Multisystems analysis of beryllium mineral stabilities: the system BeO–Al₂O₃–SiO₂–H₂O

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Abstract

Seven commonly associated minerals in the system $BeO-Al_2O_3-SiO_2-H_2O$ include chrysoberyl, phenakite, euclase, bertrandite, beryl, kaolinite, and quartz. The phase rule implies that not more than six of these minerals can coexist at an invariant point, and, with the addition of an aqueous phase, the association constitutes an $(n + 4)$ phase (negative two degrees of freedom) multisystem. The apparent incompatibility of kaolinite with phenakite allows the splitting of this unwieldy multisystem into two smaller $(n + 3)$ phase multisystems, which may be labeled ⟨Kao⟩ and ⟨Phe⟩. Molar volume data, computer program REACTION, and natural assemblages can then be used to derive the presumably stable configuration of these multisystems on an isothermal P_s-minus μH_2O diagram. A $P-T$ diagram projected through the aqueous phase should have the same topology, and can similarly be drawn.

On the resulting diagrams, three invariant points labeled [Chr], [Btr], and [Qtz] are stable in the multisystem ⟨Kao⟩, and three distinct but identically-labeled points are stable in the multisystem ⟨Phe⟩. An implication of this topology via the "metastable–stable correspondence," is that the assemblage phenakite + euclase + beryl (+ aqueous phase) has a finite range of stability in $P-T$ space. More importantly, this topology implies that the beryl stability field pinches out at high P and T, with beryl eventually breaking down to chrysoberyl + phenakite + quartz. The topology also explains why euclase is much rarer than bertrandite. Euclase is a comparatively high-density phase, and its stability field, especially in the presence of quartz or amorphous silica, pinches out at low P and T. Most reactions involving the hydrous phases bertrandite and euclase probably occur at temperatures too low for convenient hydrothermal experimentation (below 400°C).

Introduction

Beryl as emerald (Gaines, 1976) and chrysoberyl as alexandrite (Okrusch, 1971) are among the more valuable synthetic and natural gemstones, yet their stability relations in the system $BeO-Al_2O_3-SiO_2$ are poorly understood. When water is added to this system, bertrandite, $Be_4(Si_2O_7)(OH)_2$, and euclase, $BeAl(SiO_4)(OH)$, become stable, but their stability relations are likewise unknown, despite the fact that bertrandite has overtaken beryl as the most important domestic source of beryllium (Petkof, 1976, p. 137–146). In this regard, one might ask, why is bertrandite so much more common than euclase in nature? Compositional considerations alone (the lack of Al in bertrandite) would suggest that the opposite should be true. (In the anhydrous system, in contrast, beryl and chrysoberyl are more common than the Al-free phase phenakite, Be_2SiO_4.)

The present paper represents a first attempt to derive the topology of the stability fields of these beryllium minerals. The derivation depends on natural assemblages (*cf.* Beus, 1960; Vlasov, 1966; Burnol, 1968; Černy, 1968), Fortran program REACTION (Finger and Burt, 1972), molar volume data (Robie *et al.*, 1967), and multisystems analysis (Korzhinskii, 1957). Reliable thermochemical or experimental data on most of the phases are lacking, so that the results are of necessity topological rather than quantitative.

Many of the results were collectively derived as a laboratory assignment by my spring term 1977 class in ore deposits at Arizona State University. The method, here summarized in advance, consisted basically of the following five steps: (1) The system $BeO-Al_2O_3-SiO_2-H_2O$ was searched for all possible phases that occur as minerals or that have been synthesized. A number of these phases were eliminated from con-

sideration, leaving seven minerals plus an aqueous fluid. (2) The resulting eight-phase multisystem was simplified to a six-phase pseudoternary system by projecting through H_2O and by noting that phenakite and bertrandite then plot at the same point. (3) An isothermal P_s–minus μH_2O diagram was plotted for this simpler multisystem. (4) Natural assemblages were used to determine the most likely intersection of the degenerate dehydration reaction of bertrandite to phenakite with the multisystem. (5) The resulting P_s–minus μH_2O diagram was transformed into a topologically identical schematic P_{H_2O}–T diagram.

Phases

The quaternary system BeO–Al_2O_3–SiO_2–H_2O contains, among others, the seven commonly associated phases listed in Table 1. Corresponding molar volumes are given in joules/bar. Eight additional phases have been omitted from the present study, largely because they have never been reported in association with beryl (Table 2). The compositions and assumed natural compatibilities of anhydrous minerals in the system BeO–Al_2O_3–SiO_2 are shown in Figure 1 (Burt, 1975a; a summary of evidence appears under the discussion of natural assemblages). Similarly, the compositions and known compatibilities of most phases in the system BeO–Al_2O_3–SiO_2–H_2O, projected through excess quartz, are shown in Figure 2. The dashed lines on this figure refer to uncertain or conflicting assemblages variously reported in the literature (again, consult the section on natural assemblages).

In the following discussion, the phases in Table 1 will be assumed to be stoichiometric. Natural beryl may contain considerable alkalis (Na, Cs, and Li)

Table 2. Abbreviations, formulas, and molar volumes* of eight additional minerals in the system BeO–Al_2O_3–SiO_2–H_2O

Name	Abbrev.	Formula	Molar Volume* (joules/bar)
Bromellite	Bro	BeO	0.831
Behoite	Beh	$Be(OH)_2$	2.22
Corundum	Cor	Al_2O_3	2.558
Diaspore	Dsp	$AlO(OH)$	1.776
Gibbsite	Gib	$Al(OH)_3$	3.196
Beryllite	Blt	$Be_3SiO_4(OH)_2 \cdot H_2O$	---
Andalusite	Als	Al_2SiO_5	5.153
Pyrophyllite	Pyp	$Al_2Si_4O_{10}(OH)_2$	12.83

*Data from Robie et al. (1967) except for behoite and pyrophyllite. Behoite from x-ray data for β-$Be(OH)_2$ in Ross (1964); pyrophyllite recalculated from Day (1976).

and water, mainly in channel positions (Bakakin and Belov, 1962; Černy, 1975; Hawthorne and Černy, 1977), and natural beryl and chrysoberyl may also contain Cr^{3+}, Fe^{3+}, V^{3+}, Sc^{3+}, and other ions substituting for Al^{3+}. Based on available data, there are no indications of major compositional variations in natural euclase, bertrandite, or phenakite.

