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Experimental determination of melting relationships of beryl in the system BeO-Al_2O_3-SiO_2-H_2O between 10 and 25 kbar

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ABSTRACT. The onset of melting of beryl+H_2O was determined experimentally in the P-T range 10-25 kbar, 900 to 1200 °C, by synthesis runs on the composition $Al_2Be_3Si_6O_{18}$. Beryl begins to melt incongruently to chrysoberyl, phenakite, and melt at temperatures slightly above 1000 °C. At higher temperatures a divariant stability field exists where beryl, chrysoberyl, phenakite, and melt coexist due to the solubility of H_2O in beryl and in the melt. The final disappearance of beryl was bracketed between 1050 and 1100 °C at 10 kbar and at 1100 °C between 10 and 20 kbar. The phases (analysed for Al and Si by electron microprobe) do not show major deviation from stoichiometric composition.

KEYWORDS: beryl, melting, chrysoberyl, phenakite.

THE mineral beryl with the idealized formula $Al_2Be_3Si_6O_{18}$ has a very wide stability field. Beryl is formed at low temperatures in tuffs, as well as at high temperatures in pegmatites, but little experimental data on its stability field are available. At atmospheric pressure Ganguli (1972) found that beryl decomposes into phenakite, chrysoberyl, and cristobalite between 1300 and 1400 °C. Barton (1981) determined this reaction (with quartz instead of cristobalite) at elevated pressures in the water-free system BeO-Al_2O_3-SiO_2 between 5 and 7 kbar; he found a negative slope with equilibrium temperatures of 1450 °C at 5 kbar and 1100 °C at 7 kbar.

Miller and Mercer (1965) found incongruent melting of beryl into phenakite and liquid at atmospheric pressure at temperatures between 1460 and 1475 °C. At elevated pressures, Munson (1967) and Wilson (1964) obtained data on a reaction of beryl into phenakite, chrysoberyl, quartz and liquid, or phenakite and liquid, respectively. These reactions probably represent metastable equilibria or must be explained by additional components such as H_2O or alkalis as concluded on the basis of the work of Ganguli (1972) and Barton (1981). The eutectic temperature was determined by Ganguli and Saha (1965) at 1515 °C. In the quaternary system BeO-Al_2O_3-SiO_2-H_2O beryl can easily be synthesized and is stable to at least 800 °C at 1 and 2 kbar P_{H_2O} (Franz and Morteani, 1981).

It is the purpose of this paper to present experimental data on the upper thermal stability of beryl in the P_{H_2O} range of 10 to 25 kbar. Two aspects are of particular interest: (i) Beryl may serve as a 'model mineral' for investigating the influence of H_2O on the upper thermal stability of minerals which incorporate H_2O into the structure. Beryl may contain up to 1 mole per formula unit H_2O within its channels, and is therefore similar to cordierite, where the same problem—influence of channel-H_2O—complicates the applicability of experimental studies on natural systems. (ii) An investigation of the melting relationships in the system BeO-Al_2O_3-SiO_2-H_2O will be a first step towards an understanding of the formation of beryl in the highly complex natural systems where beryls crystallize from granitic or pegmatitic melts. Of course, any application of the results presented here must be done with caution.

Experimental procedure. Starting mixtures of the composition $Al_2O_3 \cdot 3BeO \cdot 6SiO_2$, the ideal composition of beryl, were made from the following: pure natural phenakite (analysis see Franz and Morteani, 1981) in order to avoid handling the extremely poisonous BeO or Be salts; γ-Al_2O_3

(corrected for 'H_2O' content); and SiO_2 (prepared from noncrystalline, gel-like SiO_2, 'Aerosil', by heating at 1100 °C). The necessary amount of the starting mixture for several runs was homogenized in an agate mortar (dry) for at least 30 minutes, and then 30 to 50 mg were placed together with 5 μl H_2O in Au or Pt capsules. The capsules were sealed.

Run durations varied between 20 and 120 hours (except one run at 1200 °C, 2 hours). A few runs were carried out without water, i.e. at conditions of room humidity and no special precautions were taken to keep the starting mixture and the capsule absolutely dry.

