THE REMOVAL OF ALKALIS FROM BERYL: STRUCTURAL ADJUSTMENTS

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ABSTRACT

A natural sample of alkali-rich beryl, placed in aqueous solutions of HCl at 600°C and 1.5 kbar, is progressively depleted of its alkalis. The changes in the chemical composition of the beryl and in its IR absorption spectra in the domain of the water vibrations show that the leaching mechanism involves an exchange of cations: $(H^+) <--> (Li^+, Na^+, Cs^+)$. This reaction is achieved partly by means of a dissolution–recrystallization process. The partitioning of protons is much in favor of beryl. The structural change in beryl is monitored through X-ray and IR analysis. The cell parameters a and c decrease as the alkalis are leached. The sharpening of the IR absorption bands indicates that the mosaicity of the structure decreases. The variations observed in the Si–O vibrations seem to reveal a general shortening of the Si–O bonds.

Keywords: beryl, alkali elements, experimental leaching, hydrothermal, infrared absorption, protons, ion exchange.

SOMMAIRE

Un échantillon de béryl naturel riche en éléments alcalins est mis en présence de solutions de HCl à 600°C et 1.5 kbar. Le béryl est progressivement vidé de ses alcalins. Les variations de la composition chimique du béryl et l'évolution des spectres d'absorption infra-rouge réalisés dans le domaine des vibrations de l'eau, montrent que le mécanisme de lessivage implique un échange cationique: $(H^+) <--> (Li^+, Na^+, Cs^+)$. Cet échange est en partie réalisé par l'action de phénomènes de dissolution–recristallisation. Le partage des protons est extrêmement favorable au béryl. Les paramètres a et c diminuent lorsque le taux de lessivage augmente. L'affinement des bandes d'absorption infra-rouge indique une diminution, au cours du lessivage, du désordre structural. Les modifications observées dans le domaine des vibrations Si–O semble traduire un raccourcissement général des liaisons Si–O.

Mots-clés: béryl, éléments alcalins, lessivage expérimental, hydrothermal, absorption infra-rouge, protons, échange d'ions.

INTRODUCTION

The symmetry of beryl, ideally $Be_3Al_2Si_6O_{18}$ (Bragg & West 1926), is hexagonal ($Z=2$), space group D^2_{6h} (Deer *et al.* 1986). Beryl is made up of rings of six SiO_4 tetrahedra, linked together by BeO_4 tetrahedra and AlO_6 octahedra (Gibbs *et al.*

1968). The rings, stacked along the Z axis, form large channels (2.8 to 5.1 Å across) in which various elements and molecules can be located (Aines & Rossman 1984). Beryl may contain up to 11 wt.% alkali oxides, mainly Li, Na and Cs (Černý 1972) and 2.9 wt.% of molecular water (Bakakin & Belov 1962).

The crystal chemistry of alkali elements in beryl has long been a controversial question. The mode of incorporation of Li, Na and Cs now accepted, first proposed by Belov (1958), consists of a substitution of Li for Be, coupled with the introduction of Na or Cs in the channel, to compensate for the charge deficiency created. Hawthorne & Černý (1977) agreed with this hypothesis, but proposed that part of the Li may be in the channels. Furthermore, they pointed out that the Na^+ ion in the channel is linked with one or two molecules of water.

On the basis of infrared (IR) and optical absorption spectroscopy, Wood & Nassau (1968) found two distinct orientations of the water molecules. Type-I water corresponds to molecules whose axis of symmetry is perpendicular to Z, whereas in type-II water, the axis of symmetry is parallel to Z. Type-I water is found in many samples of beryl, including those free of alkali, whereas type-II water is closely related to the presence of alkalis.

The addition of alkalis in the beryl structure involves a notable increase in the c parameter (De Almeida *et al.* 1973, Bakakin *et al.* 1970, Aurisicchio *et al.* 1988) and alteration of IR absorption spectra (Plyusnina 1964, Hanson *et al.* 1988). The interpretation of IR spectra is made easier by the assignments of absorption frequencies (Gervais *et al.* 1972, 1973, Adams & Gardner 1974, Hofmeister *et al.* 1987).

On the basis of these findings, we propose to follow the leaching of alkalis from beryl, using IR and X-ray spectroscopy. For this purpose, a sample of natural beryl, rich in Li, Na and Cs, was gradually leached in a hydrothermal medium (600°C, 1.5 kbar) using hydrochloric acid of solutions. Structural transformations were observed by X-ray diffraction and IR absorption spectroscopy.