Review of experimental studies

This review of experimental studies and the following review of natural occurrences have been made as complete as possible, in order to succinctly summarize in one place the conflicting data initially available on the system BeO–Al_2O_3–SiO_2–H_2O. Much of this data is seen to be unnecessary for the multisystems analysis that follows, and these two sections may therefore be skimmed during a first reading without much loss of continuity.

Phase equilibria in the system Al_2O_3–SiO_2–H_2O have recently been summarized by Burt (1976, 1978)

Table 1. Abbreviations, formulas, and molar volumes* of seven minerals in the system BeO–Al_2O_3–SiO_2–H_2O

Name	Abbrev.	Formula	Molar volume (joules/bar)
Chrysoberyl	Chr	$BeAl_2O_4$	3.432 ± .002
Phenakite	Phe	Be_2SiO_4	3.719 ± .004
Euclase	Euc	$BeAlSiO_4(OH)$	4.657 ± .010
Bertrandite	Btr	$Be_4Si_2O_7(OH)_2$	9.217 ± .050(?)
Beryl	Brl	$Be_3Al_2Si_6O_{18}$	20.355 ± .025
Kaolinite	Kao	$Al_2Si_2O_5(OH)_4$	9.952 ± .026
Quartz	Qtz	SiO_2	2.2688 ± .0001

*Data from Robie et al. (1967) except for bertrandite. The bertrandite value was calculated from unit cell dimensions given by Solov'eva and Belov (1961), and cited in Ross (1964). Slightly different unit cell dimensions in Solov'eva and Belov (1964) give a value of 9.177; use of densities measured on natural materials (2.60 ± .03) gives a value of 9.16 ± .10.
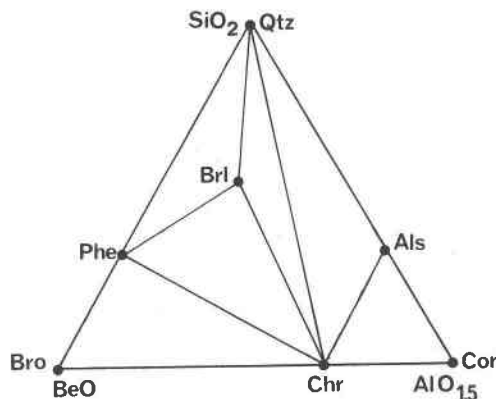

Fig. 1. Moderate P and T mineral compatibilities deduced for the system BeO–Al_2O_3–SiO_2, based on natural assemblages.
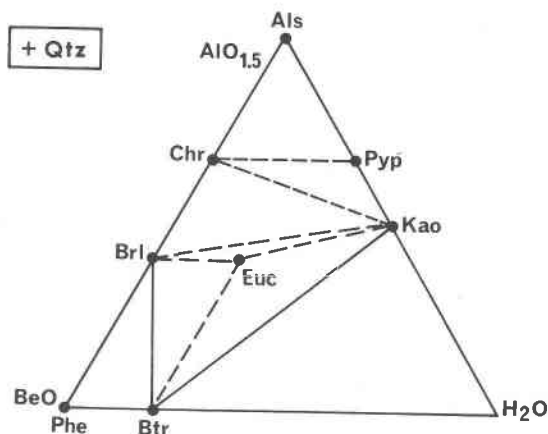
Fig. 2. Compatibilities among some minerals in the system BeO–Al₂O₃–SiO₂–H₂O, based on natural assemblages. Quartz is assumed present. Dashed lines indicate uncertain or conflicting mineral compatibilities.

and Day (1976, 1978), and little need be added here.

In high-temperature studies of the system BeO–Al₂O₃, Foster and Royal (1949) and Lang et al. (1952) synthesized chrysoberyl and a second phase BeO·3Al₂O₃. In nature, chrysoberyl is the only intermediate phase yet described, and any others will be assumed to be unstable at low to moderate temperatures. Studies of the related binary system BeO–SiO₂ by Morgan and Hummel (1949) revealed phenakite as the only intermediate phase; it melts incongruently. In the binary system BeO–H₂O, Newkirk (1964) dehydrated behoite to bromellite at 170°C, 1.3 kbar and 200°C, 4.1 kbar, but this reaction was not reversed. In the ternary BeO–SiO₂–H₂O, Bukin (1967) readily synthesized both bertrandite and phenakite between 300 and 500°C, 720 atm, but bertrandite appeared favored below 400°C.

The anhydrous ternary BeO–Al₂O₃–SiO₂ has been extensively studied, mainly with regard to the synthesis of emeralds. Early attempts involving fluxes and hydrothermal growth are thoroughly reviewed by Flanigen et al. (1967), who also report their own flux growth of emerald in the range 700–1200°C and hydrothermal syntheses under unspecified conditions (500–600°C, 0.7–1.4 kbar according to Nassau, 1976).

Studies of the incongruent melting behavior of beryl by Ganguli and Saha (1965) and Miller and Mercer (1965) were confirmed by Riebling and Duke (1967). Liquid immiscibility occurs in the melts. Ganguli and Saha (1965) delineated a ternary eutectic at 1515±5°C involving chrysoberyl, phenakite, and cristobalite, and Ganguli (1972) in a subsolidus study

determined that beryl breaks down to chrysoberyl, phenakite, and cristobalite between 1300 and 1400°C.

