

# Molecular water in beryl, ${}^{\text{VI}}\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}]\cdot n\text{H}_2\text{O}$ , as a function of pressure and temperature: An experimental study

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## ABSTRACT

The incorporation of molecular water into the *c*-parallel structural channels in end-member beryl  ${}^{\text{VI}}\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}]\cdot n\text{H}_2\text{O}$ , where  $n_{\text{H}_2\text{O}} = 1.00$  corresponds to 3.24 wt%  $\text{H}_2\text{O}$ , was studied experimentally in the temperature-pressure range 400–950 °C and 1–14.5 kbar ( $P_{\text{H}_2\text{O}} = P_{\text{tot}}$ ). Time-dependent studies ensured that the incorporation of water by beryl had reached the equilibrium  $n_{\text{H}_2\text{O}}$  values in the hydration experiments.

Increasing water contents were found to enhance the refractive indices of beryl as follows:

$$n_e = 1.5585 + 0.0080 \cdot \text{wt\% H}_2\text{O} \quad (r = 0.986)$$

$$n_o = 1.5616 + 0.0086 \cdot \text{wt\% H}_2\text{O} \quad (r = 0.978)$$

These relations were used to determine the water contents attained in the equilibrium experiments, and were calibrated using synthetic beryls, the water contents of which had been determined gravimetrically with an accuracy of  $\pm 0.06$  wt%  $\text{H}_2\text{O}$ . The incorporation of water into the structural channels of beryl leaves the hexagonal *a*-axis unchanged,  $a = 9.2110(10)$  Å, *c* and *V* increase as:

$$c \text{ (Å)} = 9.1893 + 0.0020 \cdot \text{wt\% H}_2\text{O} \quad (r = 0.974)$$

$$V \text{ (Å}^3\text{)} = 674.98 + 0.203 \cdot \text{wt\% H}_2\text{O} \quad (r = 0.936)$$

Two isobars at 3.4 and 10.8 kbar with  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  could be modeled as:

$$\text{wt\% H}_2\text{O} (P) = a - bT \text{ (}^\circ\text{C)} + cT^2 \text{ (}^\circ\text{C)}^2$$

$$3.4 \text{ kbar: } a = 4.10, b = 5.90 \cdot 10^{-3}, c = 0.31 \cdot 10^{-5} \quad (r = 0.963)$$

$$10.8 \text{ kbar: } a = 3.31, b = 0.514 \cdot 10^{-3}, c = 0.00 \quad (r = 0.941)$$

Similarly, the two isotherms at 600 and 900 °C could be modeled as:

$$\text{wt\% H}_2\text{O} (T) = a + bP \text{ (kbar)} - cP^2 \text{ (kbar)}^2$$

$$500 \text{ }^\circ\text{C: } a = 0.94, b = 0.261, c = 0.0075 \quad (r = 0.949)$$

$$900 \text{ }^\circ\text{C: } a = 0.19, b = 0.331, c = 0.0092 \quad (r = 0.964)$$

These relations together with data points from additional experiments were used to construct a ( $P_{\text{H}_2\text{O}} = P_{\text{tot}}$ ) – *T* field of isohydrans for the system end-member beryl- $\text{H}_2\text{O}$ . Comparing  $n_{\text{H}_2\text{O}}-P$  sections at 600 °C for beryl obtained in this study with data for Mg-cordierite obtained from the literature, proves nearly the same equilibrium contents of water in both minerals.

## INTRODUCTION

End-member beryl has the crystal-chemical formula,  ${}^{\text{VI}}\text{Al}_2[{}^{\text{IV}}\text{Be}_3{}^{\text{IV}}\text{Si}_6\text{O}_{18}]\cdot n\text{X}^{(\text{Chan})}$ , where X represents molecular or/and ionic constituents in channel sites of the structural framework, as discussed below. The hexagonal structure (Bragg and

West 1926; Gibbs et al. 1968) with space group *P6/mcc*, contains *Z* = 2 formula units in the unit cell. The structure is made up of hexagonal rings of corner-connected  $\text{SiO}_4$ -tetrahedra, T1, with point symmetry *6/mmm*. These rings of T1-tetrahedra are stacked over each other along [0001], alternating rings being rotated relative to each other by  $\pm 30^\circ$ . The T1 tetrahedral rings are interconnected by additional, Be-centered tetrahedra, T2, in such a way that a tetrahedral framework is formed that contains isolated Al-octahedra outside the T1-rings stacked over each other along [0001]. The stacking of the T1-rings along [0001] produces channels of interconnected “pumpkin-like” cavities with maximum diameter of 5.15 Å between the rings

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at  $z = 1/4$ , and “bottle-necks” with a diameter of 2.49 Å at the horizontal mirror plane of the rings. Such dimensions can be calculated from the structural data of Gibbs et al. (1968) using the ionic radius of  $O^{2-}$  given by Shannon and Prewitt (1969),  $I.R.(CN = 2) = 1.35 \text{ \AA}$ .

