

Preliminary petrogenetic grids for sodium and calcium zirconosilicate minerals in felsic peralkaline rocks: The $\text{SiO}_2\text{-Na}_2\text{ZrO}_3$ and $\text{SiO}_2\text{-CaZrO}_3$ pseudobinary systems

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ABSTRACT

Although zircon is the most common Zr mineral, a wide array of alkali and alkaline earth zirconosilicates are known to occur in felsic peralkaline rocks in addition to or in place of zircon. The current lack of experimental phase equilibrium and free energy data for these phases precludes a quantitative understanding of their relative stabilities in P - T space. Therefore, fixed-slope $P_s\text{-}\mu_{\text{H}_2\text{O}}$ diagrams have been generated for the pseudoternary systems $\text{SiO}_2\text{-Na}_2\text{ZrO}_3\text{-H}_2\text{O}$ and $\text{SiO}_2\text{-CaZrO}_3\text{-H}_2\text{O}$ as first approximations to P - T phase relations among the sodium and calcium zirconosilicates, respectively. These two pseudoternary systems contain quartz, H_2O , and either elpidite, vlasovite, catapleiite, gaidonayite, hilairite, and parakeldyshite, in the first case, or gittinsite, armstrongite, calcium catapleiite, and calciohilairite, in the latter case. The phase relations of these two systems, which are subsets of the larger $\text{Na}_2\text{O-ZrO}_2\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-ZrO}_2\text{-SiO}_2\text{-H}_2\text{O}$ systems, serve as starting points for understanding the more complex phase relationships of the complete systems. The phase compositions in the two pseudoternary subsystems were projected through H_2O . Two possible $P_s\text{-}\mu_{\text{H}_2\text{O}}$ topologies were determined for each pseudoternary, based on an interchange of stable and metastable invariant points. Although for the $\text{SiO}_2\text{-Na}_2\text{ZrO}_3\text{-H}_2\text{O}$ system the correct topology cannot yet be resolved, owing to a lack of constraints from experimental and field observations, chemographic analysis reveals that the critical observation would be either the coexistence or incompatibility of the divariant assemblage elpidite + parakeldyshite. However, both possible topologies are consistent with vlasovite and parakeldyshite as high-temperature phases, limited in upper thermal stability only by their incongruent melting at temperatures in excess of 1200 °C. Parakeldyshite stability is unrestricted at low temperatures, but vlasovite is unstable at low temperatures relative to assemblages involving either catapleiite or elpidite, depending on the P - T topology. The observed replacement of armstrongite by gittinsite + quartz in the Strange Lake peralkaline complex, Canada, suggests that the preferred topology for the $\text{SiO}_2\text{-CaZrO}_3\text{-H}_2\text{O}$ system may be the one in which the calcium catapleiite-, quartz-, and calciohilairite-absent invariant points are stable. In either topology for the latter system, the stability field of the assemblage gittinsite + quartz increases to high temperatures and low pressures.

INTRODUCTION

Alkali and alkaline-earth zirconosilicates are common accessory minerals in felsic peralkaline rocks. In some cases (e.g., the Strange Lake complex, Quebec-Labrador, Canada) these minerals can constitute several volume percent of certain zones (Miller, 1986). In fact, at Strange Lake minerals such as elpidite and gittinsite (Table 1) are potential ore minerals of Zr. The alkali and alkaline-earth zirconosilicates could be useful petrogenetic indicators of P - T - f_v conditions of formation and subsolidus modification of peralkaline rocks. However, to our knowledge, only one set of reversed subsolidus phase equilibrium

experiments involving these minerals has been attempted (Currie and Zaleski, 1985), and there are few thermodynamic data available for these phases. Several workers have carried out hydrothermal syntheses of zirconosilicates (Maurice, 1949; Christophe-Michel-Lévy, 1961; Baussey et al., 1974; Caruba, 1975) and have used the information gained from these studies to outline rough fields of stability for these minerals in pressure-temperature-composition space. However, synthesis studies are liable to metastability problems (Fyfe, 1960). Indeed, based on his inability to synthesize any calcium zirconosilicates, Caruba (1975) concluded that such phases did not exist. The only other pertinent experimental studies are those of Gardinier (1980) and Lazutkina et al. (1980), who described the melting behavior of some sodium zirconosilicates. Clearly, for zirconosilicate minerals to be

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useful petrogenetic indicators, phase diagrams based on reversed experiments must be determined. In order to provide a framework for future experiments on the calcium and sodium zirconosilicate systems and for the interpretation of phase relations in nature, we present here preliminary schematic pressure-temperature grids constructed using the theoretical methods of Korzhinskii (1959) and Burt (1978), combined with the molar volumes of the phases, the results of the experiments of Currie and Zaleski (1985), and information available from natural occurrences. As will be evident below, our work has been hampered somewhat by the lack of sufficiently detailed descriptions of natural occurrences of the zirconosilicates. Although many zirconosilicate-bearing rocks have been described in the literature, one is often simply presented with a list of the minerals that occur in a given locality, and it is difficult, if not impossible, to determine the stable assemblage from these descriptions. Thus, we hope that this paper will encourage further well-documented descriptions of natural zirconosilicate phase assemblages.