Studies of beryl synthesis at high pressures were initiated by Wilson (1965), who reported direct synthesis of beryl from its melt at pressures to 20 kbar. Beryl and phenakite reportedly were synthesized by Takubo et al. (1971) to 20 kbar at 1600°C. The phase characterizations (or quenching procedures) in the above two studies are questionable (cf. Nassau, 1976) in light of the results of Munson (1967). His reconnaissance studies indicated that natural beryl breaks down to chrysoberyl, phenakite, and quartz at approximately 15.5 kbar and 1340°C and to chrysoberyl, phenakite, and coesite at 45.5 kb, 1050°C. As discussed below, this high P subsolidus breakdown of beryl is consistent with molar volume data (Table 1).
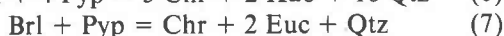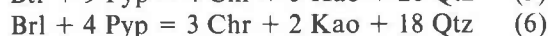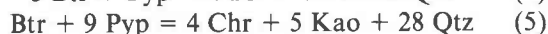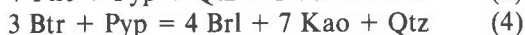
Studies of the complete quaternary BeO–Al₂O₃–SiO₂–H₂O initially involved hydrothermal syntheses of beryl and emerald. Van Valkenburg and Weir (1957) synthesized beryl between 500 and 850°C at 1 to 2 kbar, but reportedly obtained phenakite plus glass above 900°C. Wyart and Scavnicar (1957) synthesized beryl between 400 and 600°C at 400–1500 bars. At 600°C they obtained beryl + chrysoberyl + phenakite, and with the addition of Cr₂O₃ to replace Al₂O₃, beryl + phenakite + quartz + Cr₂O₃. Frondel and Ito (1968) readily obtained beryl at 680° and 2 kbar, and also synthesized the Sc–Fe analogue of beryl (bassite), with phenakite, quartz, and hematite. Other syntheses are reviewed by Nassau (1976).

Beus et al. (1963) studied the hydrothermal alteration of beryl in various HF-bearing solutions between 500 and 600°C. They altered beryl to quartz, to bertrandite, and to bertrandite + muscovite. A similar series of leaching experiments was performed by Syromyamnikov et al. (1972). They altered beryl to chrysoberyl + phenakite at temperatures above 300°C and 500 kg/cm² (approximately 500 bar). They also leached phenakite in alkaline solutions to produce a surface coating of chkalovite, Na₂BeSi₂O₆.

A synthesis study of the complete system BeO–Al₂O₃–SiO₂–H₂O between 300 and 700°C, 1 kbar is reported by Ganguli and Saha (1967). They produced beryl, chrysoberyl, phenakite, bromellite, bertrandite, quartz, mullite, pyrophyllite, and kaolinite. They hydrated phenakite to bertrandite at about 500°C and broke beryl down to bertrandite solid solution plus pyrophyllite at about 485°C. The probable lack of equilibrium in these experiments is indicated by the fact that they reportedly grew pyrophyllite to 550°C, which is about 200° above the 1

kbar equilibrium dehydration temperature determined by Haas and Holdaway (1973).

Ganguli and Saha's experiments involving pyrophyllite are also inconsistent with natural assemblages, as shown by the following compositional relations (abbreviations in Tables 1 and 2):

$$2 \text{ Brl} + 2 \text{ Btr} + 5 \text{ Pyp} = 14 \text{ Euc} + 22 \text{ Qtz} \quad (1)$$
$$\text{Phe} + \text{Pyp} = 2 \text{ Euc} + 3 \text{ Qtz} \quad (2)$$
$$7 \text{ Phe} + \text{Pyp} + \text{Qtz} = 2 \text{ Btr} + 2 \text{ Brl} \quad (3)$$
$$3 \text{ Btr} + \text{Pyp} = 4 \text{ Brl} + 7 \text{ Kao} + \text{Qtz} \quad (4)$$
$$\text{Btr} + 9 \text{ Pyp} = 4 \text{ Chr} + 5 \text{ Kao} + 28 \text{ Qtz} \quad (5)$$
$$\text{Brl} + 4 \text{ Pyp} = 3 \text{ Chr} + 2 \text{ Kao} + 18 \text{ Qtz} \quad (6)$$
$$\text{Brl} + \text{Pyp} = \text{Chr} + 2 \text{ Euc} + \text{Qtz} \quad (7)$$
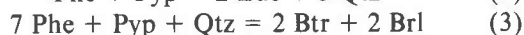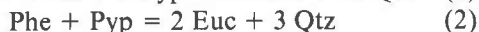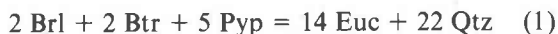
As discussed below, most of the assemblages on the right sides of the above equations have been reported from nature; the alternative assemblages involving pyrophyllite are unknown, and pyrophyllite was therefore omitted from the multisystems analysis.

In summary, virtually all experimental studies involved short-duration synthesis runs rather than equilibrium (stable or metastable) reversals. Nevertheless, it appears that beryl breaks down both at high T and at high P, and that bertrandite is stable at lower temperatures than phenakite. It is also probable (Wyart and Scavnicar, 1957, and later studies) that beryl-phenakite-quartz, beryl-chrysoberyl-phenakite, and less clearly beryl-chrysoberyl-quartz are stable assemblages at moderate P and T, as shown on Figure 1. None of the above studies involved the synthesis of euclase, and thus its role in the above equilibria will have to be answered from natural assemblages.

Natural assemblages

The moderate P and T compatibilities among the anhydrous beryllium minerals have been deduced from numerous natural occurrences (Fig. 1; cf. Burt, 1975a). Examples of the incompatibility of beryl with the aluminosilicate minerals in pegmatites are given by Heinrich and Buchi (1969); the stable assemblage is chrysoberyl-quartz. Chrysoberyl-phenakite (±beryl) assemblages are reviewed by Okrusch (1971), who also reviews chrysoberyl-corundum and chrysoberyl-aluminosilicate localities. To the best of my knowledge, beryl has not been found with bromellite or corundum, although Bank (1974) has apparently found corundum (ruby), beryl (emerald), and chrysoberyl (alexandrite) in a single hand specimen. Similarly, phenakite, chrysoberyl, and quartz may occur as associated minerals, but they have not all been found in direct contact (implying the instabil-

ity of beryl). Four reported bromellite occurrences are mentioned in Burt (1975b); a fifth from China is mentioned by Chao (1964) and is described by Shabynin (1974, p. 228).