The cavities may contain molecular constituents,  $X_{Mol}^{[Chan]}$ , as water or carbon dioxide (Wood and Nassau 1967, 1968), or/and ionic constituents,  $X_{Min+}^{[Chan]}$  as e.g., alkali ions. The latter may be the case in chemically complex natural beryls (e.g., Bakakin et al. 1970; Hawthorne and Černý 1977. In the latter case, charge compensation may be achieved by cation substitutions as such,  $^{IV}Al^{3+}$  for  $^{IV}Si^{4+}$  or  $^{VI}M^{2+}$  for  $^{VI}Al^{3+}$ . As the present paper deals with results for end-member beryl,  $^{VI}Al[Be_3Si_6O_{18}] \cdot nX_{Mol}^{[Chan]}$ , such effects will not be discussed further in this paper.

The aforementioned “pumpkin-like” cavities have dimensions that allow for the incorporation of just one water molecule with diameter of about 2.8 Å, i.e., for  $n_{H_2O} = 1.00$  in beryl crystals free of ionic channel constituents,  $X_{Min+}^{[Chan]}$ , as is the case in end-member beryl. In this case, water molecules held in the channels, are oriented with their H-H vector statistically along [0001] (Wood and Nassau 1967, 1968) and show nearly free rotation down to very low temperatures (Rehm 1974; Winkler 1996).

Clearly, the water held in the structural channels of  $X_{Min+}^{[Chan]}$ -free beryls depends not only on the geometric properties of the cavities but also on the physical-chemical conditions of  $P_{tot}$ ,  $P_{H_2O}$ , and  $T$ . Nothing is known about the influence of pressure and temperature on water contents of beryl. Therefore, it was the aim of the present study to address this knowledge gap by an experimental investigation of the dependence of equilibrium water content in end-member beryl on  $T$  and  $P_{H_2O} = P_{tot}$ . The basis for this is the knowledge that the stability field of end-member beryl in the presence of water ranges to pressures well above 25 kbar and to temperatures of 1050 °C (Čemić et al. 1983, 1986).

The results of the present study will be important for understanding the thermodynamics of beryl reactions in the presence of water, thoroughly studied by Barton (1986), for understanding the crystal-chemical behavior of water in end-member beryl, and for evaluating how the water contents of chemically complex natural beryl crystals depend upon their conditions of formation. As systematic data on the water content of natural beryls from different geological environments are lacking, we confine the evaluation of our results to the  $P,T$  dependence of water in synthetic end-member beryl, and related crystal-chemical aspects, and to the possibility of using our data for routine water determinations in natural beryls.

## EXPERIMENTAL METHODS

### Starting materials

Starting materials for syntheses of end-member beryl were as follows. (1) Natural phenakite, San Miguel de Piracicaba, Minas Gerais, Brazil, with the composition (in wt%)  $SiO_2$  53.91,  $Cr_2O_3$  0.006,  $MgO$  0.001,  $CaO$  0.008,  $SrO$  0.008,  $Na_2O$  0.001,  $K_2O$  0.007,  $BeO$  45.43 (Franz and Morteani 1981). (2)  $\gamma$ - $Al_2O_3$ , prepared from 4N Al-ribbon (Merck no. 1057). The water con-

tent of this alumina material, equilibrated at room atmosphere, was determined by heating at 1300 °C to constant weight. From the results of the heating process, a correction factor of 1.029 was calculated for the weight of the starting material. (3)  $SiO_2$ , noncrystalline, prepared from 5N Aerosil (Heraeus), which had been heated for 12 at 1000 °C.

These starting materials were combined in the molar ratio 3  $Be_2SiO_4$ :2  $Al_2O_3$ :9  $SiO_2$ , which corresponds to the composition of end-member beryl, and then carefully mixed and sealed with some water in gold capsules for large-volume synthesis runs in the piston-cylinder-apparatus (see below). The run products (Table 1) were fine-grained single-phase beryl crystals containing some water (Table 1) that was subsequently removed (see below). The necessary temperature and time to achieve this had been determined previously using small fractions of one of the synthetic beryl crystals. The water-free, synthetic end-member beryl crystals served as starting materials for the equilibrium experiments at varying  $P_{H_2O} = P_{tot}$  and  $T$  conditions. For this purpose, the dehydrated beryl crystals of Table 1 were carefully mixed to obtain a sufficient amount of homogeneous starting material.