EXPERIMENTAL PROCEDURE

The beryl used in the experiments is a colorless gemstone rich in the rare alkalis. The composition

TABLE 1. COMPOSITION AND STRUCTURAL FORMULA* OF THE NATURAL
BERYL USED AS STARTING MATERIAL

	SiO_2	Al_2O_3	BeO	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O	FeO	H_2O	sum
wt%	62.59	17.06	11.11	1.26	1.23	0.08	0.02	3.45	0.09	2.05	99.17
SD	0.76	0.14	0.17	0.04	0.12	0.006	0.005	0.33	0.006	0.10	1.7
nb	10	3	8	4	5	3	2	8	3	2	
at.	6.04	1.94	2.57	0.49	0.23	0.01	--	0.14	0.01	0.66	

* calculated on the basis of 18 oxygen atoms.   at.: atom per formula unit.
wt.%: weight percent of oxides, SD: standard deviation, nb: number of analyses.

of the beryl, along with its structural formula, cal-
culated on the basis of 18 oxygen atoms, are given
in Table 1. Its chemical homogeneity has been
checked by electron microprobe and using images
of the chemical distribution of elements, as provided
by an ion-microprobe analyzer. About 100 mg of this
beryl, ground into particles of 10 to 50 μm, were
placed in presence of 20 to 200 μL of a solution of

TABLE 2. EXPERIMENTAL CONDITIONS AND COMPOSITION OF LEACHED
BERYL FRACTIONS

N°	Duration	Beryl	Solution		final solid comp.		
	days	mg	μL	mole/L	Li ppm	Na ppm	Cs ppm
A	0	--	--	--	6038	10116	33228
2	42	100.0	100	0.10	5163	7955	30303
3	32	100.2	100	0.11	5510	8460	29639
4	17	99.5	20	0.55	5698	9771	29373
5	32	100.6	100	0.22	4997	7587	27379
6	31	99.5	100	0.50	3796	5656	23658
B	42	99.0	100	0.50	4532	4897	24057
8	17	100.2	50	1.10	4296	5334	27911
9	17	99.4	100	0.50D	4414	5954	25917
10	17	100.5	200	0.55	2845	3081	15683
11	31	98.7	100	1.00	2436	3747	13823
C	17	100.2	100	1.10	1978	3885	13025
13	17	99.5	100	1.10D	2519	2483	13956
14	17	99.6	50	2.20	2262	2851	12495
15	32	100.6	100	1.65	805	621	5449
16	32	99.9	100	1.65	548	1563	4519
17	17	99.3	200	1.1	715	1471	3400
D	17	99.5	100	2.20	319	759	4918
19	17	99.7	100	2.20D	402	299	4120
E	18	--	--	0.0	35	230	270

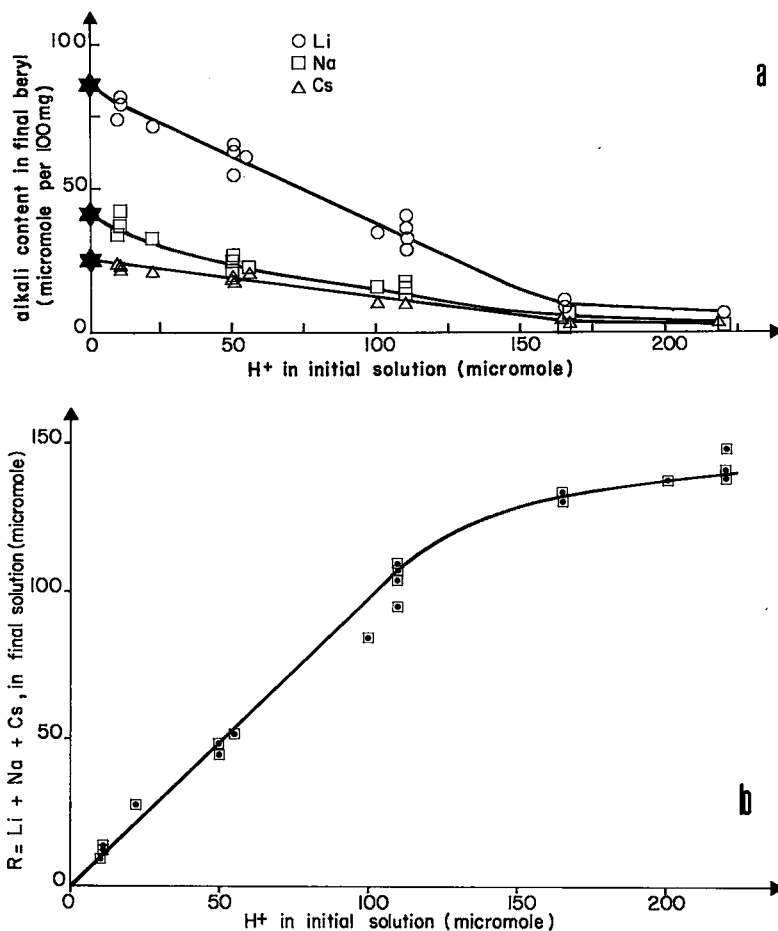D: experiments with DCl in the initial solution.