Natural assemblages involving the hydrous phases could be shown on a tetrahedron, but most assemblages involve quartz, so that a triangular diagram in the presence of excess quartz should be adequate initially (Fig. 2). Solid lines on Figure 2 depict well-documented and/or common natural assemblages; dashed lines indicate poorly documented and/or conflicting assemblages. Unfortunately, most of the uncertainties again involve euclase.

As examples of these uncertainties, consider that the assemblage beryl-bertrandite-kaolinite has been described or implied (Aver'yanova, 1962; Gallagher and Hawkes, 1966), but the conflicting assemblage euclase-quartz is more common, with beryl (Gallagher and Hawkes, 1966), kaolinite (Olsen, 1971; Cassedanne, 1970), or bertrandite + beryl (Strand, 1953; Mårtensson, 1960; Sharp, 1961). The assemblages euclase-bertrandite (Sainsbury, 1968) and euclase-bertrandite-beryl (Komarova, 1974) are also known from silica-undersaturated environments.

The extremely common assemblage bertrandite-beryl rules out the assemblage phenakite-euclase-quartz, which has apparently not been documented, although all three minerals may occur in the same deposit (Mårtensson, 1960, and others). In silica-undersaturated environments, however, euclase-phenakite assemblages are described from the Soviet Union (Kalyuzhnaya and Kalyuzhnyi, 1963; Novikova, 1964; 1967; Getmanskaya, 1966; Komarova, 1974; Ginzburg et al., 1974).

Kaolinite-beryl assemblages are also described (Černy, 1968; Kerr, 1946; Kayode, 1971); the alternative assemblage chrysoberyl-euclase-quartz has apparently not been reported. A bertrandite-kaolinite-quartz assemblage is reported by Levinson (1962) and chrysoberyl-kaolinite-quartz assemblages probably occur in hydrothermal alteration zones (cf. Govorov, 1968; Sainsbury, 1968), although they are not definitely reported.

As regards some of the minerals in Table 2, behoite is known from only two localities (Montoya et al., 1964; Ehlmann and Mitchell, 1970); at neither does it occur with any of the minerals of Table 1. In the system $BeO-SiO_2-H_2O$, it presumably is stable with bertrandite and bromellite, but not with phenakite or quartz. In the system $BeO-Al_2O_3-H_2O$ it presumably is stable with diaspore, but not with chrysoberyl. These remain conjectures.

Beryllite, reported from a single locality (data summarized in Kuz'menko, 1966), is compositionally equivalent to a mixture of bertrandite, behoite, and water, but it only occurs with the poorly characterized phases "sphaerobertrandite" and "gelbertrandite" (hydrated bertrandites, more or less). Like behoite it is probably stable only at such low temperatures that it can safely be neglected.

As mentioned in the review of experimental studies, pyrophyllite presents a particular problem among the hydrated aluminous minerals, inasmuch as it apparently has never been reported as occurring with any beryllium mineral. I have tentatively shown it as being compatible only with chrysoberyl in silica-saturated environments.

Finally, diaspore, like andalusite and corundum, is known only with chrysoberyl (Apollonov, 1967; Sainsbury, 1968), and, like the other minerals in Table 2, will not be considered further.

To summarize, the natural assemblages have not elucidated the unknown role of euclase. The assemblage beryl–bertrandite–kaolinite suggests that euclase is unstable with quartz, but euclase typically occurs with quartz. The assemblage euclase–phenakite suggests that euclase is stable at higher temperatures than bertrandite (chemically, hydrated phenakite), but euclase is much less common than bertrandite.

These ambiguities suggest that there may exist solid–solid, P- and T-dependent reactions among the Be-bearing phases; such reactions can be investigated by means of multisystems analysis (Korzhinskii, 1959; Burt, 1971) and a computer program to generate the relevant reactions (e.g., REACTION: Finger and Burt, 1972).

Multisystems analysis

Simplifying the multisystem

In the quaternary system $BeO-Al_2O_3-SiO_2-H_2O$, not more than six phases can stably coexist at an invariant point. If H_2O fluid is added to the seven phases in Table 1, the resulting eight-phase association constitutes an $(n + 4)$-phase multisystem, where n is the number of components. In terms of the phase rule, this multisystem has negative two (-2) degrees of freedom.

Such a multisystem is unwieldy; how can it be simplified? A first step is to recognize that only equilibria occurring in the presence of aqueous fluid are of practical interest; "projecting through water" eliminates one of the eight phases and topologically

reduces the number of components by one, to three. Nevertheless, an $(n + 4)$-phase multisystem still remains, and previous analytical considerations of three-component systems (Zen and Roseboom, 1972; Day, 1972) have only considered $(n + 3)$-phase multisystems. Another simplification is needed. [Note that "projecting through quartz" still leaves an $(n + 4)$-phase binary multisystem, and results in a loss of generality.]

The second simplification is made possible by the fact that, projected through H_2O, two of the phases, bertrandite and phenakite, plot at the same point (Fig. 3). A P–T diagram will therefore be split in two by the degenerate dehydration reaction converting bertrandite to phenakite. Reactions involving either phase will be refracted as they cross this line, but the underlying topology will be unaffected. For topological purposes, then, the system already constitutes an $(n + 3)$-phase multisystem. It belongs to chemography type Qc of Zen and Roseboom (1972, Figs. 3 and 8) and Day (1972, Fig. 8).

Using molar volume data

Purely topological approaches to multisystems analysis can become exceedingly cumbersome (Burt, 1978). A less cumbersome procedure in the present case is to use the molar volume data in Table 1 to construct an isothermal P_s–minus μH_2O diagram (Marakushev, 1973, and earlier papers going back to 1964; cf. Zen, 1974). This construction is based on the thermodynamic relation

$$\left(\frac{\partial P_s}{\partial \mu H_2O}\right)_T = \frac{-\Delta n H_2O}{\Delta V_s} \qquad (8)$$

where $\Delta n H_2O$ is the number of moles of water involved in a dehydration reaction, and ΔV_s is the reaction volume change for the solids. If it is assumed that decreasing μH_2O corresponds to increasing T, this diagram should, in general, have the same topology as a P–T diagram in the presence of an aqueous fluid.