### High-pressure runs

High-pressure runs in the ranging up to 14.5 kbar were performed either in a conventional cold-seal hydrothermal apparatus or in a piston-cylinder apparatus with high-pressure cells of the Neuhaus and Steffen (1970) type using pyrophyllite as the pressure transmitting material. For runs in the cold-seal apparatus up to 5 kbar, the starting materials (beryl plus water) were encapsulated in 2 mm diameter gold tubes, 30 mm long. The capsules were checked to be water-tight before and after the runs. Temperature calibration in the autoclaves showed the temperature recordings to be accurate to within  $\pm 10$  °C. To quench the temperature from 400, 600, or 700 °C to 110 °C at the end of the runs required 6, 7, or 8 minutes, respectively. Pressures were accurate to within  $\pm 100$  bar.

In the case of the piston-cylinder runs, temperature regulations and recordings were accurate to within  $\pm 5$  °C in synthesis

**TABLE 1.** Synthetic beryl samples,  $Al_2[Be_3Si_6O_{18}] \cdot nH_2O$ , used after dehydration, as starting materials in the hydration equilibrium experiments

Sample no.	Pressure (kbar)	Temperature (°C)	Duration (h)	Water content	
				wt%	$n_{H_2O}$
Be-Sy-1	14.5	950	24	2.95	0.91
Be-Sy-2				2.77	0.85
Be-Sy-3				2.84	0.88
Be-Sy-4				2.90	0.90
			( $x \pm 1s$ )	2.87 $\pm$ 0.08	0.89 $\pm$ 0.03
Be-Sy-5	14.5	950	24	(1)* 2.91	0.90
				(2)* 2.79	0.86
				(3)* 2.91	0.90
				(4)* 2.88	0.89
			( $x \pm 1s$ )	2.87 $\pm$ 0.06	0.89 $\pm$ 0.03

Note: The beryl crystals were synthesized in the piston-cylinder-apparatus under  $P_{H_2O} = P_{tot}$  and were analyzed for their water contents as described in the experimental section. The samples proved to be single phase beryl.  $n_{H_2O} (plu) = wt\% H_2O/3.24$  (see text).

\* Analysis number.

runs where large-volume gold capsules were used (5.5 mm in diameter and ca. 9.5 mm long). In the case of hydration experiments using capsules 3.5 mm in diameter and 5.5 mm long, the temperature recordings were accurate to within  $\pm 3$  °C. To quench the runs from 900 to 300 °C required 15 s, from 600 to 300 °C required 10 s, and from 600 to 110 °C required 27 s. Nominal pressures were calculated as  $P_{\text{nom}} = f/a$ , where  $f$  is the pressing force generated, measured, and regulated to  $\pm 2\%$  in the hydraulic system, and  $a$  is the working area of the piston acting on the high-pressure insert. The nominal pressures were corrected for frictional losses in the pressure-transmitting material using the equation experimentally determined by Čemić et al. (1983) with a reliability parameter of  $r = 0.992$ , to obtain the true pressures acting on the samples:

$$P_{\text{true}} = -0.283 + 0.740 \cdot P_{\text{nom}} \quad (1)$$

Piston-out runs were performed exclusively.

### Phase identification

The crystalline run products were identified by powder X-ray diffraction (XRD) and by microscopic examination. All 19 diffraction peaks observed in the  $2\theta$ -range 5 to 60° (taken with  $\text{CuK}\alpha$  radiation) could be assigned to the XRD pattern of beryl (Borg and Smith 1962). No run product produced extra peaks. Lattice constants were calculated from  $2\theta$ -values obtained with Si as an internal standard. Optical examination failed to reveal the presence of phases additional to beryl. The bulk of the run products consisted of idiomorphic, short prismatic hexagonal beryl single crystals with sharp extinction although some hypidiomorphic crystals were also present. Crystal sizes were in the range 5–70  $\mu\text{m}$ , such that both refractive indices  $n_e$  and  $n_o$  could be measured.

### Water determination

Water contents of the beryl crystals were determined gravimetrically by heating about 30 mg of sample to constant weight at 920 °C after drying them at 110 °C, a temperature at which no water is removed from the structural channels. A constant weight was reached after 2.5 h. The samples were held in a small Pt container folded from carefully cleaned and dried foil. The weighings were performed on an electronic ultra-micro balance (Perkin-Elmer AD-2Z) with the measurement range 0 to 200 mg and an accuracy of  $\pm 10$   $\mu\text{g}$ . Repeated analyses of the same sample showed the precision of the water determination to be  $\pm 0.06$  wt% (Table 1, experiments on sample Be-Sy-5).

To be sure that the uptake of water by beryl has reached constant values in our equilibrium hydration experiments, we studied the time dependence of water contents at  $P_{\text{H}_2\text{O}} = P_{\text{tot}} = 3.4$  kbar. We found constant values after 100 h at 400 °C or after 10 h at 600 °C. The precision of the water contents obtained under the chosen  $P,T$ -conditions and appropriate run times were determined to be  $\pm 0.08$  wt% (Table 1) in repeated experiments.

