Egypt (Grubessi *et al.* 1990). Analytical data are given in Table 1. Table 2 is a list of all the samples, with details of color and provenance. For the chemical composition, structural parameters and mineral associations of the samples other than the three new ones, the reader is referred to Tables 3 and 4 in Aurisicchio *et al.* (1988).

Infrared-absorption spectra were recorded in the 4000 to 300 cm^{-1} region using the Perkin Elmer models 580B and 983 spectrometers. Both instruments gave a resolution better than 3 cm^{-1} across the range examined. Samples were prepared as compressed disks of powdered beryl and KBr (2 to 5 weight %) to minimize polarization effects. To avoid the effect of absorbed water, the KBr was dehydrated at 150°C for 24 hours prior to analysis. Transparent KBr disks were prepared always using the same amount (200 mg) of a mechanically ground powder compacted under 10^{10} Pa pressure. Experiments were performed at room temperature and at –180°C on the same disks, using a liquid-nitrogen-cooled cell. The temperature was monitored *via* a thermocouple placed close to the disk. Control measurements were performed on a sample of powdered beryl, before and after heating at 1000°C. As to the potential freezing of H_2O in beryl or in KBr (moisture), its absorption band should be in the range from 3350 to 3150 cm^{-1} (Farmer 1974); none was observed.

The spectra collected at the temperature of liquid nitrogen showed the best resolution of specific absorption bands, permitting better insight into the spectra. The actual IR spectra can be obtained from the authors. Correlations with structural parameters are based on a smaller number of points because only 15 samples of beryl were analyzed by single-crystal X-ray diffraction.

DISCUSSION

OH-stretching region, 3800 – 3400 cm^{-1}

In the 3800–3400 cm^{-1} frequency range, absorption bands were assigned by Wood & Nassau (1968) to two types of H_2O molecules, defined as type I (the 2-fold axis of symmetry of the H_2O molecule normal to the crystal's 6-fold axis) and type II (the 2-fold axis of symmetry of the H_2O molecule is parallel to the crystal's 6-fold axis). Our observations confirm the existence of these two types of H_2O, and they also suggest the presence of OH groups associated with the alkalis in the channels (Figs. 1A, B, C), as explained below. At room temperature, absorbances due to molecular H_2O are easily distinguished: 3698 cm^{-1} generated by H_2O of type I, and 3663 cm^{-1} plus 3600 cm^{-1} indicative of H_2O of type II (Fig. 2). Samples of "normal" beryl (*e.g.*, sample 11) show the almost exclusive presence of type-I H_2O. However,

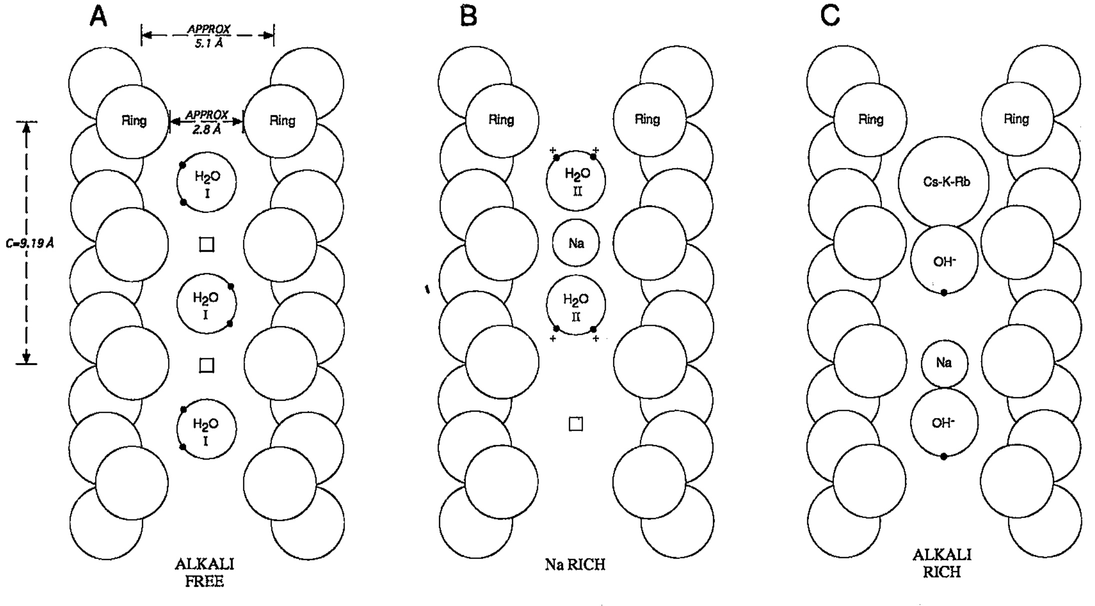


FIG. 1. A. Channel configuration of alkali-free beryl, with H_2O of type I, □: vacancies. B. Channel configuration of sodium-rich beryl, with type-II H_2O. C. Channel configuration of alkali-rich beryl promoting a OH^- group. Modified after Aines & Rossman (1984).