The main advantage of the isothermal P_s–minus μH_2O diagram is that the reaction slopes are determined by the molar volumes of the solids, as shown by equation (8) above. If compressibilities and solid solution are neglected, the slopes are constant (i.e., the reactions define straight lines). This constraint is analogous to the compositional constraints that fix the slopes on, e.g., a $\mu H_2O-\mu CO_2$ diagram involving pure substances (cf. Korzhinskii, 1957).

On such fixed-slope diagrams, any $(n + 3)$-phase

multisystem has only two alternative topologies, related to each other by an interchange of stable and metastable invariant points (Korzhinskii, 1957). The use of molar volume data to construct a P_s-minus μH_2O diagram therefore yields only two possible topologies for each $(n + 3)$-phase multisystem—a simplification when compared to the several topologies yielded by compositional considerations alone (*cf.* Day, 1972).

The metastable–stable correspondence

For each topology, the labels of the invariant points that are *metastable* correspond to the phase assemblage that is *stable,* and *vice versa* (Burt, 1971). This proposition could be called the metastable-stable correspondence for $(n + 3)$-phase multisystems. A simple derivation is given below.

The first step of the derivation consists of noting that an $(n + 3)$-phase multisystem can be derived from an invariant point involving an equal number of phases by subtracting one degree of freedom (*i.e.,* by arbitrarily fixing one of the intensive parameters at a value to one side or the other of its value at the invariant point). By this treatment the univariant reactions around the invariant point transform into stable and metastable invariant points in the resulting multisystem, and divariant fields transform into univariant lines. An example of such a transformation is given in Burt (1971, p. 192–193). In the present study, a more complicated example involves the derivation of the two multisystems ⟨Phe⟩ and ⟨Kao⟩ on Figure 4 by fixing the temperature at its value at the left margin of Figure 6.

Without invoking a magnetic field or other unconventional degree of freedom (*cf.* Pippard, 1957, p. 63–

Fig. 4. Schematic isothermal P_s-minus μH_2O diagram of the multisystem of Table 1, if kaolinite–phenakite is unstable and phenakite–euclase–beryl is stable. Solid circles indicate stable invariant points, open circles metastable points. Invariant points are labeled by absent (non-participating) phases in the multisystems ⟨Kao⟩ and ⟨Phe⟩, which are, respectively, above and below the Btr/Phe line. Lines are labeled by their slopes (in bars/joule/mole of H_2O). Corresponding reactions are listed in Table 3. The saturation line for pure H_2O is not shown.

68), one might experience some conceptual difficulty in deriving multisystems on P_s–T diagrams by this method. Nevertheless, the analogous nature of the constraints imposed on the slopes, and the identical topologies, suggest that such multisystems should obey the same relations as those on μ–μ and μ–T(or P) diagrams.

The second step of the derivation consists of pointing out that a straight line cutting an invariant point divides the immediate vicinity of the invariant point into two sectors, in which stable and metastable univariant reactions are interchanged (as they pass through the invariant point). This line corresponds to the value of the "fixed" intensive parameter at the invariant point. If the line is moved slightly in one direction, one configuration of the resulting multisystem net results; and if it is moved in the other direction, the alternative configuration ("residual net") results. It now remains to demonstrate that the labels of the univariant reactions that are *metastable*

Fig. 3. Projected compositions of some phases in the system $BeO–Al_2O_3–SiO_2–H_2O$, in the presence of H_2O.

on one side of the dividing line correspond to the phase assemblage that is *stable* on this side of the line, and *vice versa*. This proposition could be called the stable–metastable correspondence for invariant points.

This latter proposition is a rather trivial consequence of the Morey-Schreinemakers rule (Zen, 1966, p. 10–11) and of Schreinemakers' concept of the univariant scheme (Zen, 1966, p. 12–14). The interested reader may verify its applicability to any invariant point involving univariant reactions that are approximated by straight lines.

It has thus been demonstrated that the correct topology for each $(n + 3)$-phase multisystem on fixed-slope diagrams is specified by the choice between the stabilities of two alternative mineral assemblages. For μ–μ diagrams, the two alternative assemblages are related to each other by a balanced solid–solid univariant reaction (Burt, 1971); for P_s–minus μH_2O diagrams a reaction (or relation) can be

stated, but not balanced chemically. (The same seems to be true for P_s–T diagrams.) The above statements are illustrated by the examples that follow.

For this discussion, angled brackets $\langle \ \rangle$ will be used to enclose the names or abbreviations (Table 1) of the non-participating phases labeling multisystems, square brackets [ ] will similarly label invariant points, and parentheses ( ) will label reactions. This usage follows Burt (1971).

P_s–minus μH_2O diagram

At low temperatures or high values of μH_2O, bertrandite is stable relative to phenakite, and the phenakite-absent $(n + 3)$-phase multisystem $\langle Phe \rangle$ can be considered. Computer program REACTION (Finger and Burt, 1972) is used to calculate all possible reactions in this multisystem (Table 3, in part). The reaction slopes (in bars/joule/mole of H_2O) are then obtained from equation 8 and the molar volume data in Table 1.