THEORY

As will be shown below, we will be dealing primarily with phase relationships in multisystems of $n + 3$ phases, where n is the number of components. In general, there are $(n + 2)(n + 3) + 2$ alternate pressure-temperature nets possible in a nondegenerate multisystem of $n + 3$ phases that are consistent with the rules of Schreinemakers (Zen, 1966; Zen and Roseboom, 1972; Mohr and Stout, 1980; Stout, 1990). Experimental constraints, such as the location of some of the univariant reactions, molar volumes, etc., and knowledge of natural occurrences, can eliminate some possibilities. However, available data are usually insufficient to identify a unique solution among the alternative nets. Another approach is to construct a fixed-slope diagram that has a topology similar to the pressure-temperature diagram. One such diagram is the P_s - μ_{H_2O} diagram (Korzhinskii, 1959; Burt, 1978), where P_s represents the pressure on the solid phases and μ_{H_2O} represents the chemical potential of H_2O . According to the thermodynamic relation

$$(\partial P_s / \partial \mu_{H_2O})_T = -\Delta n H_2O / \Delta V_s$$

the slopes of univariant reactions on such a diagram can be determined from the molar volumes of all the solids in the reaction and the number of moles of H_2O involved. The univariant reactions on such a diagram should approximate straight lines (i.e., constant slopes), assuming that there is no solid solution and that the compressibilities of the solid phases are negligible.

The main advantage of a fixed-slope diagram is that a multisystem of $n + 3$ phases has only two alternative topologies for such a diagram (Korzhinskii, 1959; Burt, 1978). One of the two topologies may be derived from the other simply by forcing stable invariant points in one topology to be metastable in the other topology. According to Burt (1978), for each topology, the labels of the

metastable invariant points reveal a phase assemblage uniquely stable in that topology, and similarly the labels of the stable invariant points indicate a uniquely metastable phase assemblage. The choice among alternative topologies for the phase diagram can then be made by identifying, from field observation or experimental results, which of the alternative phase assemblages are actually stable.

Once the appropriate choice of alternative P_s - μ_{H_2O} diagrams is made, the topology of the corresponding P - T diagram is also determined, because decreasing μ_{H_2O} generally corresponds to increasing temperature (Burt, 1978). However, experimental studies are still required to determine the exact positions of the invariant points and the univariant curves in the P - T plane.

MINERAL RELATIONS OF ZIRCONOSILICATES

As a first step in the analysis of phase relations among alkali and alkaline earth zirconosilicates, we restrict our treatment to phase relations in the separate Na_2O - SiO_2 - ZrO_2 - H_2O and CaO - SiO_2 - ZrO_2 - H_2O systems. Some of the known phases in each of these systems are listed with their formulae and molar volumes in Table 1. Phases in the quinary CaO - Na_2O - SiO_2 - ZrO_2 - H_2O system, in addition to those listed in Table 1, include zirsinalite ($Na_6CaZrSi_6O_{18}$), loudounite [$NaCa_5Zr_4Si_{16}O_{40}(OH)_{11} \cdot 8H_2O$] and eudialyte [$Na_3Ca_2ZrSi_6O_{17}(OH)_2$]. This quinary system represents an unmanageable multisystem with $n + 16$ phases that we shall not consider in this paper. It

TABLE 1. Formulae and molar volumes of sodium and calcium zirconosilicates and related minerals

Mineral	Formula	V (J/bar·mol)	Abbrev.
NSZH system			
Catapleite	$Na_2ZrSi_3O_9 \cdot 2H_2O$	14.385(1)	Ct
Elpidite	$Na_2ZrSi_5O_{15} \cdot 3H_2O$	23.118(2)	EI
Gaidonnayite	$Na_2ZrSi_3O_9 \cdot 2H_2O$	15.161(3)	Gdn
Hilairite	$Na_2ZrSi_3O_9 \cdot 3H_2O$	15.352(4)	Ht
Lovozerite	$Na_2Ca(Zr, Ti)Si_6(O, OH)_{18}$	23.570(5)	Lv
Parakeldyshite	$Na_2ZrSi_5O_{17}$	8.973(6)	Pk
Petarasite	$Na_5Zr_2Si_6O_{18}(Cl, OH) \cdot 2H_2O$	28.676(7)	Ptr
Terskite	$Na_4ZrSi_6O_{15}(OH)_2 \cdot H_2O$	23.520(8)	Tk
Vlasovite	$Na_2ZrSi_4O_{11}$	13.853(9)	VI
CSZH system			
Armstrongite	$CaZrSi_5O_{15} \cdot 3H_2O$	22.017(10)	Arm
Baghdadite	$Ca_3(Zr, Ti)Si_2O_9$	11.729(11)	Bg
Calciohilairite	$CaZrSi_3O_9 \cdot 3H_2O$	15.145(12)	Cht
Calcium catapleite	$CaZrSi_3O_9 \cdot 2H_2O$	14.385(13)	Cct
Gittinsite	$CaZrSi_2O_7$	8.198(14)	Gs
Quartz	SiO_2	2.267(15)	Qtz
Zircon	$ZrSiO_4$	3.931(16)	Zrn
Baddeleyite	ZrO_2	2.187(17)	Bd

Note: Cell dimensions used in calculation of molar volume data obtained from following sources: (1) Chao et al. (1973), (2) Cannillo et al. (1973), (3) Chao and Watkinson (1974), Chao (1985), (4) Chao et al. (1974), (5) Il'yukhin and Belov (1960), (6) Raade and Mladeck (1977), (7) Ghose et al. (1980), (8) Khomyakov et al. (1983), (9) Tikhonenkova and Kazakova (1962), (10) Jambor et al. (1987), (11) Al-Hermezi et al. (1986), (12) Boggs (1988), (13) Portnov (1964), (14) Ansell et al. (1980), Roelofsen-Ahl and Peterson (1989), (15) Hurlbut and Klein (1977), (16) Robinson et al. (1971), (17) Hiernstra (1955).

should be noted that phases in the K_2O - CaO - Na_2O - SiO_2 - ZrO_2 - H_2O system, including wadeite ($K_2ZrSi_3O_9$), dalyite ($K_2ZrSi_6O_{15}$), umbite [$K_2(Zr,Ti)Si_3O_9 \cdot H_2O$], khibinskite ($K_2ZrSi_2O_7$), georgechaoite ($NaKZrSi_3O_9 \cdot 2H_2O$), and kostylevite ($K_4Zr_2Si_6O_{18} \cdot 2H_2O$), also occur in peralkaline rocks. Because of the overwhelming complexity of the complete system K_2O - CaO - Na_2O - SiO_2 - ZrO_2 - H_2O and the relative paucity of hydrated phases in the subsystem K_2O - SiO_2 - ZrO_2 - H_2O , for which it is impossible to construct meaningful P_s - μ_{H_2O} diagrams, these phases are also not treated in this preliminary investigation. It should also be noted that the potassium zirconosilicates are often spatially and temporally separated from the sodium and calcium zirconosilicates in a given paragenesis (Harris et al., 1982; Birkett et al., 1992).