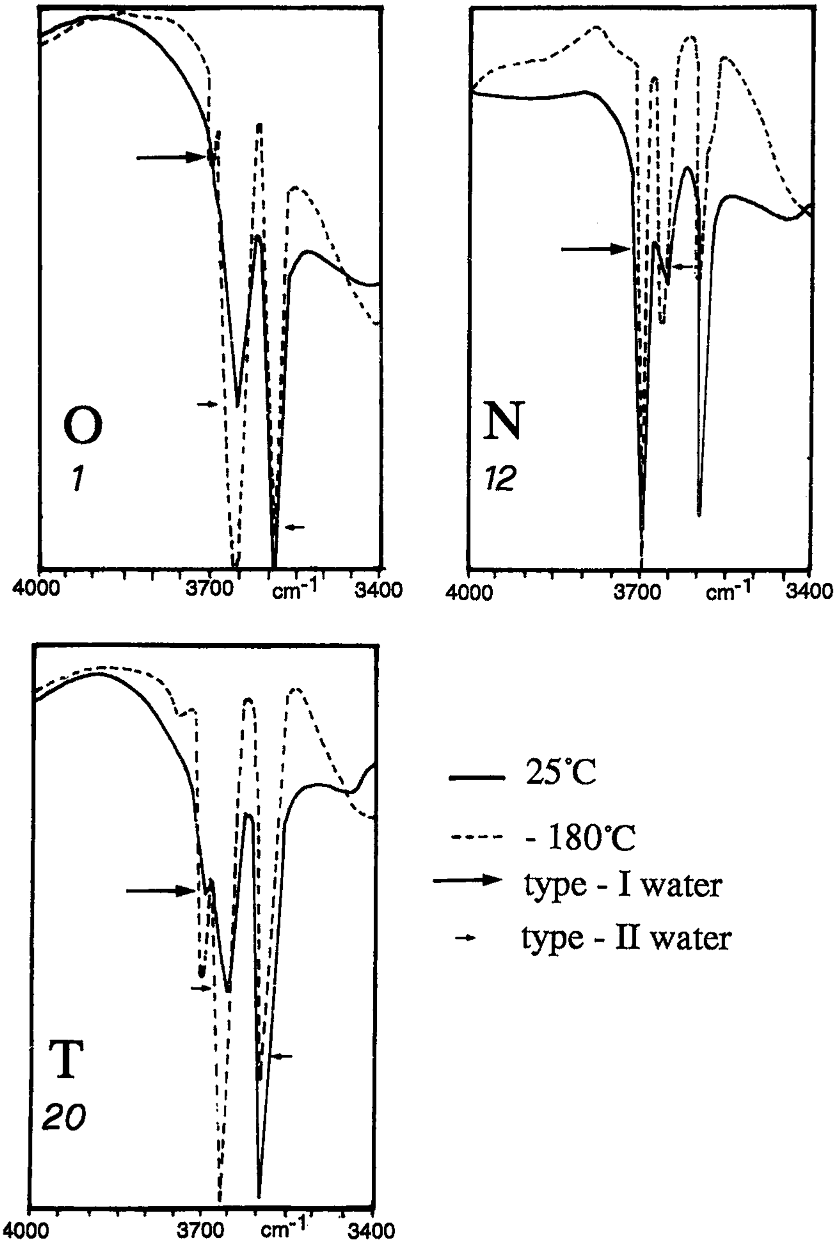


FIG. 2. IR spectra showing evidence of type-I and type-II H_2O in beryl: O: octahedrally substituted beryl, T: tetrahedrally substituted beryl, N: normal or unsubstituted beryl; samples 1, 12, and 20 (see Table 2).

with increased substitutions for Al (octahedrally substituted beryl: *e.g.*, sample 1) and for Be (tetrahedrally substituted beryl: *e.g.*, sample 20), coupled with incorporation of alkalis into channels, type-II H_2O becomes dominant; the dipole effect of H_2O molecule attracts its oxygen to the alkali cation in the 2*a* site, and turns its 2-fold axis parallel to the channel, *i.e.*, parallel to the 6-fold axis of beryl.

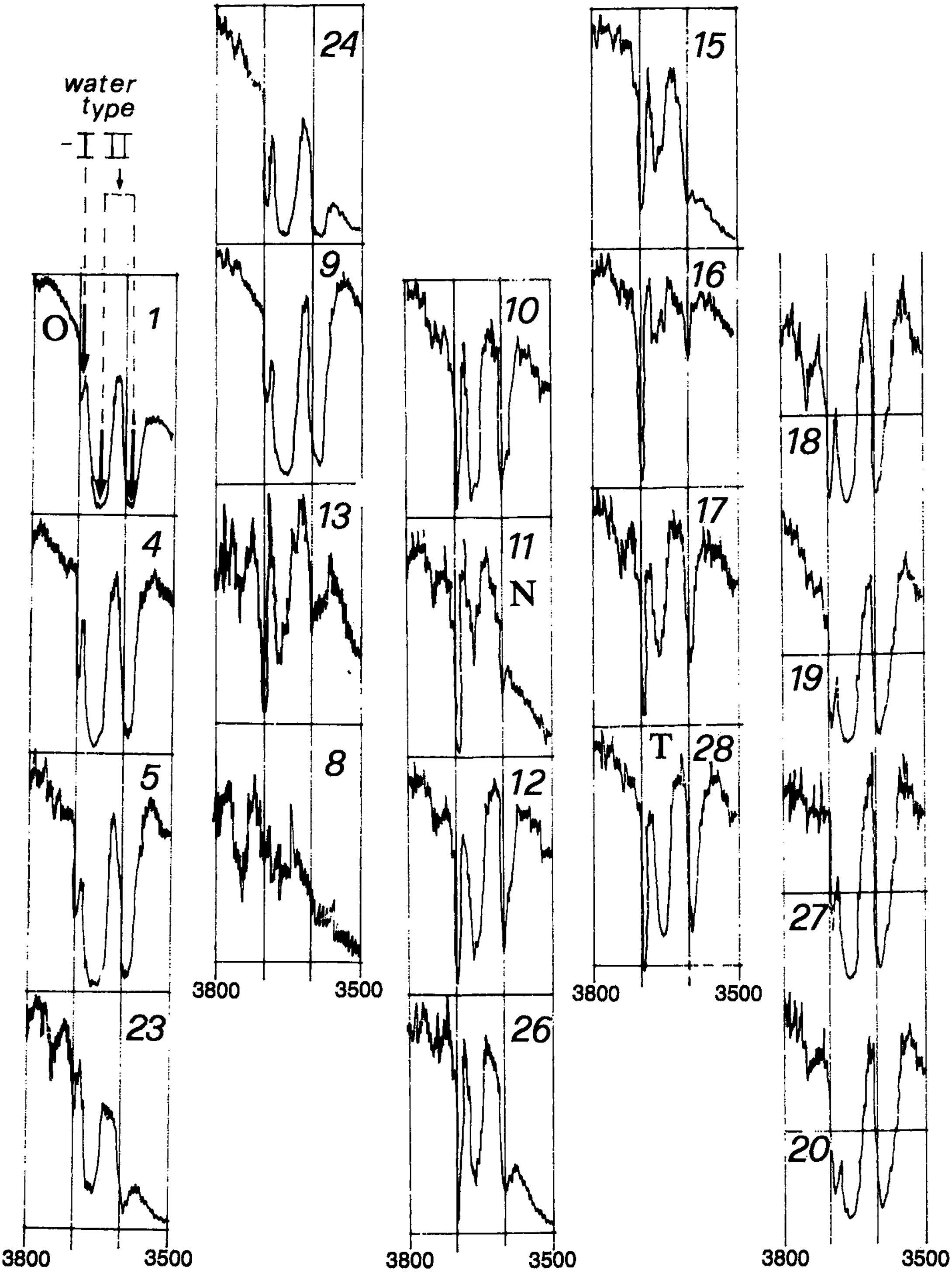


FIG. 3. Transmission infrared spectra of beryl in the range 3800 – 3500 cm^{-1} at the temperature of liquid nitrogen (–180°C).