In the results section, the water contents are reported as wt%  $\text{H}_2\text{O}$  and as  $n_{\text{H}_2\text{O}}$  (moles  $\text{H}_2\text{O}$  per formula unit of beryl). In end-member beryl, 3.24 wt%  $\text{H}_2\text{O}$  corresponds to  $n_{\text{H}_2\text{O}} = 1.00$ .

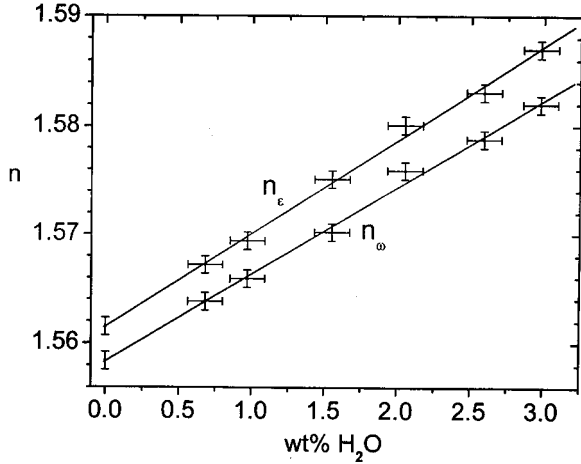
## EXPERIMENTAL RESULTS

Results of all hydration runs are presented in Table 2. Lattice constants, refractive indices, and birefringence of hydrated and water-free beryl samples are presented in Table 3. Both refractive indices,  $n_e$  and  $n_o$ , increase with increasing water content, the latter at a slightly higher rate such that the birefringence, small in both dry and hydrous beryl, increases slightly with water content (Table 2 and Fig. 1). The solid lines in Figure 1 represent the linear regression functions:

**TABLE 2.** Conditions and results of equilibrium runs of  $\text{H}_2\text{O}$ -incorporation in synthetic end-member beryl

Run no.	Apparatus	$P_{\text{H}_2\text{O}} = P_{\text{tot}}$ (kbar)	$T$ (°C)	Duration (h)	$\text{H}_2\text{O}$ Content		
					wt%	$n_{\text{H}_2\text{O}}$	
1	Hy	1	700	23	0.68	0.21	
				22	0.96	0.30	
1	W	3.4	300	22	1.78	0.55	
				23	1.75	0.54	
					2.16	0.67	
3h	Hy	5		500	2.22	0.69	
				850	2.22	0.69	
4	W	3.4	500	22	2.06	0.64	
				23	1.92	0.59	
6			600	0.5	1.88	0.58	
				2	1.95	0.60	
				4	1.72	0.53	
				16	1.72	0.54	
				22	1.66	0.51	
11	47	1.63	0.50				
5h	Hy	5		23	2.07	0.64	
12	W	3.4	700	22	1.39	0.43	
				22	1.34	0.41	
				23	1.31	0.40	
				22	1.24	0.38	
				22	1.99	0.61	
				22	2.05	0.63	
18			900	22	1.55	0.48	
				22	2.31	0.71	
20				23	2.09	0.65	
				23	1.87	0.58	
21	7.1		600	23	2.40	0.74	
22				700	23	2.45	0.75
23				900	22	1.87	0.58
24		8.6	600	23	2.59	0.80	
				23	900	23	2.47
26		10.8	500	23	3.04	0.94	
				22	2.99	0.92	
				23	2.98	0.92	
				23	2.83	0.87	
30		14.5	600	23	3.12	0.96	
				23	900	23	2.99

*Note:* Starting materials were dehydrated synthetic beryls (Table 1). Hy = runs in the cold seal hydrothermal apparatus, W = runs in the piston-cylinder-apparatus (see text).



**FIGURE 1.** Dependence of the refractive indices of  $\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}]$  beryl on the content of molecular water in the structural channels. Because of crystal sizes, beryls from the following runs were studied (samples in the order of increasing  $\text{wt}\%\text{H}_2\text{O}$ ): dehydrated BeSy-1 (Table 1); 1h, 2h, 18, 5h, 24, 29 (Table 2).