Experiments were carried out in a piston cylinder apparatus with a NaCl cell (Neuhaus and Steffen, 1970). Pressure is held constant to about ± 200 bar and, for 'piston in' runs, is approximately 5 % lower than nominal pressure (Kirfel, pers. comm.). Pressure calibration (Hoyer, pers. comm.) has been performed by means of the Bi I $\rightleftharpoons$ Bi II transition at 25.48 kbar (Peerdeman *et al.*, 1980). Temperatures are held constant to within ± 0.5 °C and are accurate to approximately ± 5 °C. No correction of the pressure dependence of the thermo-emf was performed.

Run products were examined with powder X-ray diffraction and optical methods as well as with the electron microprobe, using natural minerals as standards for Al, Si, Fe, Na. Both systems, WDS and EDS, of a CEMEBAX automated probe (ZAF correction program) were used.

Results. The results of the piston cylinder runs are presented in Table I and fig. 1. At $P_{H_2O} = 25$ kbar, $T = 1000$ °C, and $P_{H_2O} = 10$ kbar, $T = 1010$ °C, beryl is the main constituent of the run products. Chrysoberyl, phenakite, and quartz are present in minor amounts only, probably of the order of $\leqslant 5$ vol. % (estimated from optical observation).

At higher temperatures (between 1025 and 1100 °C) the run products consist of various amounts of beryl, phenakite, chrysoberyl, and melt. Minor amounts of quartz which were formed among the run products at 25 kbar could not be

Table 1. Run data for piston-cylinder runs with the composition 1 $Al_2O_3 \cdot 3\ BeO \cdot 6\ SiO_2$

No	P (kbar)	T (° C)	t (h)	H_2O (μl)[1]	run products[2]	
CF 3	10	1000	24	-	Be, Ph, Cb, Qz	
4	15	1000	24	-	Be, Ph, Cb, Qz	
5	15	1000	120	-	Be, Ph, Cb, Qz	
6	25	1100	20	-	Be, Ph, Cb, Qz	
15	10	1010	42,5	5	Be, (Ph), (Cb)	*
16	10	1050	21	5	Be, Ph, Cb, L	*
19	10	1100	18	5	L, Ph, Cb, (Be?)	
18	10	1150	15	5	L, Ph, Cb	
14	17,5	1025	64	5	Be, Ph, Cb, L, (Qz?)	*
7	20	900	41	5	Be, (Ph), (Cb), (Qz)	
1[4]	20	950	20	5	Be, (Ph), (Cb), (Qz)	*
8	20	950	20	5	Be, (Ph), (Cb)	
13	20	1025	48	5	Be, Ph, Cb, L, (Qz?)	
12	20	1050	72	5	Be, Ph, Cb, L, (Qz?)	*
2[3]	20	1100	25	2	Be, Ph, Cb, L	*
17	20	$\gtrsim$1200	1,5	5	L, Ph, Cb	*
9	25	1000	20	5	Be, (Ph), (Cb), (Qz)	
11	25	1050	96	5	Be, Ph, Cb, L, (Qz)	*
10	25	1100	24	5	Be, Ph, Cb, L, Qz	

1) water added to approximately 30 - 50 mg solid starting material

2) Be = beryl, Cb = chrysoberyl; Ph = phenatite; Qz = quartz; L = liquid; ( ) = minor amounts; *) = microprobe analyses

3) starting material: natural alkali-poor beryl from Kolsva/Sweden (analysis see Franz and Morteani, 1984)

4) seeds of natural beryl added

identified unequivocally at 20 and 17.5 kbar and are absent at 10 kbar.

When no water was added to the run charge, the products consisted of a mixture of beryl, phenakite, chrysoberyl, and quartz. At 1100 °C the amount of beryl compared to phenakite, chrysoberyl, and quartz is lower than at 1000 °C. Increasing the run duration from 24 to 120 hours at 1000 °C did not change the relative amounts of the run products. At 10 kbar and at temperatures of $\geqslant 1100$ °C no beryl was found among the run products while at 20 kbar, $\geqslant 1200$ °C, melt is the main constituent, and phenakite and chrysoberyl are the only crystalline phases.