Table 3. Possible reactions (and corresponding molar volume changes for the solids in joules/bar) among water and the phases in Table 1, assuming that phenakite-kaolinite is an unstable assemblage. This is the output of computer program REACTION (Finger and Burt, 1972)

Chr	Phe	Euc	Btr	Brl	Kao	Qtz	H_2O	ΔV_s
	-2		1				-1	1.779
-1	-1			1		-5		1.860
		6	3	-4	4	10	-11	8.727
			-2		-1	8	-1	-4.570
		-4	1		-2		-3	5.955
		8	1	-4		14	-5	-3.184
		-10	4	-2	7		-13	19.252
		-22	1	6	5	-26		19.664
	1	4		-2		7	-2	-2.481
	-5	-4	2	2		-7		6.039
-3				1	2	-10	-4	7.275
-4			1		4	-10	-9	12.609
2			1	-2		10	-1	-1.941
-1			1	-1	2		-5	5.334
-11			-4	9	2	-50		15.039
-2		2			1	-4	-3	3.327
-1		4		-1	2	-2		-0.621
-4		10		-2	1		-7	2.084
-1		-8		3	2	-14		8.518
-4		8	-1			-6	-3	0.698
2		-10	2		3		-3	8.584
-2		6	-1		-1	-2		-2.629
-7		20	-1	-3			-9	-1.166
-5		4	-2	3		-18		3.261
-13		50	-7	-3	-9			-26.918
-2	-1	4				-3	-2	1.239
-7	-2	20		-3			-10	0.613
-2	3	4	-2			-3		-2.319
-7	18	20	-10	-3				-17.177

The next step is to plot the multisystem ⟨Phe⟩ on an isothermal P_s–minus μH_2O diagram. When this is done (as seen in the lower left part of Fig. 4), the two alternative topologies are given by the following relation among the stable and metastable invariant points:

$$Qtz + Chr + Btr + Kao = Brl + Euc \quad (9)$$

As discussed above, beryl–euclase is a relatively common assemblage, whereas the alternative four-phase assemblage quartz–chrysoberyl–bertrandite–kaolinite is unknown. The two invariant points labeled [Brl] and [Euc] must then be metastable, as shown, and the points [Qtz], [Chr] [Btr], and [Kao] are stable. (Point [Kao], labeled [Phe] on Fig. 4, becomes metastable when phenakite is considered, as described below.) On Figure 5, an enlargement of the stable part of Figure 4, the assemblage beryl–euclase is stable inside the closed polygon formed by joining the two points labeled [Qtz], the two points labeled [Chr], and the upper point labeled [Btr].

The final step is to determine how the degenerate dehydration reaction Btr/ Phe cuts the multisystem ⟨Phe⟩ determined above. Inspection of Figure 4 reveals that it may do so (1) below point [Qtz], (2) between [Qtz] and [Chr], (3) between [Chr] and [Btr], (4) between [Btr] and [Kao] (labeled [Phe] on Fig. 4 because this is where I placed the reaction), or (5) above point [Kao] (labeled [Phe] on Fig. 4). Possibilities (1) and (2) above would imply that phenakite, rather than bertrandite, would typically occur with kaolinite and euclase (in other words, that bertrandite would have a very low dehydration temperature indeed). This implication conflicts with the widespread natural occurrences of bertrandite, and possibilities (1) and (2) may therefore be rejected. Possibility (3) is for practical purposes indistinguishable from possibility (4), because the dehydration reaction Btr/Phe is independent of the Btr-absent point [Btr].

The above arguments leave only possibilities (4) and (5). In other words, the dehydration reaction Btr/Phe can intersect the multisystem either above or below the point [Kao] (labeled [Phe] on Fig. 4). These alternatives correspond to a second ($n + 3$)-phase multisystem ⟨Kao⟩, the two topologies of which are given by the relation

$$Chr + Qtz + Btr = Phe + Brl + Euc \quad (10)$$

Neither the left nor the right assemblage has been reported from nature. Phenakite, beryl, and euclase are, however, known as associated minerals (*cf.* Mår-
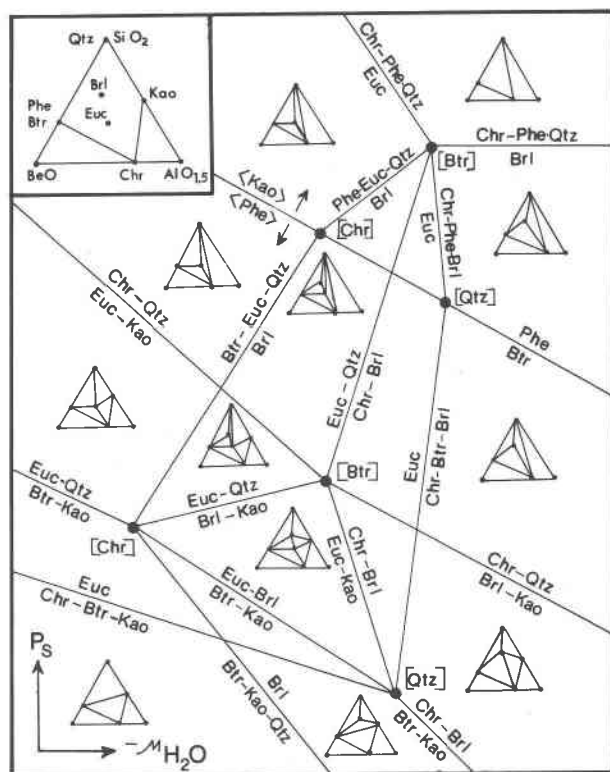
Fig. 5. Enlargement of the central part of Fig. 4, showing stable reactions and invariant points. Inset shows chemography (*cf.* Fig. 3). Tie lines to kaolinite are omitted in the upper right area of the diagram where other aluminosilicates probably become stable.

tensson, 1960; Kalyuzhnaya and Kalyuzhnyi, 1963). Tentatively then, phenakite–beryl–euclase is assumed to be a stable assemblage, and Figure 4 has been constructed accordingly from the data in Table 3. The rarity of phenakite–beryl–euclase is probably due to the fact that it is a quartz-absent assemblage.

With regard to the multisystem ⟨Kao⟩, shown in the upper right part of Figure 4, the metastable invariant points are then [Phe], [Brl], and [Euc], and the stable ones are [Chr], [Qtz], and [Btr]. The metastable point [Phe] of multisystem ⟨Kao⟩ corresponds to the formerly stable point [Kao] of the multisystem ⟨Phe⟩. (Strictly speaking, with regard to the full ($n + 4$)-phase multisystem of Table 1, the point [Phe, Kao] is metastable.)