Fig. 1. Evolution of alkali contents (Li, Na and Cs) in leached beryl fractions (a)
and variation of the sum of the three alkalis in final solution (b), as a function
of the number of protons available in the initial solution.

hydrochloric acid of various concentrations (0.1 to 2.2 M). DCl was used instead of HCl in some experiments, so as to facilitate the interpretation of the IR spectra in the zone of water vibrations.

Solids and solutions were introduced into gold capsules, welded at both ends, and heated at 600°C and 1.5 kbar in a pressure vessel. The experiments lasted from 17 to 42 days. We ascertained that a steady state was reached after 17 days. Once the experiments were run, solids and solutions were separated by centrifuging, and were analyzed. Na and Cs were sought by emission spectrometry, and Li and Be, by atomic absorption. The solids were identified by X-ray diffraction (XRD) and observed by scanning electron microscope (SEM).

Products

The XRD spectra show no crystalline phase other than beryl, except in experiments D and 19, in which small quantities of quartz and cristobalite were detected (about 2 wt.%, by comparison with standards). Beryl is clearly the only phase containing significant amounts of alkalis.

A control sample of beryl was synthesized from a dehydrated gel. This gel was obtained from a mixture, in nitric acid solution, of $BeCO_3$ (Carlo Erba), of tetraethylorthosilicate (Merck) and of $AlNO_3$ (Johnson Matthey). The mixture was dehydrated, powdered, and then heated to 800°C, in order to break down the nitrates. The stoichiometry of the dehydrated gel was tested by wet-chemical analysis. Finally, the mineral was synthesized in deionized water, the conditions of pressure and temperature being identical to those in the leaching experiments.

Determination of the unit-cell parameters

The digitalized diffractograms were recorded step by step in the following conditions: 0.005° 2θ steps, 10 s per step, operating voltage 35 kV, current 40 mA, CuKα radiation. Quartz was used as internal standard. The angles were measured with a precision of 0.01° 2θ. The unit-cell parameters were calculated using the program of Appleman & Evans (1973).

Infrared absorption spectroscopy

The absorption spectra, obtained over a frequency range of 400 to 4000 cm^{-1} on powders, were recorded with a single-beam IR spectrometer with Fourier transform (Nicolet 5DX). The precision of the peak measurements is 2 cm^{-1} for the narrow bands and 5 cm^{-1} for shoulders. The samples were diluted in KBr in proportions ranging from 1 to 5 wt.%.
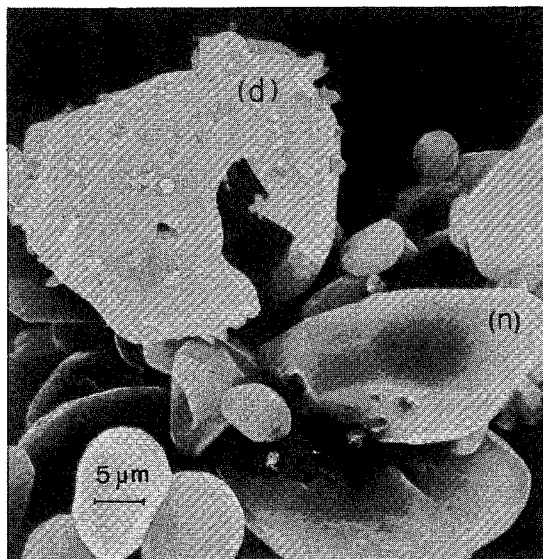

FIG. 2. SEM image of a representative sample from experiment 20. Symbols: (n) newly formed beryl, (d) grain of initial beryl showing signs of dissolution.

RESULTS

Evolution of chemical composition of the beryl with leaching

The concentration of alkalis in the beryl fractions leached by solutions of HCl or DCl are given in Table 2. The initial composition of the beryl (A) and that of the synthetic reference sample (E) also are given for comparison. The traces of beryllium found in solution are negligible (< 0.5 micromole) compared to the quantities of Li, Na and Cs leached out of the beryl (5 to 140 micromoles of $Li + Na + Cs$). Beryllium, therefore, does not take part in the leaching process.