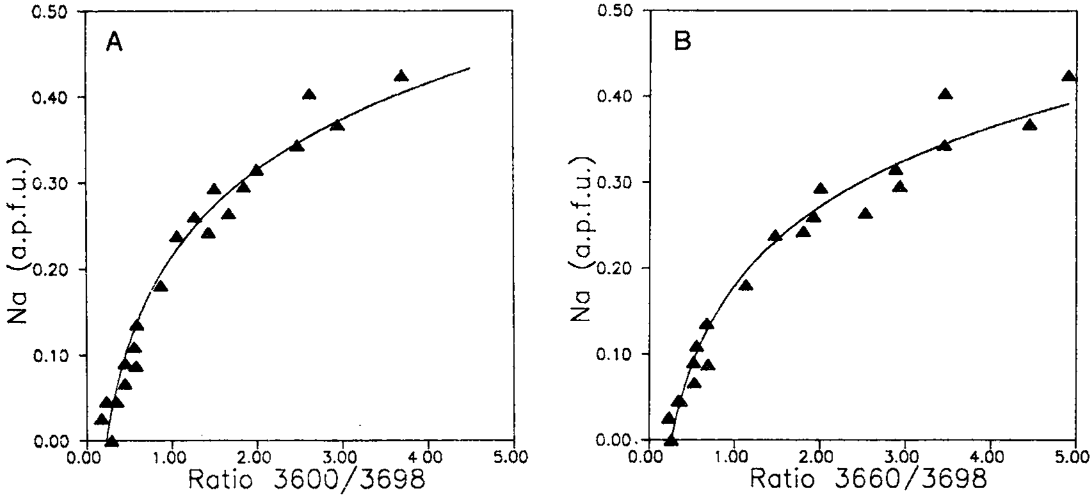


FIG. 4. Ratios of the intensities of the absorption bands 3600/3698 (A) and 3660/3698 (B) (type II/type I) at –180°C *versus* the sodium content, in atoms per formula unit. A logarithmic function fits the experimental data very well.

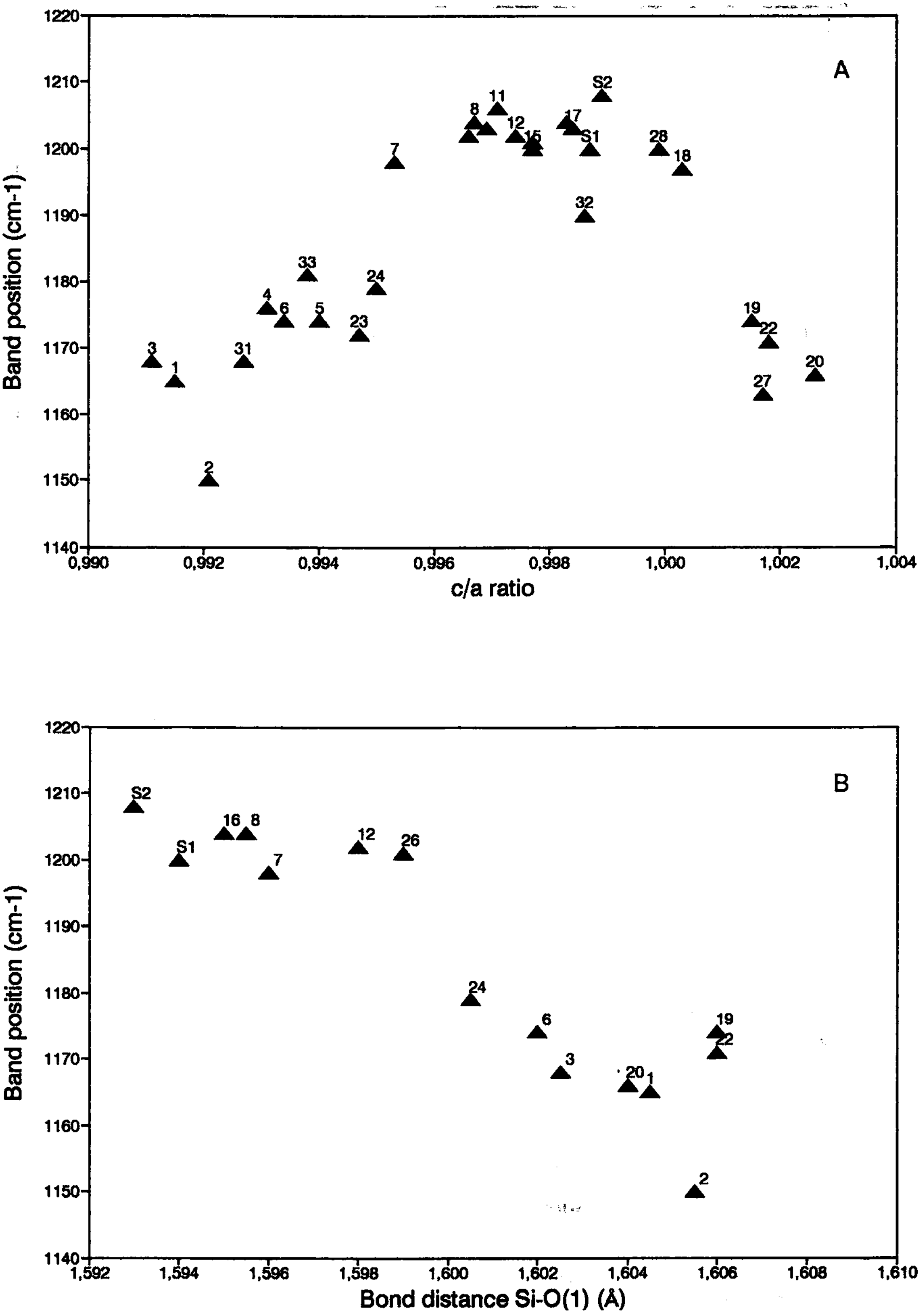
The same effect was observed in the closely related structure of cordierite; Wallace & Wenk (1980) and Armbruster (1986) obtained similar H_2O spectra for this mineral, and correlated type-II H_2O with the presence of alkali ions in the channels.