On Figure 5, the assemblage phenakite–beryl–euclase is stable only inside the small triangle whose apices are labeled [Chr], [Qtz], and [Btr] in the multisystem ⟨Kao⟩. The size of this area could be enlarged by moving the Btr/Phe line down, even to below the lower point [Btr]. As long as this line does not intersect the lower points [Chr] and [Qtz], the mineral compatibility relations, and the fundamental to-

pology of the diagram, remain unchanged. The area of stability of the assemblage was made small because the assemblage is not yet described from nature.

Incompatibility of phenakite and kaolinite

The two multisystems ⟨Phe⟩ and ⟨Kao⟩ are stable on opposite sides of the Btr/Phe line (Figs. 4 and 5). Extending somewhat the generalization that stable arrays of *points* correspond to unstable assemblages, consider that stable arrays of *multisystems* also correspond to unstable assemblages (Burt, 1971). That is, phenakite–kaolinite must be an unstable assemblage at the temperature considered. (A close examination of Figure 5 also reveals that phenakite–kaolinite must be unstable.)

In order to justify this more-or-less *a posteriori* observation, the following compositional relations should be noted (*cf.* Fig. 2):

$$2\ Kao + 11\ Phe + 5\ Qtz = 4\ Btr + 2\ Brl \quad (11)$$

$$Kao + 3\ Phe = 2\ Euc + Btr + Qtz \quad (12)$$

$$7\ Kao + 26\ Phe = 10\ Euc + 9\ Btr + 2\ Brl \quad (13)$$

The left-hand assemblages are unknown; the right-hand assemblages are well-known, as described above. Kaolinite–phenakite could therefore be submitted as the *only* incompatibility when program RE-ACTION was used to generate the reactions in Table 3.

P_s–T diagram (fluid-absent)

The stable multisystems ⟨Kao⟩ and ⟨Phe⟩ on P_s-minus μH_2O diagrams (Figs. 4 and 5) can also be drawn as the stable invariant points [Kao] and [Phe] on a P_s–T diagram that omits water. The result is seen on Figure 6, part of a possible $(n + 3)$-phase multisystems array for the seven minerals in Table 1. Each water-absent line on Figure 6 corresponds, in general, to an invariant point on Figure 4. The exception is the degenerate line (Btr, Euc) which is also a line on Figure 4.

The left axis of Figure 6 is positioned at the temperature for which the isothermal diagrams Figures 4 and 5 were drawn; T could either increase or decrease to the right (as shown by the label $\pm T$ on the horizonal axis). Unfortunately, with only molar volume information available, it is unknown whether the points [Kao] and [Phe] are stable or metastable if water is added to this multisystem, or whether other invariant points exist stably or metastably.

At this point it can be noted that on Figure 6,

Fig. 6. Schematic fluid-absent P_s–T diagram of part of the multisystem of Table 1. The left axis is drawn at the temperature for which Figs. 4 and 5 are drawn; T might increase or decrease to the right. Inset shows chemography for quartz-saturated equilibria (*cf.* Fig. 2).

invariant point [Kao] corresponds to type IV-21 of Dolivo-Dobrovol'skii (1969; type III-5 if projected through quartz) and that point [Phe] corresponds to type IV-13 (type III-2 if projected through quartz). Projected through quartz, as shown on the inset, the overall chemography of this multisystem belongs to type Q3 of Day (1972, Fig. 8). The multisystems net type of Figures 4 and 5 corresponds to type 2 of Day (1972, Fig. 7).

P–T diagram (fluid-present)

As stated above, the topology of Figures 4 and 5 should be equivalent to that of a *P*–*T* diagram drawn for excess water, because decreasing μH_2O should, in general, correspond to increasing T. This relation is evident on Figure 7. Topologically, there is a one-to-one correspondence between Figures 5 and 7 (Fig. 7 was so drawn).

Of course, some of the invariant points on Figure 7 may be metastable, due to the participation of other phases, or they may be physically unrealizable (*i.e.,* they may occur at negative pressures). Most natural

assemblages appear to form at pressures above the two invariant points labelled [Qtz] on Figure 7. That is, euclase and euclase–phenakite seem to be stable with regard to the alternative assemblages Chr–Brl–Btr–Kao and Chr–Brl–Btr (*cf.* Fig. 6). Natural assemblages further appear to form below the lower point labeled [Btr] on Figure 7. That is, beryl–kaolinite seems to be stable relative to Chr–Euc–Qtz. Only the invariant point [Chr] seems to fall within the *P–T* range normally involved in the formation of hydrothermal beryllium deposits. Nevertheless, as discussed below, the presence of bertrandite–beryl–kaolinite instead of euclase–quartz could be due to supersaturation of low-temperature solutions with amorphous silica in place of quartz.

The low *P* and *T* reactions on Figure 7 are schematically shown in more detail in Figure 8. Possible positions for the two dehydration curves involving the creation and destruction of pyrophyllite are marked by dashed lines. The pyrophyllite curves are drawn consistent with the assumption that chrysoberyl is the only Be-bearing mineral stable with py-
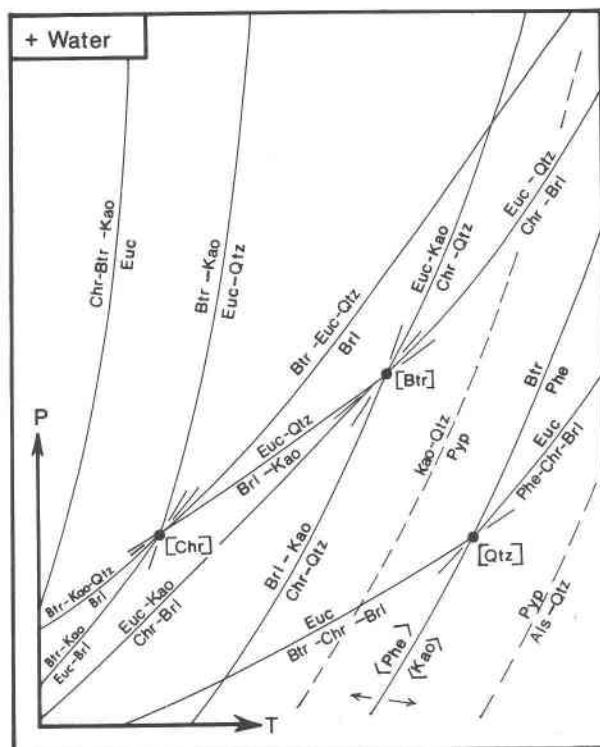
Fig. 8. Enlargement of the low pressure part of Fig. 4, showing dehydration reactions and invariant points possibly encountered in nature. Dashed lines show a permitted stability field for pyrophyllite.

rophyllite. In other words, kaolinite–quartz assemblages are assumed to break down at higher temperatures than kaolinite–beryl or kaolinite–euclase assemblages, as shown. Chrysoberyl–quartz–kaolinite is stable in the intermediate zone. The pyrophyllite curves could easily be moved to higher temperatures on Figure 8.