Sodium zirconosilicates

The chemography of part of the system Na_2O - SiO_2 - ZrO_2 - H_2O is depicted in Figure 1a. We make the simplifying assumption that H_2O is either always present as a separate phase or that its fugacity is controlled by factors external to the system, and therefore we project compositions from H_2O onto the Na_2O - SiO_2 - ZrO_2 plane. The probable presence of a separate H_2O phase during the formation of most sodium zirconosilicates can be inferred from the fact that these are often late-crystallizing, interstitial phases, occur in miarolitic cavities, or replace earlier Zr-bearing phases (Vlasov et al., 1966; Linthout, 1984; Horvath and Gault, 1990). The advantages of this assumption are twofold: first, the complexity of the system is reduced by one component and one phase; and second, it eliminates the need to consider the H_2O -absent invariant point, which is difficult to represent in P_s - μ_{H_2O} space, because all associated univariant H_2O -absent reactions have zero slopes. The drawback to projection from H_2O is that the schematic P - T nets that we will ultimately derive are not applicable to those situations where the activity of H_2O is not fixed either externally or by the presence of a vapor phase.

In addition to the sodium zirconosilicate minerals whose compositions are plotted in Figure 1a, a variety of sodium zirconosilicates have been synthesized in the laboratory, e.g., $Na_4Zr_2Si_3O_{12}$, $Na_4Zr_2Si_5O_{16}$, $Na_6Zr_2Si_4O_{15}$, $Na_{14}Zr_2Si_{10}O_{31}$, and Na_2ZrSiO_5 (Baussy et al., 1974), none of which has yet been reported to occur in nature. Furthermore, several minerals exist in the subsystem Na_2O - SiO_2 - H_2O , such as natrosilite ($Na_2Si_2O_5$), etc. However, these minerals, to our knowledge, are rarely associated with the zirconosilicate minerals considered here. We therefore exclude all these compounds from this preliminary analysis.

The system depicted in Figure 1a is a multisystem of $n + 9$ phases, which is still too complicated to represent graphically. It is necessary to simplify this system further by systematically excluding phases until a multisystem of $n + 3$ phases that can be handled by established methods has been obtained. Criteria for initial exclusion of phases

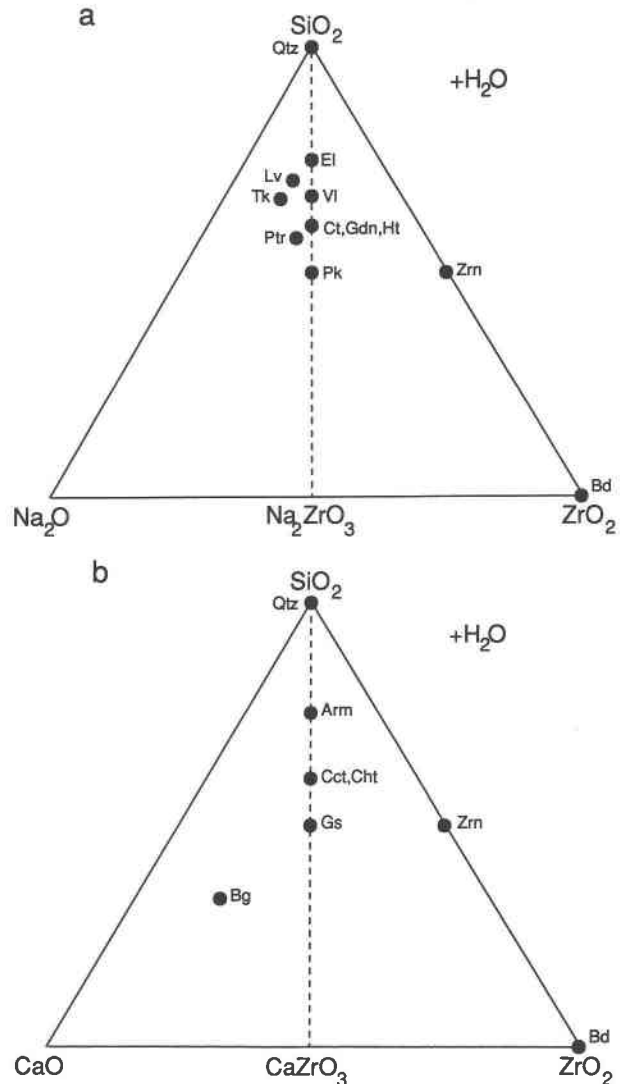


Fig. 1. (a) Chemography of some phases in the Na_2O - ZrO_2 - SiO_2 - H_2O pseudoternary system with the Na_2ZrO_3 - SiO_2 binary indicated by a dashed line. (b) Chemography of some phases in the CaO - ZrO_2 - SiO_2 - H_2O pseudoternary system with the $CaZrO_3$ - SiO_2 binary indicated by a dashed line. All compositions in both diagrams have been projected from H_2O .

include rarity and exhibition of substantial solid solution, which could potentially invalidate the assumptions required to use P_s - μ_{H_2O} diagrams. The simplifying steps taken here may reduce somewhat the generality of the schematic P - T nets derived. However, once the phase relations in the simpler multisystem of $n + 3$ phases are well understood, the excluded phases may be reintroduced into the system in a stepwise fashion.