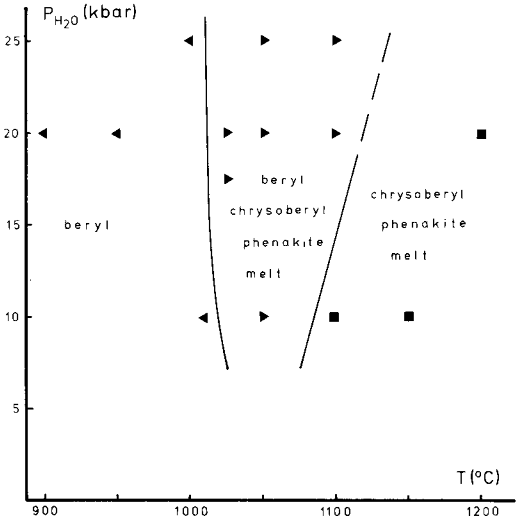

FIG. 1. Experimental results of synthesis runs on the composition $Al_2Be_3Si_6O_{18}$ ($+H_2O$).

Composition of phases. The phases obtained in the 'synthesis runs' performed were analysed by electron microprobe. Two water-free beryls obtained by hydrothermal syntheses at 20 kbar, 950 °C, and 5 kbar, 700 °C, and subsequent dehydration at 920 °C, 1 atm., 14 h, gave both a mean Al_2O_3 content of 18.6 wt. % and SiO_2 content of 67.8 wt. %, close to the ideal values of 18.96 and 67.07 wt. %, respectively. Water-bearing beryls coexisting with melt and/or other solid phases also have Al_2O_3 and SiO_2 present in values near to the ideal for hydrous or anhydrous beryl, respectively (see Table II). The analyses indicate that the beryls are close to their ideal compositions. Substitutions $2\,\mathrm{Al^{IV}} = \mathrm{Be^{IV}} + \mathrm{Si^{IV}}$ or $2\,\mathrm{Be^{IV}} = \mathrm{Si^{IV}} + \square^{\mathrm{IV}}$ may be operative to a minor extent.

The measured total varies between 89 and 94 wt. % leaving 11 to 15 wt. % for the undetermined oxides BeO and H_2O. The variation is probably due to a variation in H_2O contents (excluding possible analytical error). However, there is no obvious systematic correlation between pressures or temperatures and wt. % total in the *P–T* range of the runs presented here.

Phenakites have 2–3 wt. % more SiO_2 than ideal phenakites and also up to 0.5 wt. % Al_2O_3 (see Table II). This indicates a slightly non-stoichiometric composition of this high-temperature phase in contrast to natural phenakites, probably formed at much lower temperatures.

Chrysoberyls have variable Al_2O_3 contents but generally close to the ideal value of 80.3 wt. % [average 80.6 % (75–83) of sixteen analyses]. SiO_2 contents are in the order of 0.1 to 0.2 wt. %, similar to those found in most natural chrysoberyls (some natural chrysoberyls from metamorphosed pegmatites may contain up to one wt. % SiO_2 (Franz and Morteani, 1984); the even higher SiO_2 values of up to 4 wt. % SiO_2 reported by Okrusch, 1971, in wet chemical analyses, are possibly due to quartz impurities).

Al_2O_3 and SiO_2 contents of the melt were determined in six run products. They vary between 4.8 to 7.0 and 80 to 87 wt. %, respectively. But within one sample the variations are much smaller, indicating a rather homogeneous melt (see Table II), except for run no. CF 17, in which the run duration was only one and a half hours. With increasing temperature the wt. % total increases probably because of the decreasing H_2O content of the melt. In the pressure range from 17.5 to 25 kbar, the Al/Si ratio does not vary significantly. Among the products of run nos. CF 17 and CF 16 which are only a few degrees above the temperature of onset of melting, the amount of melt is generally too small to yield good analyses without overlap with beryl.

Nothing can be said, of course, about the BeO and H_2O contents of the melt. In terms of Al/Si ratio, the composition of the melt lies between the composition at the eutectic point E_1 (at 1 atm.) and the peritectic point P_2 as determined by Ganguli and Saha, 1965 (see fig. 2 and Table II).

Run no. CF 2, which has a natural, alkali-poor and Fe_2O_3-bearing beryl as starting material, produced higher Al_2O_3 contents (7.5 wt. %) and lower SiO_2 (77.8 wt. %) in the melt. Fe_2O_3 is 0.9 wt. % and Na_2O in the range of the detection limit of the EDS microprobe (*c.*0.5 wt. %). The wt. % total of this melt is lower than that of the synthetic run products despite the rather high temperatures. This indicates an increased BeO content.