The low-temperature infrared-absorption spectra show a marked increase in absorbances due to both type-I and type-II H_2O (Fig. 3). Moreover, a change in the ratio of intensities of the bands attributed to type-II H_2O bands was observed. The absorbance at 3663 cm^{-1} increases, whereas that at 3600 cm^{-1} decreases. This observation may be explained by assuming that at room temperature, the 3663 cm^{-1} band is not a single absorption, but in fact a combination of at least two absorption bands, one due to type-II H_2O at 3663 cm^{-1} (a very weak shoulder may be seen on some spectra), and one at 3658 cm^{-1} due to the OH–Na association. Na-poor samples generate only a minor effect at 3658 cm^{-1} (samples 10, 12, 26, 28), but the absorbance increases for Na-rich beryl (samples 1, 4, 23). This correlation, coupled with the increase in absorbance at a low temperature (Katz 1962), explains the increased absorbance and broadening of the 3663 cm^{-1} band. Figure 1C shows a possible configuration for an OH and an alkali cation. Several authors (Wickersheim & Buchanan 1959, 1967, Manier-Glavinaz *et al.* 1989, Schmetzer and Kiefert 1990) suggested the presence of $(OH)^-$ groups in the beryl structure, either in the oxygen sites or in the channels; Sherriff *et al.* (1991) found the presence of OH compatible with the available evidence and discussed its potential site-allocation. However, a definite structural assignment is not feasible at present. We favor the channel hypothesis, because the measured frequency of absorption fits that of hydroxyl linked to an alkali cation (Ross 1972). Charge balancing of underbonded oxygen seems to rule out such a link; however, the $(OH)^-$ group may be attracted to a channel cation in a similar fashion as the H_2O dipole. Taking into account the absorbances, I_{3600}, I_{3660} (= overlap of 3663 and 3658 cm^{-1}) and I_{3698} of the three bands, correlated to type-II, type-(II+OH), and type-I H_2O, respectively, the ratios $R1 = I_{3600}/I_{3698}$ and $R2 = I_{3660}/I_{3698}$ have been calculated. The sodium content (Figs. 4A, B) shows a good positive correlation with both ratios, indicating a preference of the type-II and type-(II+OH) configurations in the presence of channel alkalis. This can be considered a reasonable configuration along the channel, and it should generate two O–H stretching frequencies.

The sodium content (y) can be expressed by a function such as $y =$

$$y_{sat}\,(1 - e^{-kRi})$$

shown on Figures 4A and 4B, where y_{sat} represents the maximum sodium content in beryl (close to 0.5 atoms per formula unit, pfu), k is a constant (close to 0.5 for $R1$ and 0.4 for $R2$). The same correlation applied to measurements made at room temperature is rather poor, with considerable scatter in the experimental data. The frequency of the broad band at 3600 cm^{-1} appears to be affected by sodium content. Samples with no sodium have a maximum absorbance at 3600 cm^{-1} (sample 11). In samples with medium to high sodium content, the frequency is displaced to 3588 cm^{-1}. If both cesium and sodium are present, the absorption band is close to 3595–3597 cm^{-1}. This suggests that the "3600 cm^{-1}" absorption frequency is


A
Band position (cm-1)
1140
1150
1160
1170
1180
1190
1200
1210
1220
c/a ratio
0,990
0,992
0,994
0,996
0,998
1,000
1,002
1,004
3
1
2
31
4
6
33
5
23
24
7
8
11
12
15
17
S1
S2
32
28
18
19
22
27
20
B
Band position (cm-1)
1140
1150
1160
1170
1180
1190
1200
1210
1220
Bond distance Si-O(1) (Å)
1,592
1,594
1,596
1,598
1,600
1,602
1,604
1,606
1,608
1,610
S2
S1
16
8
7
12
26
24
6
3
20
1
19
22
2