Discussion

Heinrich and Buchi (1969) have shown that beryl is unstable with aluminosilicates, the stable assemblage being chrysoberyl–quartz. This fact explains the occurrence of chrysoberyl in alumina-contaminated pegmatites. The present study suggests that chrysoberyl–quartz remains a stable assemblage to fairly low temperatures, but eventually is replaced by kaolinite–euclase or, more probably, kaolinite–beryl.

The stability relations of beryl itself are of particular interest. It has earlier been shown (Burt, 1975b) that under high fluorine activities beryl breaks down to the assemblage phenakite–topaz–quartz or, in the presence of fluorapatite and high P_2O_5 activities, to herderite ($CaBePO_4F$)–topaz–quartz. The present
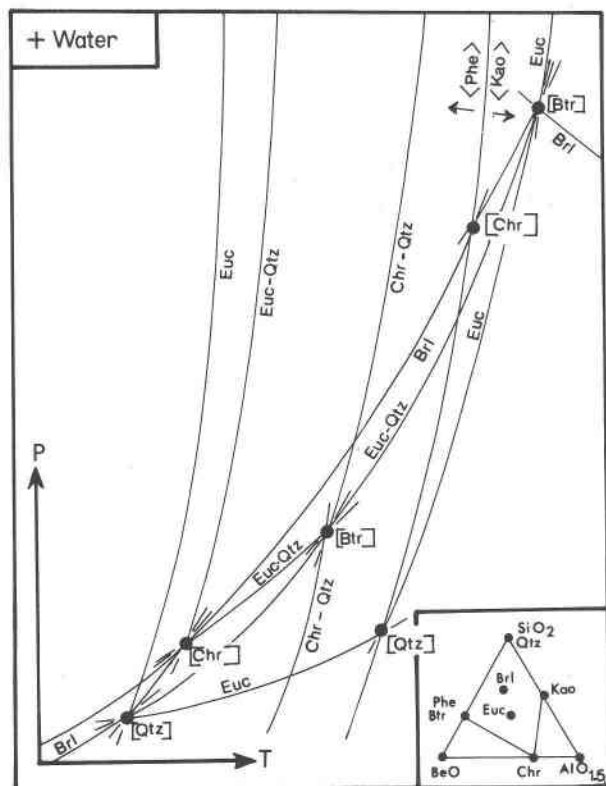

Fig. 7. Schematic, fluid-present *P–T* diagram of the multisystem of Table 1, drawn topologically identical to Figs. 4 and 5. Metastable points and lines are omitted. Inset shows chemography (*cf.* Fig. 3).

study suggests that beryl should hydrate at moderate pressures to bertrandite–euclase–quartz, or at low pressures to bertrandite–kaolinite–quartz. These and more complicated natural hydrothermal alterations of beryl are extensively reviewed by Černy (1968, 1970).

When this analysis was first performed I was unaware of the reconnaissance experimental work on beryl stability at high pressure by Munson (1967) and at high temperature by Ganguli (1972). It was therefore gratifying that the multisystems analysis correctly predicted the high P and T breakdown of beryl to chrysoberyl + phenakite + quartz (Figs. 4 and 5). The experimental data explain the steep negative slope of the breakdown curve shown on Figure 7.

The fact that beryl is unstable under upper mantle conditions is undoubtedly of some academic interest, although geologists appear to agree that beryl-bearing pegmatites are crustal phenomena. In any case, the exact high P and T breakdown curve of beryl remains to be determined. Inasmuch as hydrothermally-grown beryl is somewhat hydrous (Flanigen *et al.*, 1967), anyone undertaking such experiments should be prepared to encounter some of the problems studied by Newton (1972). He studied the influence of water activity on the high pressure breakdown of cordierite, another low-density ring silicate.

Moving on to the hydrous phases bertrandite and euclase, what does the analysis have to say? First, it provides two plausible explanations for the comparative rarity of euclase. Figures 7 and 8 show that euclase, although stable to higher temperatures than bertrandite, is stable only over a limited range of P and T. Its stability is reduced in the presence of quartz to a narrow slice of P–T space, possibly with a pressure minimum at the point [Chr] (Fig. 8). Supersaturation of hydrothermal fluids with amorphous silica might further reduce its stability in natural environments, and might alone be responsible for its failure to appear (*i.e.*, it would metastably shift the following reaction at invariant point [Chr] to the right: 22 Euc + 26 SiO$_2$ (amorphous) → Btr + 6 Brl + 5 Kao).

Assemblages that could take the place of euclase-quartz include bertrandite–kaolinite with falling T, and beryl–kaolinite or beryl–chrysoberyl with rising T. Euclase itself probably dehydrates to bertrandite–chrysoberyl–beryl or (more probably, or with rising P) to phenakite–chrysoberyl–beryl.

These hypotheses could be tested by a careful experimental study of the dehydration equilibria of ber-

trandite and euclase in silica-saturated and unsaturated solutions. The recent economic importance of bertrandite as an ore of beryllium would justify such a study. A difficulty might be the low temperatures involved—probably below 400°C. Should such experiments be impractical, carefully-documented studies of selected natural assemblages might still prove to be the best test of the multisystem topology here proposed. Assemblages of diaspore or pyrophyllite with Be minerals other than chrysoberyl, or of kaolinite with phenakite, would be especially interesting in this regard.

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