**TABLE 3.** Lattice constants, refractive indices, and birefringence of hydrated and dehydrated synthetic beryl Be-Sy-1 (see Table 1)

	Hydrated $n_{\text{H}_2\text{O}} = 0.91$	Dehydrated
<b>Hexagonal lattice constants (P6/mcc)</b>		
$a$ (Å)	9.2112 (7)	9.2092 (6)
$c$ (Å)	9.1958 (8)	9.1895 (8)
$V$ (Å <sup>3</sup> )	675.65 (16)	674.94 (13)
<b>Refractive indices and birefringence</b>		
$n_\epsilon$	1.5820 (7)	1.5585 (7)
$n_\omega$	1.5872 (7)	1.5617 (7)
$\Delta n$	0.0052 (14)	0.0032 (14)

Note: Uncertainties in parantheses.

$$n_\epsilon = 1.5585 + 0.0080 \cdot \text{wt}\% \text{H}_2\text{O} \quad (r = 0.986) \quad (2)$$

$$n_\omega = 1.5616 + 0.0086 \cdot \text{wt}\% \text{H}_2\text{O} \quad (r = 0.978) \quad (3)$$

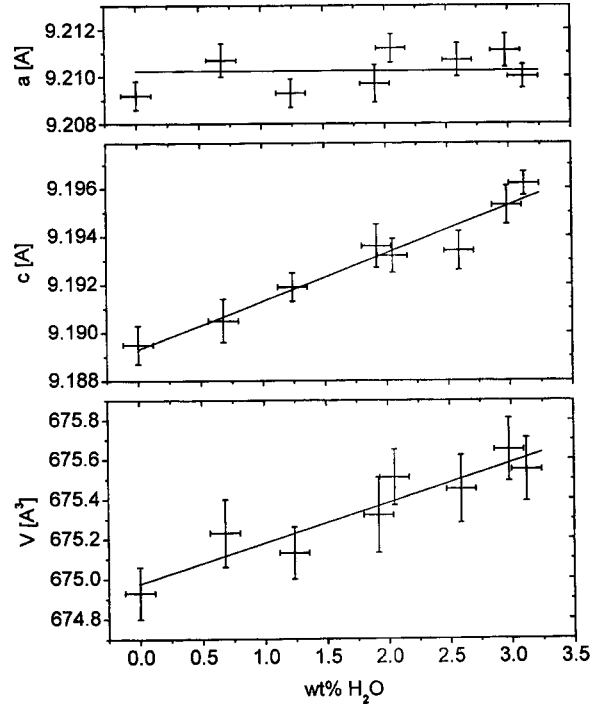
The dependencies of the refractive indices on the water content were used for routine water determinations in the hydration runs of Table 2. For this purpose, Equations 2 and 3 were rewritten as:

$$\text{wt}\%\text{H}_2\text{O} = (n_{\epsilon, \text{hydrated}} - 1.5585)/0.0080 \quad (2a)$$

$$\text{wt}\%\text{H}_2\text{O} = (n_{\omega, \text{hydrated}} - 1.5616)/0.0086 \quad (2b)$$

The dependence of the lattice constants on the water contents of end-member beryl is shown in Figure 2. Obviously, the  $a$ -parameter of the hexagonal unit cell is not affected by the incorporation of water molecules into the structural channels of beryl. However, filling of the channel by  $\text{H}_2\text{O}$  results in a relatively strong increase in the  $c$ -parameter by 0.071% for one mole water per formula unit, considering the above relation between  $\text{wt}\%\text{H}_2\text{O}$  and  $n_{\text{H}_2\text{O}}$ . The variations of  $c$  and cell volume with the water content are:

$$c \text{ (Å)} = 9.1893 + 0.0020 \cdot \text{wt}\%\text{H}_2\text{O} \quad (r = 0.974) \quad (3)$$



**FIGURE 2.** Dependence of the lattice constants and unit-cell volume of  $\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}]$  beryl on the contents of molecular water in the structural channels. The products of the following runs were studied (samples in the order of increasing  $\text{wt}\%\text{H}_2\text{O}$ ): dehydrated BeSy-1 (Table 1); 1h, 2h, 4, 5h, 24, 28, 30 (Table 2).

$$V \text{ (Å}^3\text{)} = 674.98 + 0.203 \cdot \text{wt}\%\text{H}_2\text{O} \quad (r = 0.936) \quad (4)$$

Equations 2 and 4 can be transformed to obtain the respective ones for moles  $\text{H}_2\text{O}$  per formula unit beryl,  $n_{\text{H}_2\text{O}}$ , by multiplying the slope of the linear regressions by 3.24 (see the experimental section).

The dependencies of the equilibrium water contents of beryl on pressure,  $P_{\text{H}_2\text{O}} = P_{\text{tot}}$ , and temperature,  $T$ , are shown for two isobars at 3.4 and 10.8 kbar in Figure 3 and for two isotherms at 600 and 900 °C in Figure 4. The two isobars can be represented by functions of the type:

$$\text{wt}\%\text{H}_2\text{O} = a - bT \text{ (}^\circ\text{C)} + cT^2 \text{ (}^\circ\text{C)} \quad (5)$$

with  $a = 4.10$ ,  $b = 5.90 \cdot 10^{-3}$ , and  $c = 0.31 \cdot 10^{-5}$  at 3.4 kbar ( $r = 0.963$ ), and  $a = 3.31$ ,  $b = 5.14 \cdot 10^{-4}$ , and  $c = 0.00$  at 10.8 kbar ( $r = 0.941$ ).