As a first step in simplifying the multisystem of $n + 9$ phases in Figure 1a, we omit petarasite, because it is quite rare and has never been reported without significant chloride (i.e., it does not strictly belong to the pseudoternary depicted in Fig. 1a). Baddeleyite is rare in felsic peral-

kaline rocks and is stable relative to zircon and the zirconosilicates only under extremely silica-undersaturated conditions. Terskite is also quite rare. Lovozerite, although more common, exhibits considerable isomorphous substitution of Ca for Na and Ti for Zr and therefore is not strictly a sodium zirconosilicate. Thus, we also omit baddeleyite, terskite, and lovozerite from our preliminary analysis. In the absence of baddeleyite, terskite, petarasite, or lovozerite, zircon becomes an indifferent phase in the system. By an indifferent phase we mean that zircon does not participate in any of the reactions among phases in the subsystem considered, and we imply that it is stable, given the appropriate rock composition, over the entire range of P - T conditions covered by our petrogenetic grid. Whether zircon or zirconosilicates or both appear in a rock seems to be more a function of composition than of P - T conditions (Caruba, 1975). According to Currie and Zaleski (1985), zircon is generally rare in felsic peralkaline rocks (although it is quite common at Strange Lake; Salvi and Williams-Jones, personal communication, 1991). Furthermore, in peralkaline rocks that do contain zircon, such as those at Strange Lake, phases with which zircon could react to form any of the remaining zirconosilicates (elpidite, vlasovite, catapleite, gaidonnayite, hilairite, and parakeldyshite) shown in Figure 1a, such as lovozerite, terskite, baddeleyite, and natrosilite, are apparently not present. Thus, our omission of zircon should not greatly reduce the utility of the schematic P - T diagrams derived in this paper. However, it should be remembered that reactions involving zircon and any of the other excluded phases could potentially render portions of our derived grids metastable; whether this occurs can only be determined experimentally.

Note that the remaining phases, elpidite, vlasovite, parakeldyshite, catapleite, hilairite, and gaidonnayite, all have the same Na-Zr ratio and plot along a pseudobinary $\text{Na}_2\text{ZrO}_3\text{-SiO}_2$, together with quartz. We have thus reduced the ternary system to a pseudobinary and a multisystem of $n + 5$ phases remains. The best-known and most widespread of the sodium zirconosilicates, catapleite and elpidite, occur in this pseudobinary system. Thus, an understanding of phase relationships along this simple pseudobinary will be quite useful in the interpretation of many sodium zirconosilicate occurrences in felsic peralkaline rocks. Furthermore, because this pseudobinary represents a degeneracy in the complete ternary system, understanding of the phase relationships in the former is a prerequisite to understanding the phase relationships in the latter.

A further simplification is possible by noting that the compositions of catapleite, hilairite, and gaidonnayite all plot at the same point when projected through H_2O . The P - T diagram for the pseudobinary will therefore be split into three parts by the three degenerate reactions among catapleite, hilairite, and gaidonnayite (cf. Burt, 1978). Reactions involving any of these three phases will change slope upon crossing any of the three degenerate reactions,

but the overall topology will remain the same. Thus, the system under consideration can be considered to be a multisystem of $n + 3$ phases, and the phase relations can be handled and depicted using standard methods.

As noted above, an implicit assumption in using P - $\mu_{\text{H}_2\text{O}}$ diagrams to discern phase relationships is the absence of significant solid solution in the phases considered. Published chemical analyses of elpidite, vlasovite, parakeldyshite, catapleite, gaidonnayite, and hilairite are scarce. Nevertheless, the available analyses suggest that only minor K, Mg, and Ca may substitute for Na, and minor Nb and Ti for Zr, usually less than 1–5 wt% combined (Tikhonenkova and Kazakova, 1962; Portnov and Rastsvetayeva, 1966; Kapustin, 1966; Fleet and Cann, 1967; Gittins et al., 1973; Chao et al., 1974; Chao and Watkinson, 1974; Raade and Mladeck, 1977; Khomyakov et al., 1983). In most cases, these are bulk analyses of mineral separates and could incorporate microscopic inclusions of other phases, so the actual extent of solid substitution may be less. We are unaware of any data that suggest that any of the above minerals exhibit substantial compositional variation.

We should also note a slight complication regarding the mineral parakeldyshite, which was previously known as keldyshite. Keldyshite was first described by Gerasimovskii (1962), who assigned it the formula $(\text{Na,H})_2\text{ZrSi}_2\text{O}_7$. Subsequently, Khomyakov et al. (1975) showed that the mineral described by Gerasimovskii is actually an intergrowth of two different triclinic minerals. One of these, with the formula $\text{Na}_2\text{ZrSi}_2\text{O}_7$, is now known as parakeldyshite, and the other, with the formula $(\text{Na,H}_3\text{O})_2\text{ZrSi}_2\text{O}_7$, is apparently as yet unnamed. Evidently, the latter mineral is a low-temperature alteration product of parakeldyshite, related to it solely by the exchange of hydronium for Na ion (Raade and Mladeck, 1977); we therefore do not consider it further in this paper.