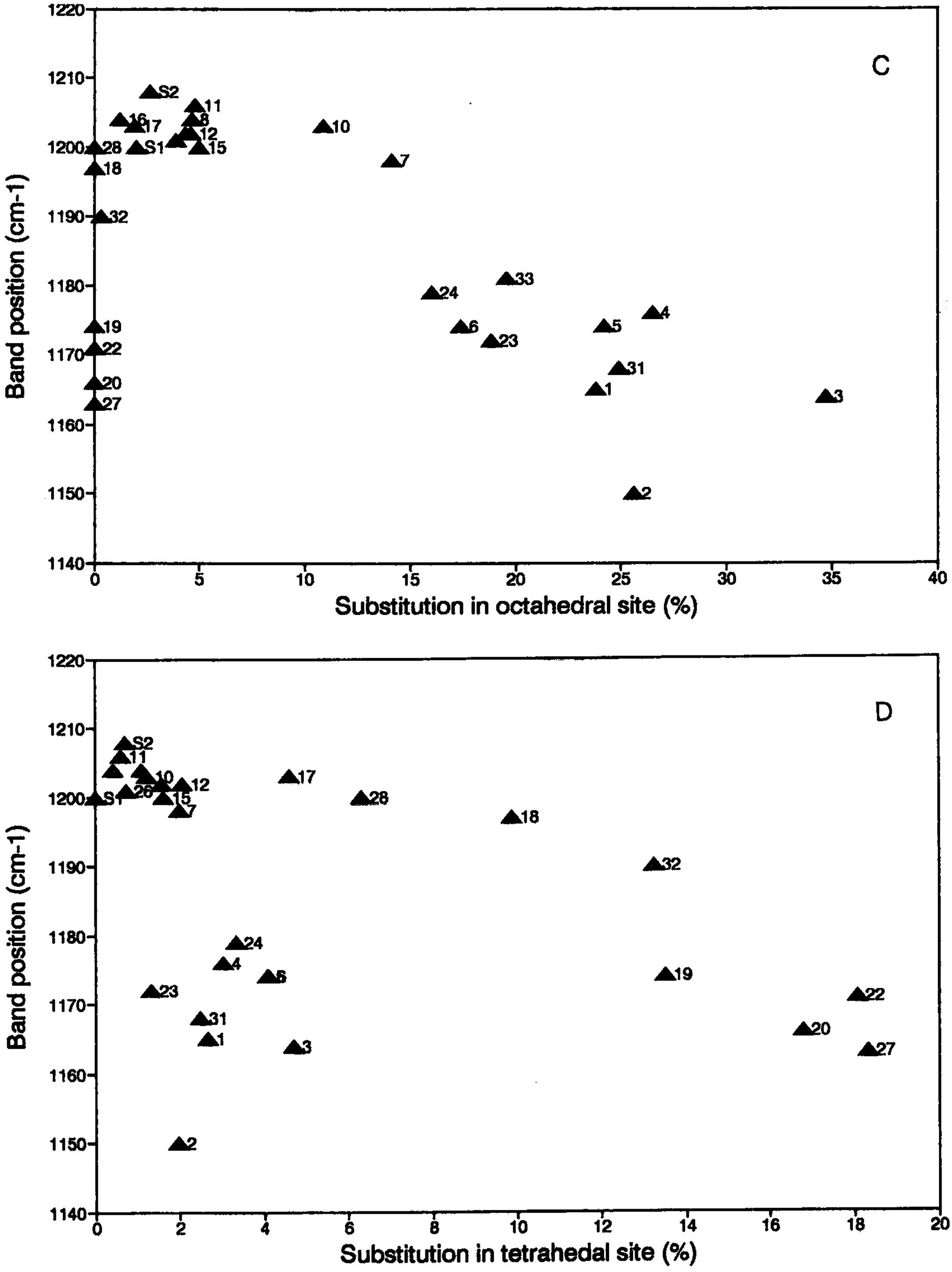


FIG. 5. Frequencies of the band at 1200 cm^{-1} *versus* the *c*/*a* ratio (A), bond distance Si–O(1) (B), substitution in the octahedrally coordinated site (C), and substitution in the tetrahedrally coordinated *T'* site (D).

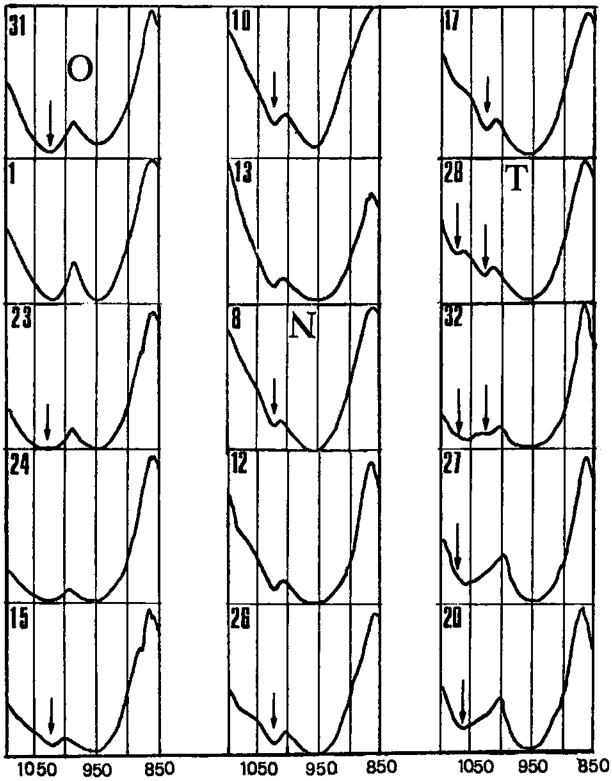


FIG. 6. Transmission infrared spectra of beryl in the range 1100–850 cm^{-1} at a T of –180°C, showing the trend of the bands at 1020 and 1060 cm^{-1}. Transition from octahedrally substituted beryl (samples 31, 1, 23, 24, 15, 10, 13), through "normal" (unsubstituted) beryl (samples 8, 12, 26, 17), to tetrahedrally substituted beryl (samples 28, 32, 27, 20).

due to a combination of at least three different absorption bands: type-II H_2O, OH–Na, and OH–Cs vibrations (Figs. 1B, C). The width of this absorption, which increases with amount of cesium, is in agreement with the hypothesis of multiple absorptions in this range of wavenumbers. This peculiar structure could support the presence of $(OH)^-$ ions in the 2*a* site.

The analytical results show that the lowest content of type-I H_2O corresponds to the highest amounts of sodium and that, at low temperature, the increasing absorption at 3658 cm^{-1} may be correlated with sodium within the channels. This is in good agreement with the assumed presence of $(OH)^-$ groups in the vicinity of sodium.

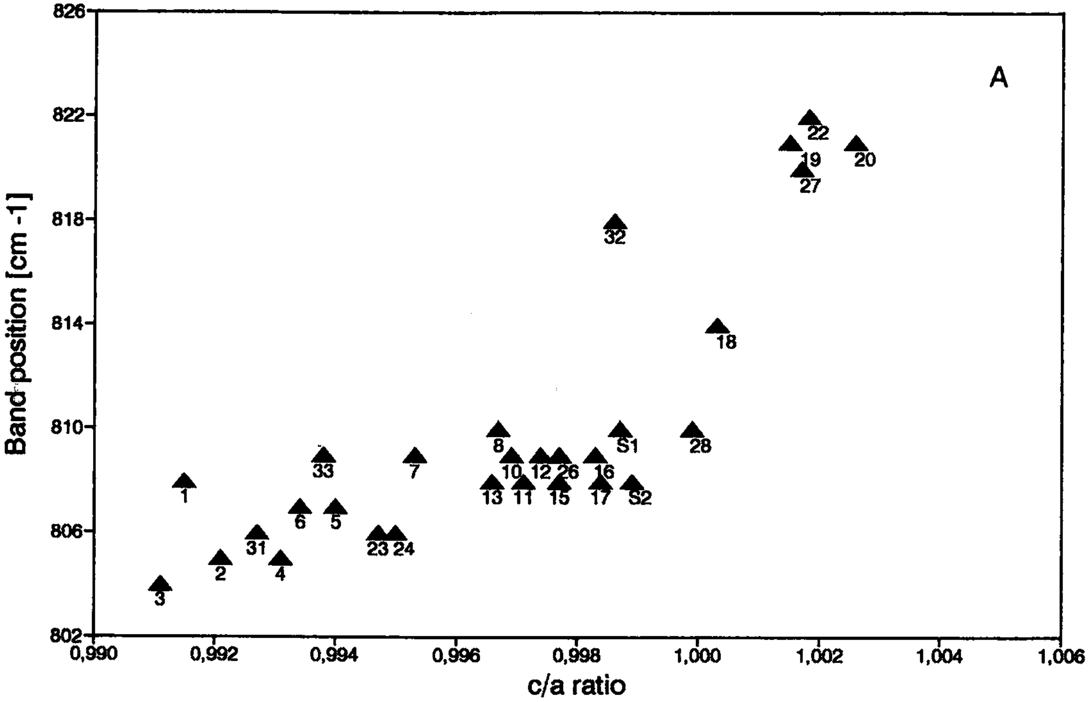
Structural vibrations in the interval 1200–400 cm^{-1}

In order to relate each absorption band in the range 1200–400 cm^{-1} to the structure, the wavenumbers were systematically correlated with structural parameters (*c*/*a* ratio, bonds lengths, site occupancies) as given by Aurisicchio *et al.* (1988), and compared with interpretations published in the literature.