Discussion. Analysis of the phase relationships

Table II. Representative electron microprobe analyses of beryl, chrysoberyl, phenakite and melt in weight % oxides

	beryl						theoretical	
run No	15	16	14	1[1]	2	11	an-hydrous	hydrous (1 H_2O per formula unit)
P (kbar)	10	10	17.5	20	20	25		
T (° C)	1010	1050	1025	950	1100	1050		
SiO_2	18.7	19.0	18.9	18.6	18.9	19.1	18.96	18.35
Al_2O_3	67.9	70.0	65.7	67.8	65.0	67.1	67.07	64.90
Fe_2O_3	-	-	-	-	0.45	-	-	-

	chrysoberyl				theoretical
run No	15	16	2	17	
P (kbar)	10	10	20	20	
T (° C)	1010	1050	1100	1200	
SiO_2	-	0.1	-	0.2	-
Al_2O_3	80.2	82.1	74.47	82.4	80.30
Fe_2O_3	-	-	2.73	-	-

	phenakite				theoretical
run No	16	14	2	17	
P (kbar)	10	17.5	20	20	
T (° C)	1050	1025	1100	1200	
SiO_2	57.4	57.1	56.0	57.5	54.57
Al_2O_3	0.1	0.5	2.5	<0.1	-

	melt					
run No	12	2	17	11	E_1	P_2
P (kbar)	20	20	20	25	0.001	0.001
T (° C)	1050	1100	1200	1050	1515	1640
SiO_2	83.0 (82.7-83.3)	77.8 (76.5-78.5)	84.0 (81.5-86.8)	82.9 (81.0-84.0)	82.8	91
Al_2O_3	5.6 (5.5-5.8)	7.5 (7.1-7.8)	5.9 (4.7-7.0)	6.1 (5.8-6.3)	11.3	4
Fe_2O_3	-	0.89 (0.84-0.92)	-	-	-	-
$\frac{Si}{Si + Al}$	95.8	94.6	96.0	95.9	92.6	97.5

1) water expelled at 1 atm, 920° C, 14 hours
2) from Ganguly and Saha (1965)

among the phases beryl (be), chrysoberyl (cb), phenakite (ph), quartz (qz), liquid (L), and vapour (V) was done by means of Schreinemaker's method. We start from the following:

(i) The solid phases do not show significant deviation from ideal composition. Microprobe analyses of the run products indicate that this is certainly true for beryl. There is, however, a slight surplus of SiO_2 in phenakite as well as a variation in Al_2O_3 contents in chrysoberyl.

(ii) The only solid phase containing water is beryl (the abbreviations be = anhydrous beryl and hbe = hydrous beryl are used). At temperatures above *c.*900 °C the water content of beryl is mainly a function of pressure and much less dependent on temperature. Lines of equal water contents in beryl, experimentally determined at 900 °C, 5 to 20 kbar, are taken from Pankrath (1984).

(iii) The eutectic temperature 1515 °C of the system $BeO-Al_2O_3-SiO_2$ is taken from Ganguli and Saha (1965), and it is assumed that, with increasing P_{H_2O}, the minimum melting temperature is significantly lowered by dissolution of H_2O in the melt. This effect is less important at pressures above *c.*5 kbar.

(iv) The 'vapour' phase is assumed to be essentially H_2O. It is known, however, that solubility in water of SiO_2 (Walther and Helgeson, 1977) as well as that of Al_2O_3 (Becker *et al.*, 1983) increases significantly with pressure. Furthermore, synthesis experiments in the subsolidus area, with varying amounts of water, showed that, with increasing H_2O content of the run charge, the amount of 'impurities' chrysoberyl and phenakite increases. This indicates incongruent solubility of beryl, with SiO_2 as the most soluble component.

(v) The composition (Be : Al : Si) of the first melt, formed at the temperature of onset of melting, is

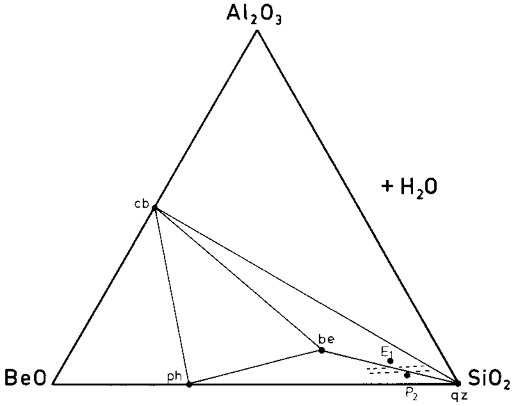

FIG. 2. Selected phases of the system $BeO-Al_2O_3-SiO_2-H_2O$ projected from H_2O. Abbreviations: be = beryl, cb = chrysoberyl, ph = phenakite, qz = quartz, E_1 = eutectic composition, P_2 = peritectic (Ganguli and Saha, 1965). The dashed lines show the range of $Al_2O_3:SiO_2$ ratios, determined in the experimentally producted melts.