Figure 1a shows the evolution of the contents of Li, Na and Cs in the beryl expressed in micromoles per 100 mg *versus* the number of protons available in the initial solution. The concentration of Li, Na and Cs in the beryl decreases as the number of ions of H^+ (or Cl^-) in the solution increases. Note that the concentration of Li and Cs in the beryl decreases linearly, so that their relative proportions remain constant. On the other hand, the concentration of

TABLE 3. NUMBER OF PROTONS* IN SOLUTION, BEFORE (Ci) AND AFTER (Cf) THE EXPERIMENT

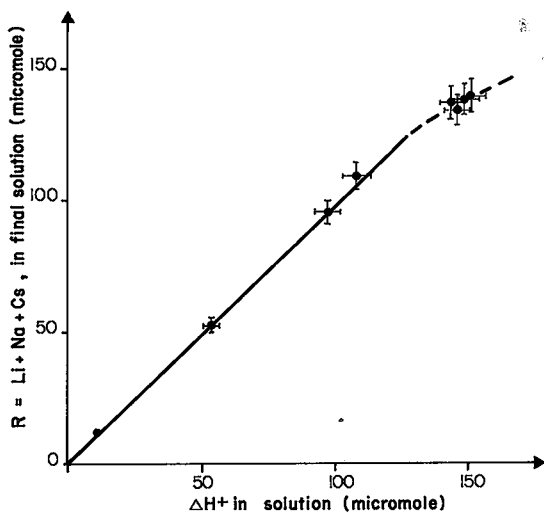| N°	Ci	Cf	N°	Ci	Cf
4	10.8	0.2	15	164.5	18.2
8	51.4	1.0	16	163.2	20.0
10	100.2	11.8	17	200.0	69.7
14	102.6	41.2			

* in micromoles

FIG. 3. Correlation between the number of alkali elements removed from the beryl and the number of protons lost by the solution, after the experiment.

TABLE 4 EVOLUTION, IN THE COURSE OF THE LEACHING, OF UNIT-CELL PARAMETERS a AND c, WITH THE BULK ALKALI CONTENT OF BERYL*

N°	a (Å)	c (Å)	N°	a (Å)	c (Å)
A	9.2214(6)	9.230(1)	C	9.207(3)	9.220(3)
4	9.220(1)	9.228(1)	13	9.211(2)	9.217(2)
5	9.2175(5)	9.227(1)	15	9.214(1)	9.197(1)
6	9.217(2)	9.226(2)	17	9.209(1)	9.197(2)
8	9.217(1)	9.220(2)	19	9.208(1)	9.194(1)
10	9.217(2)	9.227(2)	E	9.194(1)	9.196(2)

* in atom per formula unit.

FIG. 4. Evolution of c and a parameters with the total alkali content (Li+Na+Cs) of beryl. Symbols: n natural beryl used in our experiments, s synthetic control sample.

Na forms a concave-upward curve, which corresponds to a more significant decrease, relative to Li and Cs. This finding implies a partition of sodium in favor of solution over beryl. This result confirms those of Manier-Glavinaz *et al.* (1989), on the partition of Li, Na and Cs between beryl and alkali chloride solutions, which show that sodium is the least well accommodated in the structure of beryl.
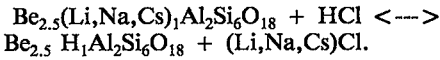
If we follow Belov's hypothesis (1958), we could expect Li to behave differently from Na or Cs, which are localized in the channel. This pattern is not observed in our experiments. However, SEM photos of the solids obtained at the end of the experiments (Fig. 2) reveal newly formed crystals of beryl, with well-developed faces, close to grains of destabilized beryl. The proportion of the starting material decreases as more and more is leached. Therefore, a dissolution–recrystallization process, at least partial, occurs, and can explain the similar behavior of the three alkali elements. We thus cannot deduce, from these results, information concerning the crystal chemistry of lithium in beryl.

The experiments carried out with varying volumes of solution but with a constant number of H^+ ions (experiments 3 and 4 or B and 8, for instance) show that the composition of beryl depends only on the number of protons available in the initial solution and not on the concentration of hydrochloric acid of the solution.

Figure 1b shows the evolution of the alkali contents (Li+Na+Cs) in the final solution *versus* the number of protons present in the initial solution. This evolution describes a straight line with a slope close to one up to 130 micromoles; it then tends asymptotically toward the limit of 150 micromoles, which corresponds to the total leaching of the initial beryl. As the number of Cl^- ions remains constant in solution, the probable mechanism of the leaching is an exchange of alkali ions and protons between beryl and solution:

$$(Li^+, Na^+ \text{ or } Cs^+)_{beryl} \longleftrightarrow (H^+)_{solution}.$$

If such is the process, there should be a noticeable increase in the pH from the initial to the final solutions, resulting from the introduction of protons in the beryl. The pH was measured in the case of experiments 4, 8, 10, and 14 to 17 on experimental solutions, diluted with deionized water to a volume of 20 mL. Results are reported in Table 3. Ci and Cf correspond to the quantities of protons (in micromoles) present in the solutions, before and after experiments, respectively. Figure 3 shows the number of alkali ions (Li+Na+Cs) present in the final solution, in relation with the number of protons missing from the final solution (introduced into the beryl). The slope close to 1 confirms the ion-exchange reaction. The reaction can be written ideally:

$Be_{2.5}(Li,Na,Cs)_1Al_2Si_6O_{18} + HCl <\text{---}>$
$Be_{2.5} H_1Al_2Si_6O_{18} + (Li,Na,Cs)Cl.$

This reaction is obtained by both leaching and dissolution–recrystallization processes.