Calcium zirconosilicates

Compositional relationships in the $\text{CaO-SiO}_2\text{-ZrO}_2\text{-H}_2\text{O}$ system are shown in Figure 1b. This diagram also is a projection from H_2O , and the justification for this is the same as that given for the sodium zirconosilicates above. The system as shown is a multisystem of $n + 6$ phases. Baghdadite is a rare mineral that apparently does not occur in the same types of environments as the other calcium zirconosilicates. The sole occurrence of baghdadite known to the authors is in a melilite skarn in Iraq (Al-Hermezi et al., 1986); it has not yet been reported from felsic peralkaline rocks. Similarly, other phases in the $\text{CaO-SiO}_2\text{-ZrO}_2\text{-H}_2\text{O}$ system not shown in Figure 1b, such as wollastonite (CaSiO_3), larnite (Ca_2SiO_4), rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$), etc., are not known to occur in felsic peralkaline rocks and have been omitted. Baddeleyite and zircon can be removed from consideration for the same reasons given above for the sodium zirconosilicates. This leaves the phases calcium catapleite, gittinsite, armstrongite, calciohilairite, and quartz, which constitute a mul-

tisystem of $n + 3$ phases along the $\text{CaZrO}_3\text{-SiO}_2$ pseudobinary. It should be pointed out that some controversy exists over the formula for armstrongite. Vladhikin et al. (1973), in their original description of this mineral, gave the formula $\text{CaZrSi}_6\text{O}_{15} \cdot 2.5\text{H}_2\text{O}$. However, Jambor et al. (1987), using electron microprobe studies, suggested that the number of H_2O molecules in the formula unit should be closer to 3. The value of 3 determined by Jambor et al. (1987) was used to construct the $P_s\text{-}\mu_{\text{H}_2\text{O}}$ net in this study. Use of the 2.5 value results in a change in the absolute values of the slopes of reactions involving armstrongite but does not change the overall topology of the diagram. In addition to the calcium zirconosilicate minerals listed in Table 1, a phase with the formula $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ has been synthesized in the laboratory at temperatures of 1000–1500 °C (Kordyuk and Gul'ko, 1962; Morgan et al., 1987), but it is not yet known to occur in nature. We have therefore not included this phase in our analysis.

As was the case for the sodium zirconosilicates, the extent of natural compositional variation of armstrongite, gittinsite, calcium catapleite, and calciophilairite appears to be relatively small. Total impurities, including Na_2O , K_2O , Al_2O_3 , TiO_2 , P_2O_5 , MgO , and Fe_2O_3 , usually amount to 2 wt% or less (Portnov, 1964; Vladhikin et al., 1973; Ansell et al., 1980; Jambor et al., 1987; Boggs, 1988; Birkett et al., 1992; Salvi and Williams-Jones, unpublished data).

EXPERIMENTAL DATA

As mentioned above, only three phase equilibrium studies involving reversed experiments have been reported in the literature. One of these established the ultimate thermal stabilities of vlasovite and parakeldyshite at 1 atm of pressure (Gardinier, 1980). In this investigation, it was found that parakeldyshite melts incongruently to $\text{ZrO}_2 + \text{liquid}$ at 1450 °C, whereas vlasovite melts incongruently to zircon + liquid at 1210 °C. In a study of the melting relations among phases in a eutectic mixture of albite + nepheline + Na_2SiO_3 and ZrO_2 , Lazutkina et al. (1980) determined that parakeldyshite melted incongruently to $\text{ZrO}_2 + \text{liquid}$ at a maximum temperature of 1275 °C at 1 atm, and that a eutectic exists at 650 °C in this system. Subsequently, Currie and Zaleski (1985) examined the dehydration reaction between elpidite and vlasovite + quartz (Reaction 6, Table 2) and found its univariant curve to pass through the brackets 550–557 °C at 500 bars, 591–599 °C at 1000 bars, 620–630 °C at 1500 bars, and 640–648 °C at 2000 bars. It is thus clear that, whereas vlasovite and parakeldyshite are each stable to very high temperatures, elpidite breaks down at much lower temperatures. Currie and Zaleski (1985) also reported the synthesis of parakeldyshite. This was accomplished using as a reactant a gel of bulk composition equivalent to pure elpidite. However, they obtained parakeldyshite + quartz only at temperatures less than 700 °C when Na was introduced as NaCl. In all cases where Na was introduced as NaHCO_3 , elpidite or vlasovite + quartz was the product. Currie and Zaleski (1985) attrib-

TABLE 2. Reactions in the Na and Ca zirconosilicate systems with ΔV_s and calculated slopes in $P_s\text{-}\mu_{\text{H}_2\text{O}}$ space

Reaction	ΔV_s (J/bar·mol)	$-dP_s/d\mu_{\text{H}_2\text{O}}$ (bar·mol/J)
Na₂O-SiO₂-ZrO₂-H₂O		
1. El = Pk + 4Qtz + 3H ₂ O	-5.077	-0.591
2. 4Ct = El + 3Pk + 5H ₂ O	-7.503	-0.666
3. El = Ct + 3Qtz + H ₂ O	-1.932	-0.518
4. Ct = Pk + Qtz + 2H ₂ O	-3.145	-0.636
5. El + 2Ct = 3Vl + 7H ₂ O	-10.33	-0.678
6. El = Vl + 2Qtz + 3H ₂ O	-4.731	-0.634
7. Ct + Qtz = Vl + 2H ₂ O	-2.799	-0.715
8. Vl = Pk + 2Qtz	-0.346	0
9. El + Pk = 2Vl + 3H ₂ O	-4.385	-0.684
10. 2Ct = Pk + Vl + 4H ₂ O	-5.944	-0.673
CaO-SiO₂-ZrO₂-H₂O		
11. Arm = Cct + 3Qtz + H ₂ O	-0.831	-1.203
12. Arm = Cht + 3Qtz	-0.071	0
13. 4Cct = Arm + 3Gs + 5H ₂ O	-10.93	-0.457
14. 4Cht = Arm + 3Gs + 9H ₂ O	-13.97	-0.644
15. Cct = Gs + Qtz + 2H ₂ O	-3.920	-0.510
16. Cht = Gs + Qtz + 3H ₂ O	-4.680	-0.641
17. Arm = Gs + 4Qtz + 3H ₂ O	-4.751	-0.631
18. Cht = Cct + H ₂ O	-0.760	-1.316

ute this curious finding to an effect of the chloride ion on the activity of either silica or H_2O . However, given that parakeldyshite was only formed in synthesis experiments and not in reversed ones, it is possible that its appearance is connected with kinetic factors.