assumed to be essentially the same in the presence of water as that at atmospheric pressure. This assumption is probably not too unrealistic since microprobe analyses of the melt of the run products, which are not formed at the beginning of melting but at higher temperatures, actually lie in the expected range between the eutectic and peritectic (P_2, Ganguli and Saha, 1965) composition with respect to Al : Si.

(vi) The subsolidus reaction be = ph + cb + 5 SiO_2 (Ganguli, 1972) is located at 1350 °C. No attempt has been made to decipher the phase relationships in the water-free system. All complications arising from the phase transformations quartz–cristobalite–tridymite are neglected. They take place at low-pressure/high-temperature and probably do not influence the phase relations in the P–T range considered here. Furthermore, they are not located exactly.

We consider the following reactions:

	Absent phases	dP/dT
(1) hbe = be + H_2O	(cb) (ph) (qz) (L)	0
(2) cb + ph + SiO_2 + V = L (at atmospheric pressure also V absent)	(be)	–
(3) hbe = ph + cb + SiO_2 + V (at atmospheric pressure with be, also V absent)	(L)	–/∞/+
(4) hbe + cb + qz + V = L	(ph)	–/∞
(5) hbe + qz + V = ph + L	(cb)	–/∞
(6) hbe + V = cb + ph + L	(qz)	–/∞
(7) hbe = cb + ph + qz + L	(V)	+

The slopes (dP/dT) of the reactions 3 to 7 depend on the equilibrium (1) defining the water content in beryl. We assume that ΔS of reaction (1) is small compared to ΔS of the other reactions, such that ΔS of the overall reactions is not strongly influenced.

At low pressures (≪ 1 kbar) high-temperature beryl is essentially anhydrous and ΔV of the reaction is mainly that of the solid components (which is −1.72 J/bar, neglecting the compressibilities of the phases). At higher pressures beryl contains appreciable amounts of water, and ΔV of the solids is relatively small compared to ΔV of the reactions. Because of the large volume of water vapour, ΔV of the reaction becomes positive, and, therefore, the slope dP/dT changes to positive.

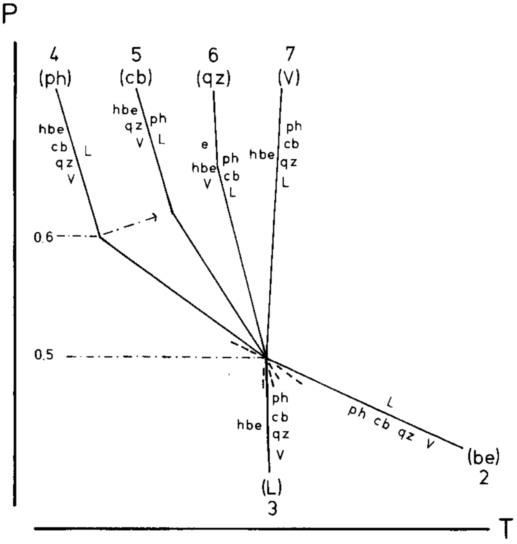

FIG. 3. Schematical phase relations of the system $BeO-Al_2O_3-SiO_2-H_2O$ at high P and T. The dashed dotted lines are lines of equal water content in beryl expressed as mole fraction of hydrous beryl. The discontinuity in the reaction slopes at the intersection with line of equal water content 0.6 is only schematical and shows the type of influence of rising water contents in beryl on dP/dT slope of the reactions. Abbreviations as in fig. 2, hbe = water-bearing beryl.

The situation is shown schematically in fig. 3. Reactions 2 (be) and 3 (L) intersect at certain P–T conditions; it is arbitrarily assumed that the water content of beryl is 0.5 mole H_2O per formula unit at these conditions. The intersection creates an invariant point from which the phenakite-, chrysoberyl-, quartz-, and vapour-absent reactions (4, 5, 6, and 7) start. In fig. 3 they are shown with a discontinuity where they intersect the next line of equal water content (0.6) for beryl, but of course the change in slope is continuous, as is shown in fig. 4, since there is an infinite number of lines of equal water content. Reactions 6 (qz) and 7 (V) represent the beginning and the end, respectively, of a continuous reaction field (cf. fig. 4). Therefore, at the high-temperature end of this field, water does not participate as a phase in the reaction (V). It participates as a component according to a distribution equilibrium between the last hydroberyl- and water-bearing liquid.