Variations of cell parameters
during the leaching of beryl

The parameters a and c have been calculated for the starting material, the synthetic beryl, and a few representative leached fractions. The results are given in Table 4. Figure 4 illustrates the evolution of a and c as a function of the overall concentration of alkalis $(Li + Na + Cs)$ in the leached beryl, expressed as atoms per formula unit (a.f.u.). The values compare well with those obtained for natural beryl by Aurisicchio *et al.* (1988).

The c parameter decreases from 9.230 to 9.217 Å as the alkali concentration is reduced from 0.9 to 0.3 a.f.u. This evolution becomes more marked between 0.3 and 0.1 a.f.u., and reaches a value close to 9.195 Å for the synthetic beryl. The a parameter decreases regularly from 9.221 to 9.211 Å between 0.9 and 0.1 a.f.u., then decreases rapidly for lower concentrations, finally to reach 9.196 Å in synthetic beryl. The dependence of the a parameter upon the alkali contents had not previously been established in studies carried out on natural beryl (Bakakin *et al.* 1970, De Almeida *et al.* 1973, Aurisicchio *et al.* 1988). According to Hawthorne & Černý (1977), the increase in the c parameter with the lithium content of the beryl is due to a lengthening of the cation–oxygen distance in the ^{IV}Be site, related to the presence of lithium in this site. We also observed this trend, which cannot be ascribed solely to lithium, because Li, Na and Cs contents of beryl decrease simultaneously.

As seen above, a dissolution–recrystallization process occurs in our experiments. Thus, these calculated parameters might be the result of superposition of data from two different populations of beryl particles: grains of the starting alkali-rich material and grains of a reprecipitated alkali-free beryl. Figure 5 shows the XRD profile of the 413 reflection in the starting material (A), in the more completely leached beryl (D) and in a beryl of intermediate composition (B). A mechanical mixing of A and D particles would lead, for B, to a broad diffraction-band in intermediate position, which is not the case in Figure 5. The B peak is as sharp as the A and D peaks and occurs in an intermediate 2θ position. Therefore, B really corresponds to grains with intermediate composition.

Evolution of the IR absorption spectra
in the domain of the network: 1600–400 cm⁻¹
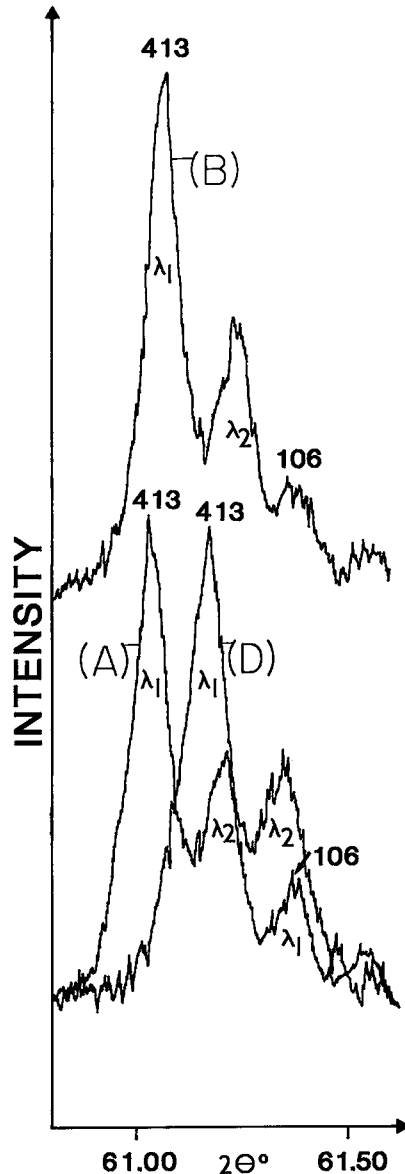
Spectra were recorded on samples A, B, C and D,

FIG. 5. XRD spectra of the 2θ (413) of starting material (A), partly leached sample (B) and completely leached sample (D).

which show the natural beryl at various stages of leaching, as well as on synthetic beryl. They appear on Figure 6. The spectra are normalized using the highest peak.