The mean deviations of the experimental water contents are  $\pm 0.07 \text{ wt}\%$  at 3.4 kbar and  $\pm 0.03 \text{ wt}\%$  at 10.8 kbar. The two isotherms of Figure 4 can be represented by functions of the type:

$$\text{wt}\%\text{H}_2\text{O} = a + b \cdot P_{\text{tot}} \text{ (kbar)} - c \cdot P_{\text{tot}}^2 \text{ (kbar)} \quad (6)$$

with  $a = 0.94$ ,  $b = 0.261$ , and  $c = 0.0075$  at 600 °C ( $r = 0.949$ ), and  $a = 0.19$ ,  $b = 0.331$ , and  $c = 0.0092$  at 900 °C ( $r = 0.964$ ).

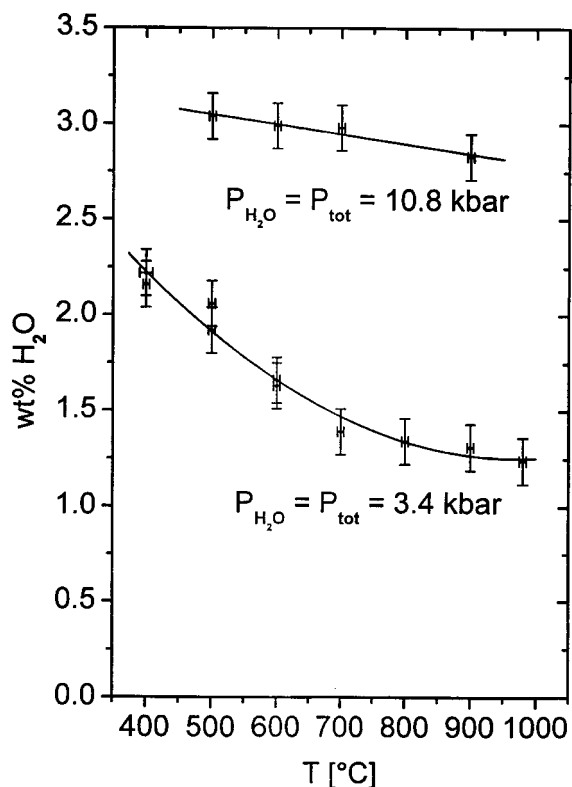


FIGURE 3. Temperature dependence of water content of  $\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}]$  beryl at  $P_{\text{H}_2\text{O}} = P_{\text{tot}}$  isobars of 3.4 and 10.8 kbar.

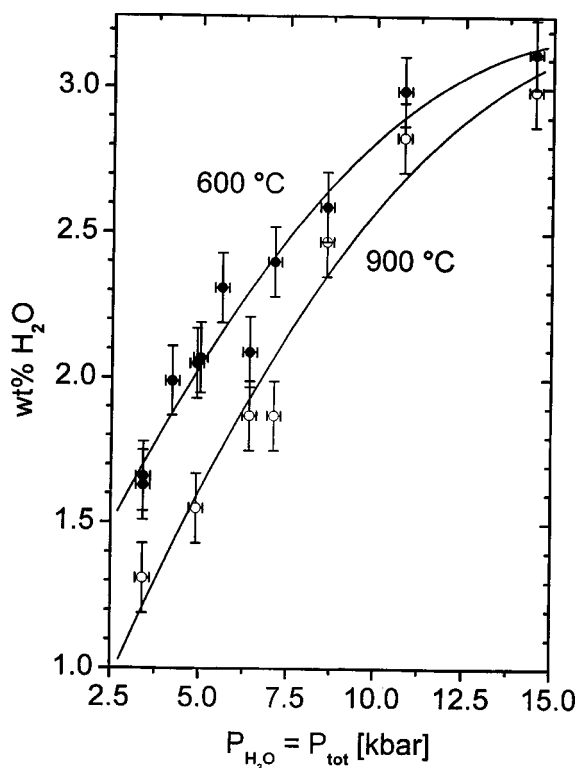


FIGURE 4. Dependence of water content of  $\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}]$  beryl on pressure for  $P_{\text{H}_2\text{O}} = P_{\text{tot}}$  at isotherms of 600 and 900 °C.

Using Equations 5 and 6 and their respective coefficients, and including the data obtained from experiments at other pressures and temperatures, one can interpolate and extrapolate all the experimental data, to calculate curves of constant water content (as wt%  $\text{H}_2\text{O}$ ) in beryl, or “isohydrans,” in the ( $P_{\text{H}_2\text{O}} = P_{\text{tot}}$ ) –  $T$  field.