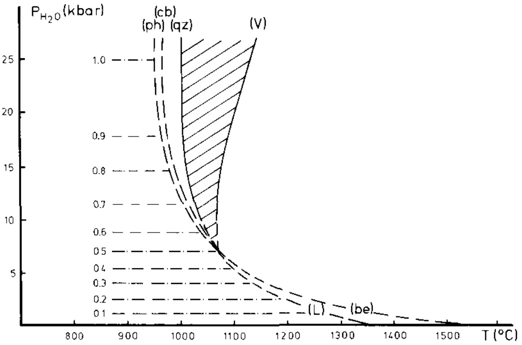

FIG. 4. Experimental high P/T results of this study compared with the experimental results of Ganguli and Saha (1965) and Ganguli (1972) at 1 atm. The dashed area shows the stability field of beryl + melt + chrysoberyl + quartz. Dashed lines are hypothetical; note that the exact position of the invariant point is unknown and that all complications involving the low-P-high-T phase transformations of SiO_2 are neglected. Lines of equal water content in beryl (dashed dotted) are taken from Pankrath, 1984 (see text).

Fig. 4. shows the reaction bundle in a P-T diagram, where the available experimental data are located. The reactions determined in this study are the quartz- and vapour-absent equilibria (6 and 7). These two reactions limit the field where beryl begins to decompose (qz) 6 until its ultimate upper thermal stability (V) 7 is reached. The location of the invariant point as well as the slopes of the reactions (L) and (V) are uncertain. Further experiments in the low-pressure/high-temperature area are necessary.

The graphical analysis allows us to interpret the experimental results. When no water was added to the run charge (runs CF 3 to 6), all available water adsorbed at the surface of the capsule and the starting mixture is incorporated into the beryl. The amount of water is not sufficient to saturate beryl, therefore chrysoberyl, phenakite, and quartz are formed too. If water is an excess phase, H_2O-saturated beryl and/or H_2O-saturated melt form. Since the composition of the melt deviates from that of beryl (towards SiO_2-richer parts of the system, fig. 2), chrysoberyl and phenakite are the only crystalline phases in addition to melt. If the temperatures are high enough (runs 17, 18, and 19) the upper thermal stability of beryl according to reaction 7 is reached and only chrysoberyl, phenakite, and melt are formed.

According to Schreinemaker's analysis, quartz should be a liquidus phase, as noted schematically in fig. 3, but it was shown that the melts formed at high temperatures have higher SiO_2 contents (see Table II) than formed at the lowest temperature.

If the minimum temperature (= eutectic) melt formed at high P_{H_2O} is significantly richer in BeO than at atmospheric conditions, such that it lies within the triangle be-ph-qz instead of the triangle be-cb-qz, reactions 4 (ph) and 5 (cb) change their relative positions. If the composition of the melt is colinear with beryl and quartz, they coincide.

Conclusions. The present study confirms that beryl is a stable phase up to high water pressures of at least 25 kbar, at temperatures up to 1000 °C. The upper thermal stability is defined by the equilibrium

$$\text{be} + \text{V} = \text{ph} + \text{cb} + \text{melt}.$$

This reaction is divariant because of the P-T-dependent solubility of H_2O in beryl. The onset of melting is almost independent of P_{H_2O} between 10 and 25 kbar; a slightly negative slope (see figs. 1 and 4) is inferred from the fact that the solubility of H_2O in silicate melts increases with increasing water pressure. The upper thermal boundary of the divariant field in which the phases beryl, chrysoberyl, phenakite, and melt coexist with 'vapour' has a positive slope. This is demonstrated by the fact that at 10 kbar, 1100 °C, beryl is not stable, whereas at 20 and 25 kbar, 1100 °C, it is stable together with phenakite, chrysoberyl, and melt. Previous discrepancies between experimental studies of the upper thermal stability of beryl (van Valkenburg and Weir, 1957; Wilson, 1964; Munson, 1967) must be due to uncontrolled H_2O content of the run charge, other impurities in the starting material, or to inaccurately determined run conditions.

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