The spectrum of the starting material (A) displays in the domain 1300–800 cm⁻¹, corresponding to the internal Si–O vibrations (Gervais *et al.* 1973), two broad composite bands centered at 1170 and 1050 cm⁻¹, and a narrower band at 956 cm⁻¹. The bands
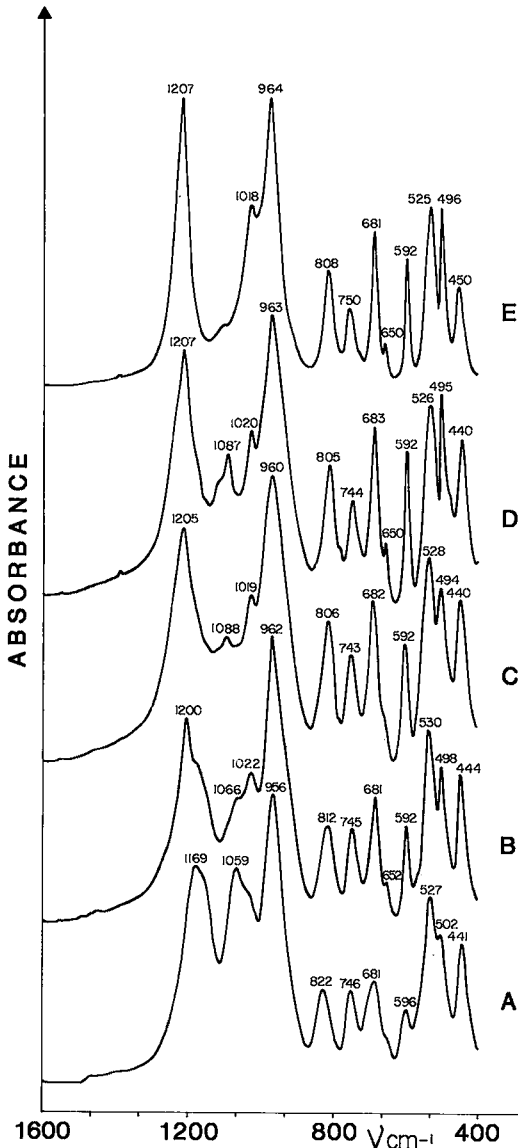
FIG. 6. Evolution of the IR absorption spectra, in the lattice-vibration domain, with increasing leaching of the beryl (A) by HCl solutions. Comparison with the synthetic control sample (E).

appearing at 820, 750 and 680 cm^{-1} are ascribed to Be–O by Hofmeister *et al.* (1987). The bands appearing at lower frequencies have not yet been attributed. The presence of the peaks at 1170 and 1050 cm^{-1}, and the absence of the one at 1200 cm^{-1} in alkali-rich beryl, had already been noted by Plyusnina (1964).

In the spectra of progressively leached samples (B, C and D), there is a general sharpening of the absorp-

tion bands; also, major transformations occur in the domain of Si–O internal vibrations. In all the spectra, the 960 cm^{-1} band is the most intense and does not seem to be affected by the concentration of alkalis, as already observed by Plyusnina (1964). We shall, therefore, select this absorption band as reference point to follow the evolution of the various peaks.

The sharpening of the the IR spectra in the course of the leaching reveals a reorganization of the structure of beryl. The removal of alkalis from the channels leads to an increase in the periodicity of the crystal (reduction in mosaicity).

In the domain 1300–900 cm^{-1}, a shift of about 30 cm^{-1} occurs toward higher frequencies in the peaks at 1170 and 1050 cm^{-1}, which correspond to Si–O bonds (Gervais *et al.* 1973, Hofmeister *et al.* 1987). The increase in energy observed may be due to shortening of these bond lengths. This explanation is compatible with the decrease in the cell parameters *a* and *c* in the course of leaching. In the leached samples B, C and D, a shoulder at 1170 cm^{-1} is visible on the peak at 1200 cm^{-1}. This shoulder decreases in the course of leaching; it does not appear in synthetic beryl. It is attributed to the inherited grains of destabilized beryl described above. The bands at 1020 and 956 cm^{-1} also are attributed to internal vibrations of the SiO_4 groups. The former does not vary, either in intensity or in frequency, whereas the latter moves slightly (10 cm^{-1}) toward higher frequencies.

These results are in agreement with the relationship between the alkali concentration of beryl and its IR spectrum, established by Plyusnina (1964) and Hanson *et al.* (1988). The variable increase in the frequency of three of the internal Si–O modes can be explained by a shortening of the bonds caused by the replacement of Li, Na and Cs by protons.

In the domain 900–600 cm^{-1}, a slight displacement (15 cm^{-1}) occurs toward lower frequencies of the peak at 822 cm^{-1}, which can be attributed to a lengthening of the Be–O bonds. Indeed, a comparison among IR reflection spectra of zircon, forsterite, phenacite, beryl and spodumene indicates that only beryllium minerals show infrared absorption bands in this frequency range (600–900 cm^{-1}). Yet, Hanson *et al.* (1988) noted the presence of some vibrations of the Si_6O_{18} rings of dioptase in this area. This shift in frequency cannot, therefore, be ascribed to Be–O only. The two bands at 750 and 680 cm^{-1}, also ascribed to Be–O by Hofmeister *et al.* (1987), are stable in frequency.