Sodium zirconosilicates have been successfully synthesized both hydrothermally and by dry methods in a variety of studies, some of which are listed in the introduction. The most useful of these with respect to determination of relative stabilities of the zirconosilicates is the investigation of Baussy et al. (1974). Their data suggest a transition from elpidite to vlasovite + quartz over a range of temperatures (450–550 °C) at 700 bars, which is in reasonable agreement with the boundary determined by Currie and Zaleski (1985), although somewhat shifted to lower temperatures. A similar temperature range is given by Baussy et al. (1974) for the transition from catapleite to parakeldyshite + quartz at 700 bars.

In the case of the calcium zirconosilicates, it is interesting to point out that, with the exception of baghdadite (Kordyuk and Gul'ko, 1962; Morgan et al., 1987), none of the naturally occurring phases listed in Table 1 has been synthesized, in spite of several attempts (Caruba, 1975; Morgan et al., 1987). As mentioned above, to our knowledge, the only other calcium zirconosilicate to have been synthesized is $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$.

DETERMINATION OF SCHEMATIC $P_s\text{-}\mu_{\text{H}_2\text{O}}$ DIAGRAMS

The univariant reactions considered for each of the two systems are given in Table 2 along with their ΔV_s values and the slopes of their corresponding $P\text{-}T$ curves. The volumes were calculated from crystallographic data from various sources (Table 1).

Na₂ZrO₃-SiO₂-H₂O

As noted above, the phase diagram for this system is affected by the compositional degeneracy among the

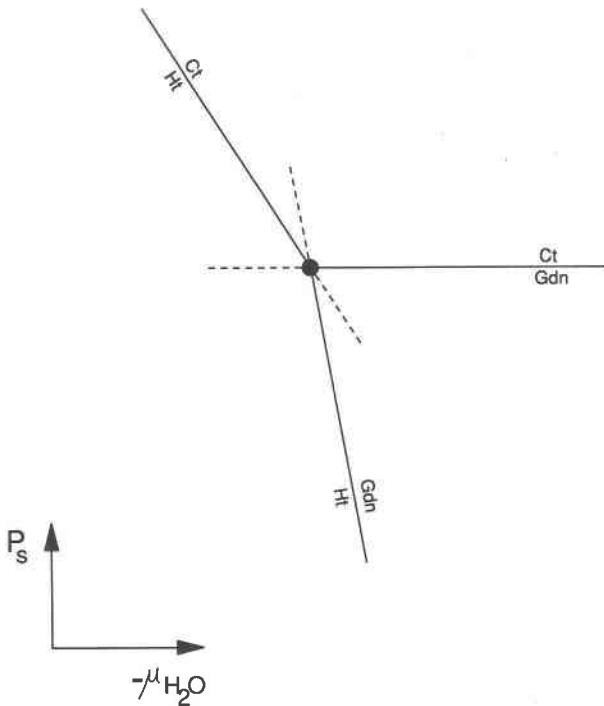


Fig. 2. Topology of the P_s - $\mu_{\text{H}_2\text{O}}$ phase diagram for the phases catapleite, gaidonnayite, and hilairite. Note: for all phase diagrams presented in this paper, solid and open circles represent stable and metastable invariant points, respectively; solid lines indicate stable univariant curves, dashed lines represent metastable univariant curves, and dotted lines represent doubly metastable univariant curves. The differences in the slopes of the univariant curves in this and all subsequent P_s - $\mu_{\text{H}_2\text{O}}$ diagrams have been exaggerated for clarity of presentation.

phases catapleite, gaidonnayite, and hilairite, which effectively splits the phase diagram into three portions without affecting the overall topology. A P_s - $\mu_{\text{H}_2\text{O}}$ diagram showing the relationships among these three degenerate phases was derived according to the data in Table 1 and is shown in Figure 2. The phase relationships among these three minerals are quite straightforward to understand: hilairite is the most hydrated phase, so it occurs at low temperatures (i.e., low $\mu_{\text{H}_2\text{O}}$), whereas catapleite has the lowest molar volume and is stable at high pressures.

We next derived the two alternative topologies for the multisystem with $n + 3$ phases involving quartz, catapleite, elpidite, vlasovite, and parakeldyshite. The two alternative P_s - $\mu_{\text{H}_2\text{O}}$ nets for this system are shown in Figure 3. Catapleite has been chosen to represent the degenerate phases in Figure 2, with the realization that the topology derived for the phase diagram will be the same no matter which phase (catapleite, gaidonnayite, or hilairite) is stable at a given set of conditions. The phase diagram depicted in Figure 2 should intersect univariant reactions from whichever topology, Figure 3A or 3B, that turns out to be the correct one, in such a way that univariant reactions involving catapleite (gaidonnayite, hilairite) are refracted as they cross the univariant reactions