The absorption band at 1200 cm^{-1} is assigned by many authors to Si–O–Si ring vibrations (Gervais & Piriou 1972, Adams & Gardner 1974, Hofmeister *et al.* 1987), or to the vibration in BeO_4 tetrahedra (Plyusnina 1964). An analysis of this absorption correlated to the *c*/*a* ratio (Fig. 5A) shows that in "normal" beryl, the frequency is close to 1200 cm^{-1}, whereas the samples with substitutions in the octahedrally and tetrahedrally coordinated (*T*) sites show a similar shift of the band to lower frequencies.

Plots of the position of the 1200 cm^{-1} band against *c*/*a* ratio (Fig. 5A) show a good positive correlation for the trend from octahedrally substituted to "normal" beryl, and a negative one for the trend from "normal" to tetrahedrally substituted beryl.

The extent of substitutions for Al and Be in beryl (Figs. 5C, D) leads to an incorporation of alkali ions (R_f^+). The two effects cause a shift and broadening of


A
Band position [cm -1]
826
822
818
814
810
806
802
c/a ratio
0,990
0,992
0,994
0,996
0,998
1,000
1,002
1,004
1,006
1
2
3
4
5
6
7
8
10
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22
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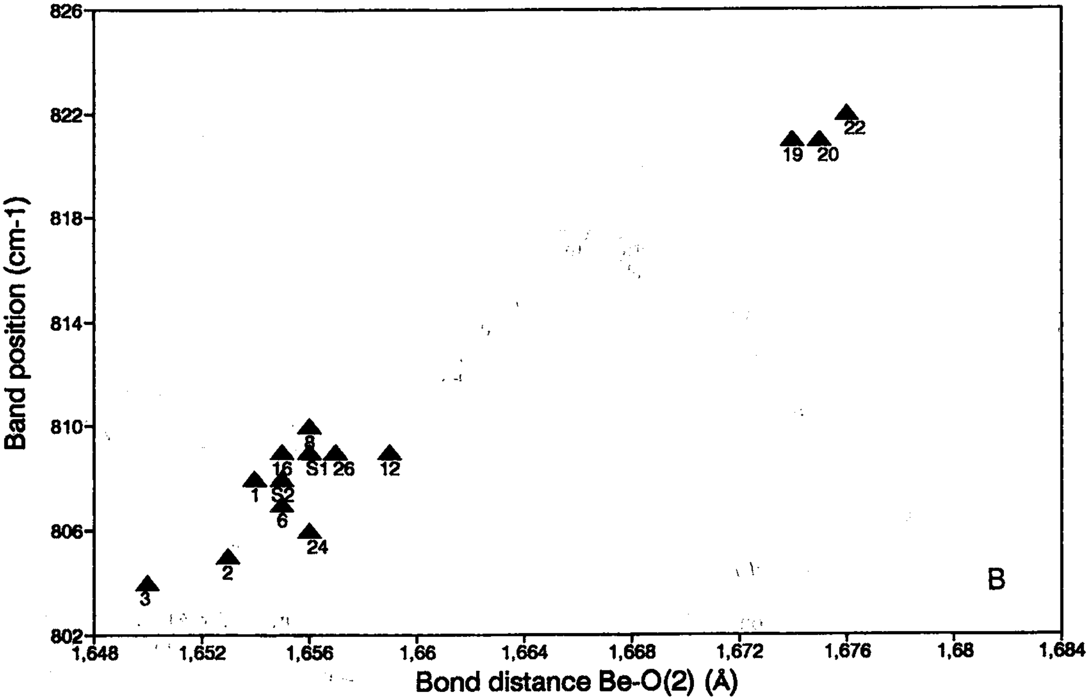
28
31
32
33
S1
S2


B
Band position (cm-1)
826
822
818
814
810
806
802
Bond distance Be-O(2) (Å)
1,648
1,652
1,656
1,66
1,664
1,668
1,672
1,676
1,68
1,684
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2
3
6
8
12
16
19
20
22
24
26
S1
S2