In the domain 600–400 cm^{-1}, the sharpening of the peaks may be accompanied by variations in intensity in the course of leaching. This domain of frequencies corresponds to that of LiO_4 vibrations, as determined by Tarte (1965). The shoulder observed in alkali-rich beryl by Vorma *et al.* (1965), which they ascribed to LiO_4 vibrations, does not occur, although the initial beryl used here is richer in Li than
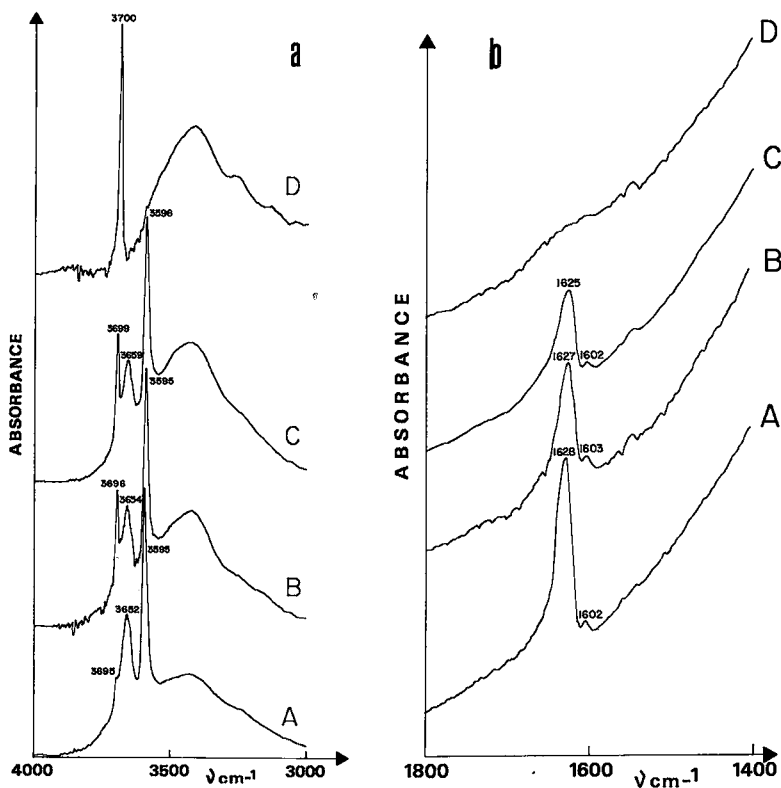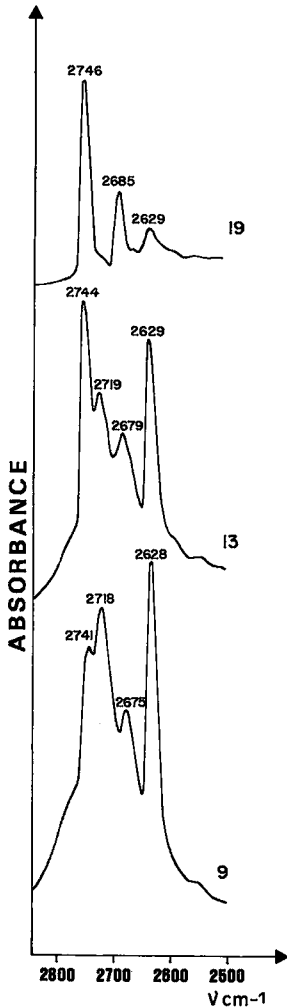
FIG. 7. Evolution of the IR absorption spectra, in the water-vibration domain, with increasing leaching of the beryl (A) by HCl solutions. (a): domain of the stretching vibrations. (b): domain of the bending vibrations.

the beryl sample studied by these authors. As Hanson *et al.* (1988) suggested, this shoulder does not seem to be linked to the presence of lithium.

Three points emerge from the present spectroscopic study: 1) The presence of alkali elements in beryl affects mostly the Si–O bonds but not the Be–O bonds. 2) No Li–O vibration can be observed in the 600–400 cm^{-1} range, although the initial beryl contains 0.5 a.f.u. of lithium, which corresponds to 15 mole of Li per 100 moles of Be. 3) The leaching of beryl results in a sharpening of the spectrum, which reveals a decreasing mosaicity in the structure. Highly leached beryl (D) and the synthetic beryl have similar spectra, which shows that the presence of protons has little influence on the structure of beryl.