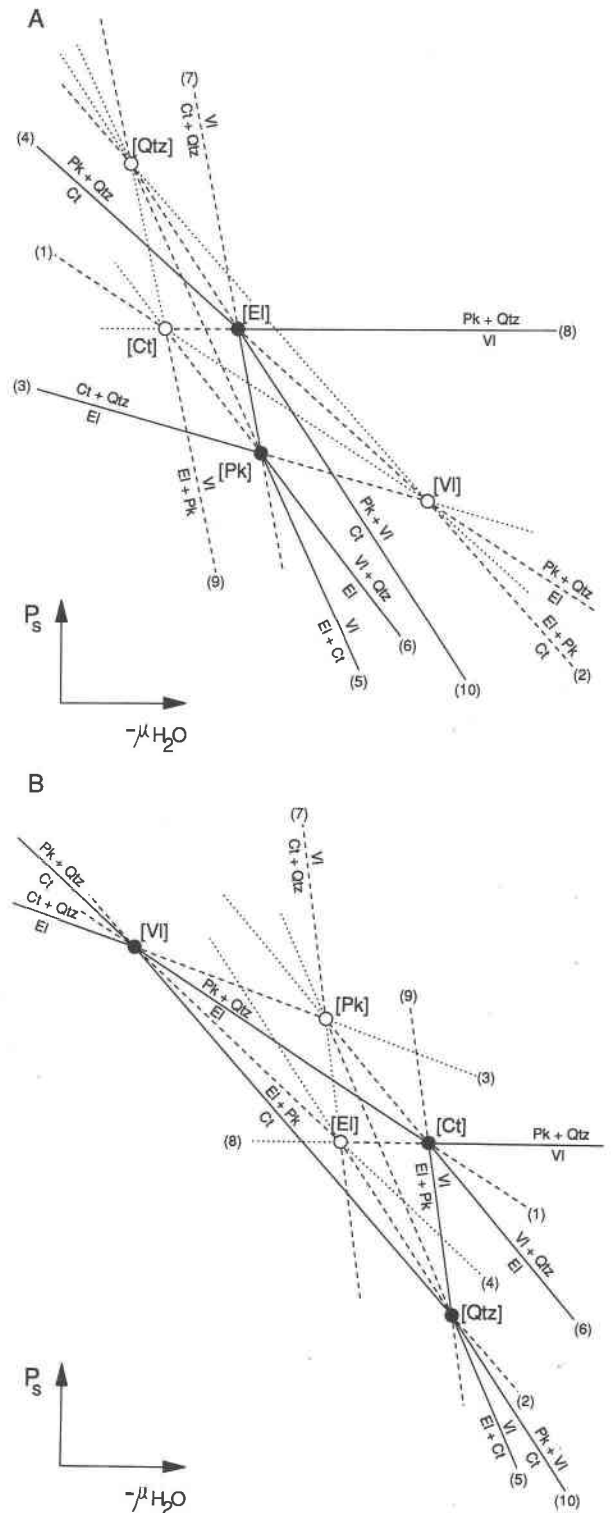
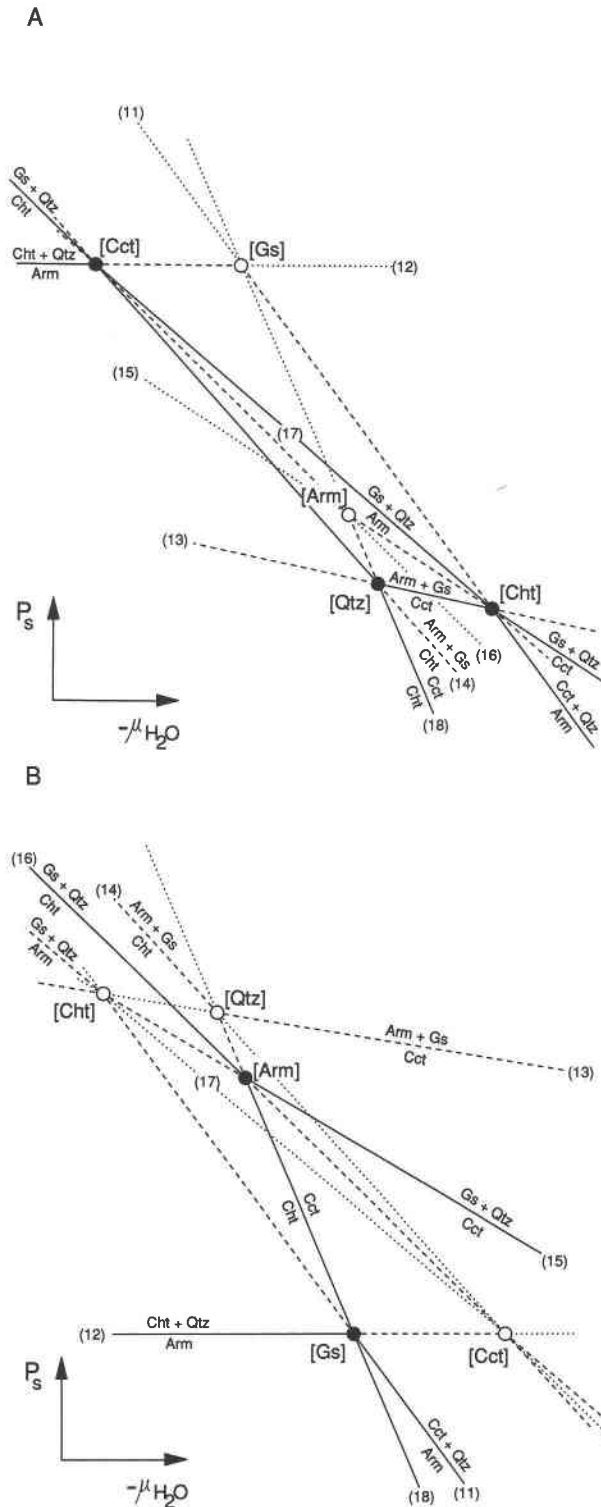


Fig. 3. The two alternative topologies of the P_s - $\mu_{\text{H}_2\text{O}}$ phase diagram for the pseudoternary system Na_2ZrO_3 - SiO_2 - H_2O . (A) The elpidite- and parakeldyshite-absent invariant points are stable, whereas the catapleite-, vlasovite-, and quartz-absent invariant points are metastable. (B) The catapleite-, vlasovite-, and quartz-absent invariant points are stable, whereas the elpidite- and parakeldyshite-absent invariant points are metastable. See caption to Figure 2 for the significance of symbols employed.



in Figure 2, and univariant reactions not involving catapleite (gaidonnayite, hilairite) will be unaffected. However, we presently have insufficient data to allow us to locate the invariant point and univariant curves in Figure 2 relative to those in Figure 3.