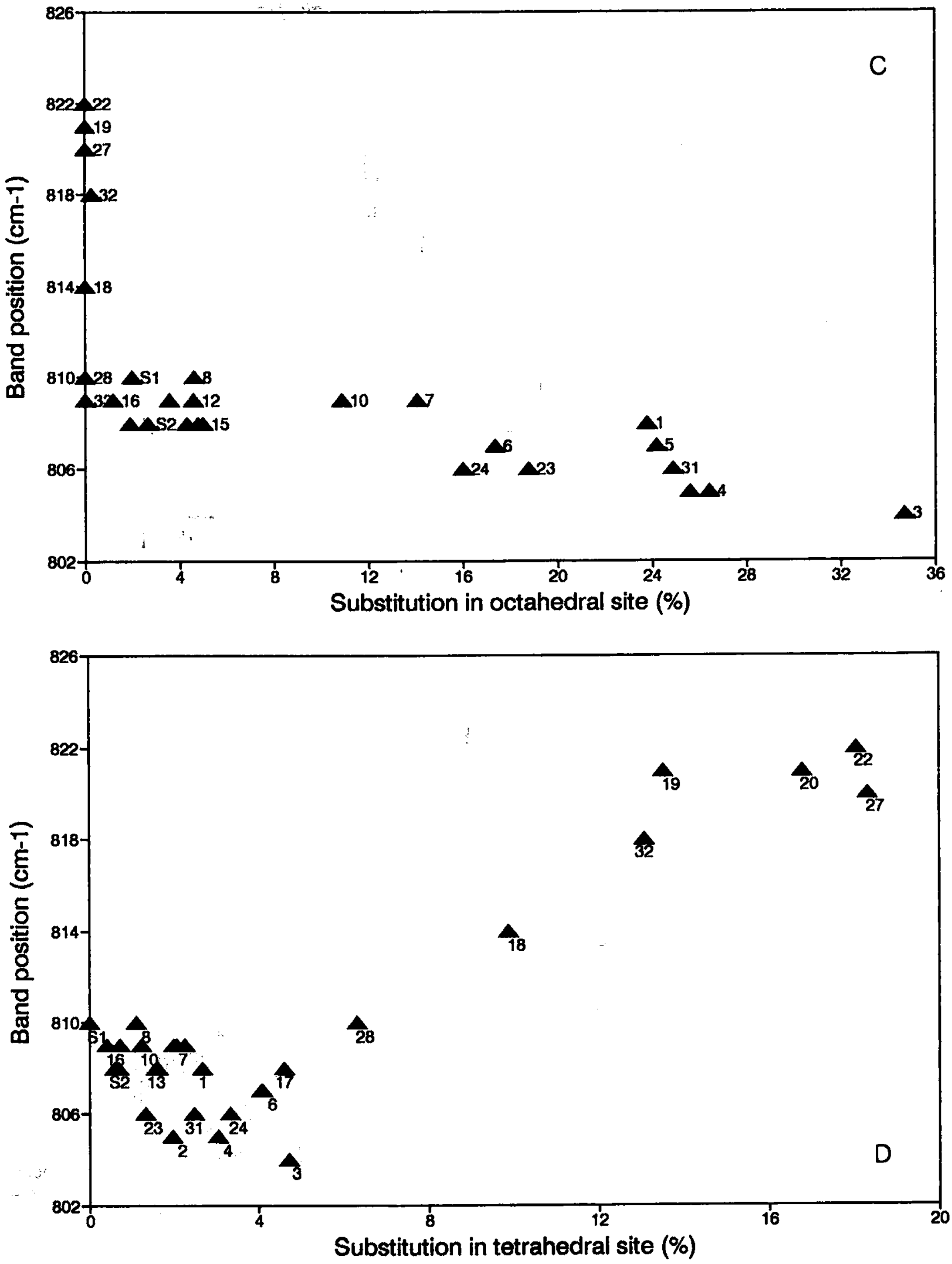

FIG. 7. Frequencies of the band 810 cm^{-1} *versus* the *c/a* ratio (A), bond distance Be–O(2) (B), substitution in the octahedrally coordinated site (C), and substitution in the tetrahedrally coordinated *T'* site (D).

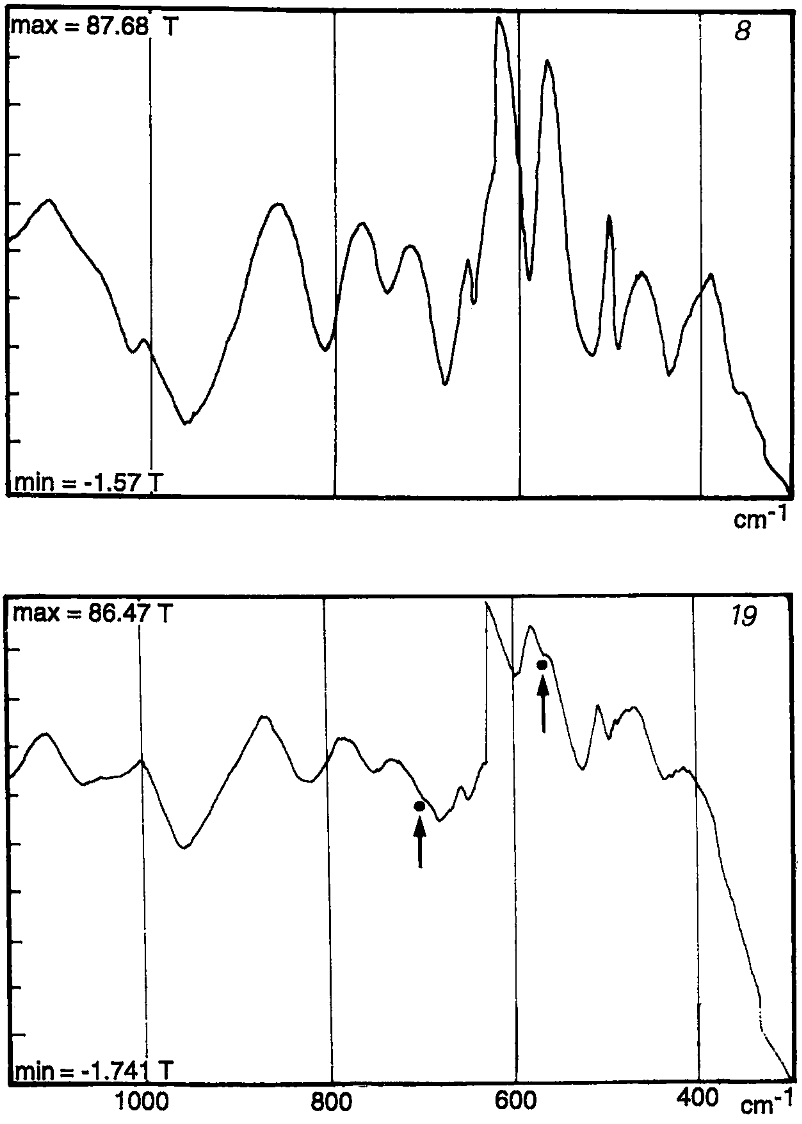

FIG. 8. Infrared absorption spectra of beryl in the range 1200–300 cm^{-1} at the temperature of liquid nitrogen, showing two weak shoulders at 700 and 560 cm^{-1}, increasing in intensity with extent of Li-for-Ba substitution. Sample 8: "normal" beryl, sample 19: alkali-rich beryl.

the band and define a good negative correlation, as does the band position as a function of Si–O bond length (Fig. 5B). In contrast, a plot of the Be–O bond length *versus* the band frequency does not show any meaningful trend. These observations confirm that (i) the 1200 cm^{-1} band (1208–1150 cm^{-1}) is generated by vibration in the (Si_6O_{18}) ring (Hofmeister *et al.* 1987); (ii) the shifts in the frequency result indirectly from substitutions in the tetrahedrally (*T'*) and octahedrally coordinated sites, which modify slightly the geometry of the ring tetrahedra; and (iii) the correlations in Figure 5 (A, B, C, and D) provide a semi-quantitative estimate of alkali content in the beryl.

"Normal" beryl shows a narrow, low-absorbance band at 1020 cm^{-1}, which increases in intensity and broadens with extent of substitution in the octahedrally coordinated site (Fig. 6, samples 31, 1, 4, 5, 23, 24). In contrast, this absorbance shrinks and ultimately vanishes with increasing extent of substitution in the tetrahedrally coordinated (*T*′) site. Instead, an absorption band at 1060 cm^{-1} appears if the extent of substitutions in the *T*′ site attains 0.19 atoms per formula unit, and its intensity increases with further substitution (Fig. 6, samples 8, 12, 26, 17, 28, 32, 27, 20). These two bands may be related to variation in the lengths of the "external bonds" Si–O–Be and Si–O–Al, respectively (Plyusnina 1964).