Such isohydrans are shown in Figure 5 for pressures up to 14.5 kb and temperatures up to 1000 °C. It should be pointed out that for the construction of isohydrans, only data obtained in the piston-cylinder apparatus, wherein very rapid temperature quenching is possible (see above), were used. Nevertheless, the possibility cannot be excluded that, at low pressures, small amounts of water might be released or incorporated by the beryl during quenching from the highest temperatures applied 1000 °C and, though with less probability, 900 °C.

### DISCUSSION

The beryl structure contains two formula units per unit cell. Furthermore, the unit cell contains two of the “pumpkin-like” cavities interconnected by “bottle-necks” to form channels along [0001], as described in the introduction. Thus, one water molecule might be held by one of the cavities when  $n_{\text{H}_2\text{O}}$  reaches a value of 1.00. From the isobars and isotherms that describe the incorporation of water (Figs. 3 and 4) as well as from the deduced field of isohydrans, it can be concluded, in beryl, that

$n_{\text{H}_2\text{O}} = 1.00$  is not exceeded. The “bottle-necks” formed by the hexagonal rings with point group  $6/mmm$  and situated with their horizontal mirror plane at structural heights of  $z = 0$  and  $z = 1/2$  have a diameter of 2.49 Å. If any  $\text{H}_2\text{O}$  with diameter of about 2.8 Å were to be located in such ring positions, then the  $a$ -parameter of the unit cell would increase dramatically. That no such increase of the  $a$ -parameter occurs on increasing  $n_{\text{H}_2\text{O}}$  (Fig. 2) proves that  $\text{H}_2\text{O}$  is exclusively incorporated in the large channel cavities in accordance with the results of structure refinement on end-member beryl (Gibbs et al. 1968). Considering the fact that the horizontal mirror planes of the six-membered tetrahedral rings are situated at a distance of  $c/2 = 4.595$  Å along [0001] from each other (dry beryl, see Table 3), then it is surprising that the  $c$ -parameter increases so strongly with increasing  $n_{\text{H}_2\text{O}}$  (Fig. 2) as the diameter of the incorporated water molecules is much smaller than  $c/2$  (see above), even if the H-H-distance in the vertical mirror plane of  $\text{H}_2\text{O}$  is considered instead of an averaged molecular diameter.

In the present paper, the equilibrium water contents of end-member beryl,  $\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}] \cdot n_{\text{H}_2\text{O}}^{[\text{chan}]}$ , were determined from their refractive indices using experimentally calibrated Equations 2a and 2b. It is worth noting that these equations can also be used to determine the water contents of any beryl that is more complex chemically than the end-member composition studied here when rearranged to the following forms:

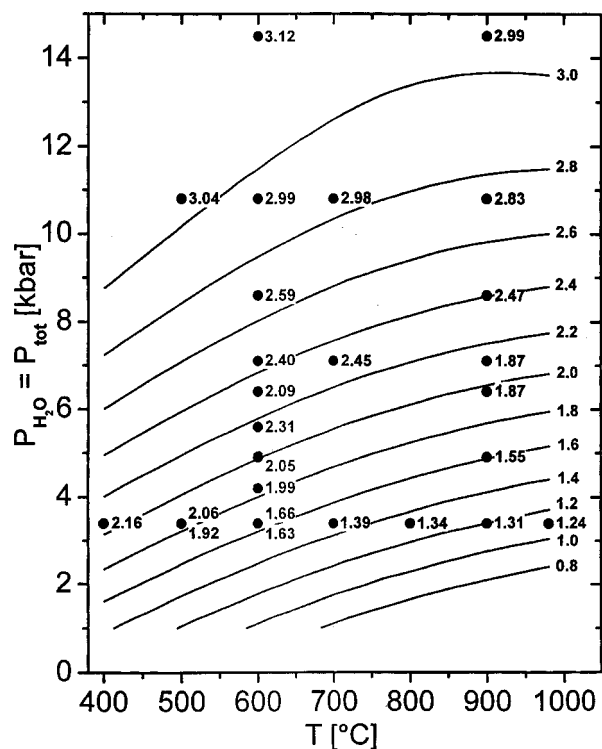


FIGURE 5. Isohydrons in the system  $\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}]\text{-H}_2\text{O}$  in the  $(P_{\text{H}_2\text{O}} = P_{\text{tot}}) - T$  field (see text). The numbers at the isohydrons and at the individual data points are wt%  $\text{H}_2\text{O}$ .

$$\text{wt}\% \text{H}_2\text{O} = (n_{\text{e}, \text{hydrated}} - n_{\text{e}, \text{dehydrated}}) / 0.0080 \quad (2c)$$

$$\text{wt}\% \text{H}_2\text{O} = (n_{\text{O}, \text{hydrated}} - n_{\text{O}, \text{dehydrated}}) / 0.0086 \quad (2d)$$

where  $n_{\text{e}, \text{hydrated}}$  and  $n_{\text{e}, \text{dehydrated}}$  are the refractive indices of the water-bearing beryl to be analyzed for  $\text{H}_2\text{O}$  in the channels and of the dehydrated form of the same beryl sample, respectively. This latter dehydrated form must be produced for the determination. The justification to deduce Equation 2c and 2d from Equation 2a and 2b is the fact that refractive indices are, to a fair approximation, sums of the molar refractivities of the components of the compound under study (e.g., Atkins 1990).