IR absorption spectroscopy in the spectral domains 4000-2500 and 1800-1500 cm^{-1}

Figure 7 shows the spectra of the same samples in the domain of the 'stretching' (4000–3000 cm^{-1}) and 'bending' (1800–1500 cm^{-1}) modes of molecular water. In natural beryl (A), both types of water, I and II, defined by Wood & Nassau (1968), are present. Type-I water, poorly developed, has two stretching bands, at 3555 and 3695 cm^{-1}, and a very weak band that appears around 1600 cm^{-1}. Type-II water has two intense stretching bands, at 3659 and 3595 cm^{-1}, and a bending band, highly developed, at 1628 cm^{-1}.

In the course of leaching, from A to D, the two stretching bands of type-II water, at 3699 and 3595 cm^{-1}, diminish and eventually disappear in the most completely leached fraction (D). In the bending mode of H_2O, the band at 1628 cm^{-1}, corresponding to type-II water, decreases rapidly and vanishes altogether. The disappearance of the three IR modes of type-II water, correlated with the decrease in alkali contents of the beryl, are in perfect agreement with the conclusions reached by Wood & Nassau (1968): the presence of type-II water is related to that of alkali elements in the beryl.

Type-I water behaves differently. The band at 3695 cm^{-1} increases very rapidly. The other stretching mode of type-I water, at 3555 cm^{-1}, is masked by the broad band of adsorbed water. Its evolution can be monitored only in beryl containing deuterium. The very weak band at 1600 cm^{-1} (bending mode) disappears.

As there is no more absorption band in the bending domain of water, we can infer that leached beryl (D) no longer contains molecular water. The band that develops at 3699 cm^{-1} must therefore correspond to the vibration in the stretching mode of an OH bond of the structure.

The use of DCl makes it possible to remove the broad band corresponding to adsorbed water (around 3450 cm^{-1}), because OD vibrations appear around 2600 cm^{-1}. As a result, there is no interference with the 3450 cm^{-1} broad band of adsorbed water. One can then follow the development of the stretching band of type I-water (3555 cm^{-1} for OH and 2630 cm^{-1} for OD). The IR spectra of deuterated beryl in the 2800–2500 cm^{-1} domain are shown in Figure 8. They clearly show that, of the two

stretching modes of type-I D$_2$O (2747 and 2630 cm^{-1}), only the band at the higher frequency seems enhanced in the course of leaching.

The above spectroscopic study thus has allowed us to follow the behavior of alkalis by observing the behavior of the water molecules associated in the channels. Type-II water disappears while the beryl is leached of its alkali ions. There is no more molecular water in the most completely leached beryl. The OH vibration developed in the course of leaching results from the incorporation of protons in the structure, compensating for alkalis. These results confirm the mechanism of exchange of alkali ions and H$^+$ or D$^+$ between beryl and solution.

CONCLUSIONS

The evolution of the chemical composition of beryl and the solutions in equilibrium, in the course of leaching, shows that the process can be considered an ion-exchange reaction of the type:

$$H^+{}_{solution} <\text{---}> (Li^+, Na^+, Cs^+)_{beryl}$$

This ion exchange is achieved by both leaching and dissolution–recrystallization. The removal of alkalis from beryl creates a charge deficiency and "unsaturated" bonds on the oxygen atoms of the structure. The protons incorporated in the beryl seem to combine with the "unsaturated" oxygen atoms.

The leaching of an alkali-rich beryl affects its structure. When the alkali contents decrease, the two unit-cell dimensions decrease, a being less affected than c. The modifications observed in the IR spectra seem to indicate a general shortening of the Si–O bonds during leaching and, at the same time, a reorganization of the structure; its periodicity increases. The shortening of Si–O bonds can be explained by the replacement of alkali cations by protons in the channels. The other vibrations, ascribed to other bonds, are unchanged. No vibrations can be assigned to the presence of lithium in the structure, although, according to Belov (1958), Li should occupy 15% of the beryllium sites. None of our results supports the substitution of Li for Be.

Beryl releases its alkalis very easily to incorporate protons. The partitioning of protons is very much in favor of beryl, compared with that of the alkalis.

The flow of acidic fluids, subsequent to crystallization, may modify the composition of beryl to a significant extent. This hypothesis appears to be in contradiction with the idea based on field observations (Gaines 1976), that beryl is chemically quite an inert mineral. Moreover, the presence of acidic fluids does not seem to favor the crystallization of alkali-rich beryl. Experiments conducted by Beus *et al.* (1963) showed that during the postmagmatic events, the beryllium-rich mineral phases precipitate when
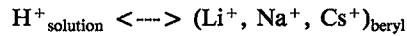

FIG. 8. Evolution of the IR absorption spectra, in the D$_2$O stretching-vibration domain, with increasing leaching of the beryl (A) by DCl solutions.

the alkalinity of the fluids increases. One can thus understand the presence of beryl enriched in alkali elements, commonly associated with late hydrothermal phases of albitization.

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