An absorption band at 950 cm^{-1} shows the same correlations as the 1200 cm^{-1} vibration. Thus the 950 cm^{-1} frequency is very likely due to another type of Si–O–Si ring vibration (Plyusnina 1964, Hofmeister *et al.* 1987).

Changes in the frequency of an absorption band at 805 cm^{-1} can be correlated with *c*/*a* ratio, bond length Be–O(2), and extent of substitution in the octahedrally and tetrahedrally coordinated (*T*′) sites (Figs. 7A, B, C, D). The correlation is particularly good in the second and fourth case. In contrast, a lot of this frequency *versus* the Si–O bond length does not show any meaningful trend. Consequently, we assign this absorption band to the Be–O vibration, in agreement with Plyusnina (1964) and Hofmeister *et al.* (1987). Gervais & Piriou (1972) assigned this band to Si–O–Si vibrations; Adams & Gardner (1974) also suggested this as a tentative interpretation. However, our observations do not support such a conclusion.

Two absorption bands at 700 and 560 cm^{-1} are evident in the spectra of tetrahedrally substituted beryl, recorded at the temperature of liquid nitrogen (Figs. 8A, B). They appear initially as a pair of small shoulders, but both absorbances increase with progressive entry of Li into the *T*′ site. However, they are not present in the octahedrally substituted series. The two bands, assigned in previous investigations to the vibrations of the BeO_4 tetrahedra in general (Plyusnina 1964, Hofmeister *et al.* 1987), seem diagnostic of tetrahedrally coordinated Li in beryl (Tarte 1964).

The absorption bands at 525 and 500 cm^{-1} can be correlated with the Al–O(2) bond length (Fig. 9 for the 525 cm^{-1} plot). The band shift increases with degree of distortion of the octahedron, particularly where larger divalent cations substitute for Al: sample 3, with 0.619 (Mg, Fe^{2+}) atoms per formula unit, lies at the extremity of the trend. Thus the pair of 525 and 500 cm^{-1} absorption bands is assigned to ^{VI}Al–O vibrations, in accordance with Plyusnina (1964); our data do not support the interpretation of Gervais & Piriou (1974), who assigned these bands to vibrations of the SiO_4 tetrahedra.

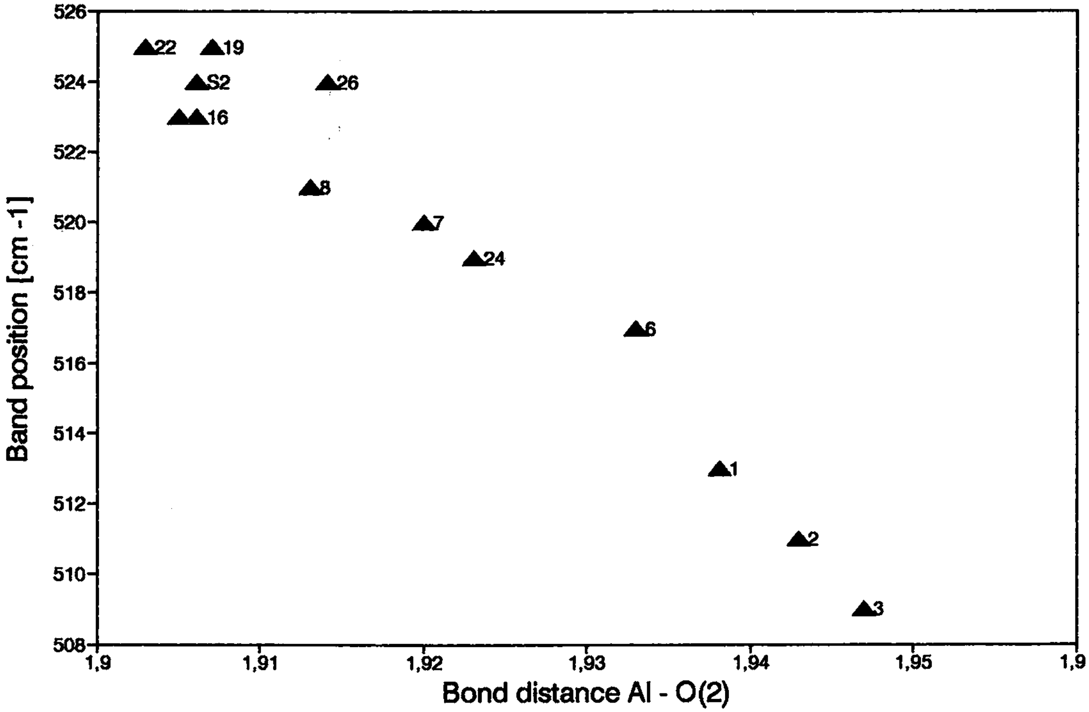

FIG. 9. Frequencies of the band at 525 cm^{-1} *versus* the bond distance Al–O(2) in Å.

CONCLUSIONS

Low-temperature studies provide improved resolution of the infrared spectra, which proves to be particularly advantageous in the H–O region. The two types of H_2O recognized previously, and hydroxyl groups associated with alkalis, can be characterized. The type-II H_2O–Na–(OH) association proposed for alkali-rich beryl correlates with its reduced content of type-I H_2O.

The principal vibrations in the 1200–400 cm^{-1} range are diagnostic of the three groups of beryl compositions: octahedrally substituted, tetrahedrally substituted and unsubstituted or "normal" (Aurisicchio *et al.* 1988).

A correlation with structural data permits the assignment of the 1200 cm^{-1} absorption band to Si–O–Si ring vibrations, and the 810 cm^{-1} absorption to vibration of the Be–O bond. The two bands at 1060 and 1020 cm^{-1} are generated by vibrations of the "external bonds" Si–O–Be and Si–O–Al, respectively; they also provide a means of identifying of the three compositional types of beryl.

The absorption bands at 700 and 560 cm^{-1} may be related to the replacement of Be by Li in the linking T' tetrahedra. In contrast, the absorbances at 525 and 500 cm^{-1} are generated by Al–O vibrations, and the patterns of the bands permit estimates of degree of substitution in the octahedrally coordinated site.

The above correlations can be used for an approximate determination of the c/a ratio, bond lengths at different sites, degree of substitution for Al and Be, and total alkali content. Such an indirect approach may be particularly valuable for the study of very small samples.

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