From the considerations of the last paragraph, it is obvious that our results on pure end-member beryl can be used to obtain  $n_{\text{H}_2\text{O}}$  systematically in natural beryls with more complicated chemistry related to different parageneses, and to obtain a comparative understanding of the role of water in their structure. Now, we shall make another step and compare our results on beryl hydration with corresponding results on the structurally related phase Mg-cordierite,  ${}^{\text{VI}}\text{Mg}_2 [{}^{\text{IV}}\text{Al}_4 {}^{\text{IV}}\text{Si}_5\text{O}_{18}] \cdot n\text{H}_2\text{O}^{(\text{Chan})}$  (Schreyer and Yoder 1964; Mirwald et al. 1979; Schreyer 1985): Figure 6 displays a comparison of hydration isotherms at 600 °C of end-member beryl, as determined in this study, and for Mg-cordierite (Mirwald et al. 1979). It is obvious that the pressure dependencies of the molecular water

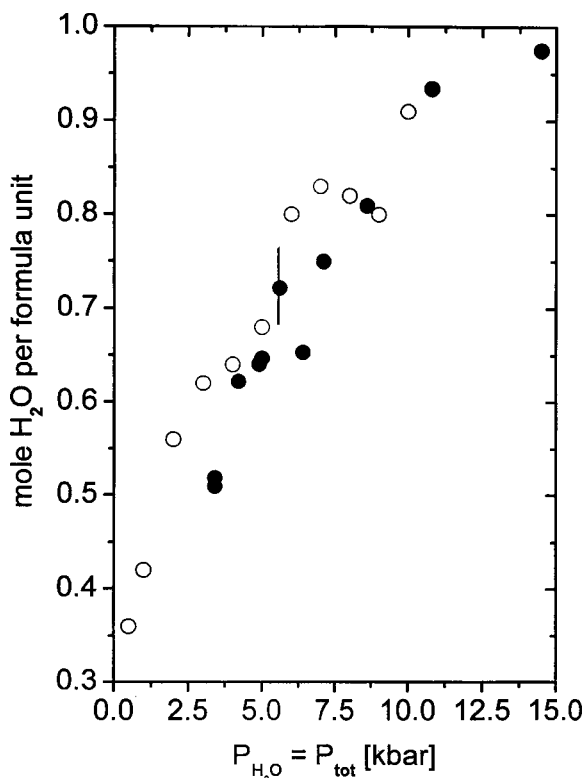


FIGURE 6. Comparison of the dependence of the equilibrium water contents in  $\text{Al}_2[\text{Be}_3\text{Si}_6\text{O}_{18}]$  beryl with those in  $\text{Mg}_2[\text{Al}_4\text{Si}_5\text{O}_{18}]$  cordierite on pressure at an isotherm of 600 °C. Symbols: Solid circle = beryl (this paper); Open circle = Mg-cordierite (Mirwald et al. 1979). The upper pressure stability of Mg-cordierite on the 600 °C isotherm at  $P_{\text{H}_2\text{O}} = P_{\text{tot}}$  (Schreyer and Yoder 1964) is marked by the vertical bar.

held in the channels of both phases are the same, within the limits of the experimental error. This result is due to the fact that the dimensions of the “pumpkin-like” cavities in beryl (see above) are very close to those in cordierite (cf., Khomenko and Langer 1999) and much larger than those of the water molecules incorporated in the structure. The “bottle-necks” of the six-membered tetrahedral rings in beryl have nearly the same diameter as in cordierite (2.49 vs. 2.5 Å). Therefore, even the hydration/dehydration kinetics are expected to be similar in both phases.

#### ACKNOWLEDGMENTS

We thank G. Franz, TU Berlin, for providing the phenakite sample from San Miguel de Piracicaba, L. Cemic, now Univ. Kiel, and G. Franz for helpful discussions, Ch. Bäumer and H.-J. Reyher, Osnabrück, for calculational work to produce the figures, as well as M. Hellwig for carefully manufacturing the high-pressure inserts for the piston-cylinder-apparatus.

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MANUSCRIPT RECEIVED DECEMBER 6, 2000

MANUSCRIPT ACCEPTED OCTOBER 23, 2001

MANUSCRIPT HANDLED BY MARK WELCH