←

Fig. 4. The two alternative topologies of the $P_s-\mu_{H_2O}$ phase diagram for the pseudoternary system $CaO-ZrO_2-SiO_2$. (A) The calcium catapleite-, calciophilairite-, and quartz-absent invariant points are stable, whereas the gittinsite- and armstrongite-absent invariant points are metastable. (B) The gittinsite- and armstrongite-absent invariant points are stable, whereas the calcium catapleite-, calciophilairite-, and quartz-absent invariant points are metastable. See caption to Figure 2 for the significance of symbols employed.

It is evident that the assemblage vlasovite + catapleite + quartz is stable only in the topology depicted in Figure 3A, whereas the assemblage elpidite + parakeldyshite is stable only in the topology shown in Figure 3B. Theoretically, it should be possible to choose between the alternative topologies given in Figure 3, if it can be demonstrated from experiment or field observation that one or the other of these two assemblages is stable. Unfortunately, there is not enough reliable information from descriptions of occurrences of these minerals to identify with certainty the correct topology. We therefore present both nets. Experiments are currently in progress to allow the determination of the correct topology and to fix the positions of the various invariant points and univariant curves in $P-T$ space.

$CaZrO_3-SiO_2-H_2O$

The two alternative topologies of the $P_s-\mu_{H_2O}$ diagram for the calcium zirconosilicate system are presented in Figure 4. The two key assemblages for selecting the correct topology in this system are gittinsite + armstrongite and calcium catapleite + calciophilairite + quartz. In this case it may be possible to make a choice between the two alternate topologies. Gittinsite and armstrongite have been reported together at Strange Lake (Miller, 1986). Our petrographic examinations (Fig. 5) suggest that, in some samples, gittinsite + quartz has replaced armstrongite. Although this cannot be taken as evidence that gittinsite + armstrongite + quartz is a stable assemblage, it does suggest that the equilibrium armstrongite = gittinsite + quartz + H_2O may be stable (it could also be metastable, but we consider this less likely). In the topology shown in Figure 4B, this equilibrium is metastable, whereas in the topology of Figure 4A, it is stable. We therefore tentatively conclude that the latter topology (Fig. 4A) is the correct one for this system. Nonetheless, further petrographic observations and experimental studies will be required to demonstrate this definitively.

DISCUSSION

Phase diagrams expressed in terms of pressure and temperature are of greater interest for representation of the phase relationships in the systems studied here. As indicated above, $P-T$ diagrams should have topologies identical to the analogous $P_s-\mu_{H_2O}$ diagram. Each of the alternative topologies in $P-T$ space for the two systems is shown schematically in Figures 6 and 7. Experiments and further careful petrographic observations will ultimately

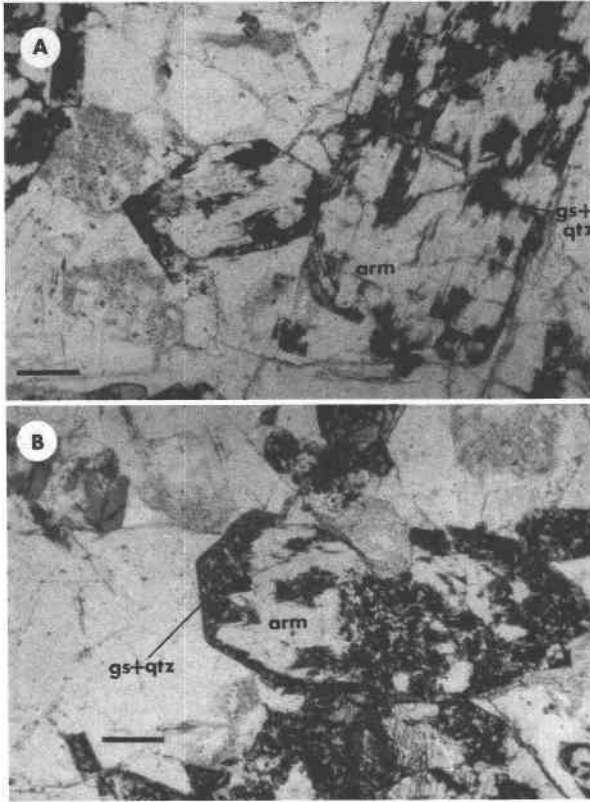


Fig. 5. Photomicrographs of sample from the Strange Lake peralkaline complex, Canada, showing the replacement of armstrongite by gittinsite + quartz along (A) cracks and (B) grain boundaries. The scale bar in both photographs corresponds to 0.1 mm. Sample courtesy of T. Birkett.

be required to establish the correct topologies and to fix the positions of the various invariant points and univariant curves in *P-T* space for each system. Nevertheless, it is possible to make a few observations relevant to natural occurrences and the planning of phase equilibrium experiments from the topologies presented here.

First of all, both topologies for the $\text{Na}_2\text{ZrO}_3\text{-SiO}_2\text{-H}_2\text{O}$ system (Fig. 6) predict that vlasovite is stable to relatively high temperature at low to intermediate pressure and that parakeldyshite + quartz is a high-temperature, high-pressure assemblage. The stability of neither parakeldyshite + quartz nor vlasovite \pm quartz is limited on the high-temperature side in either topology. As mentioned above, reactions neglected in this study involving additional phases (e.g., vlasovite = zircon + lovozerite + terskite) in the complete $\text{Na}_2\text{O-ZrO}_2\text{-SiO}_2\text{-H}_2\text{O}$ system could potentially lead to limitations in the higher temperature stability of parakeldyshite + quartz and vlasovite \pm quartz. In this regard it is interesting to recall that the few experimental data available (Gardinier, 1980) suggest that, at 1 bar at least, vlasovite and parakeldyshite remain the stable phases until incongruent melting occurs at comparatively high temperatures ($> 1200^\circ\text{C}$). This is not surprising for parakeldyshite alone because the chemography of the system $\text{Na}_2\text{O-ZrO}_2\text{-SiO}_2\text{-H}_2\text{O}$ does not permit

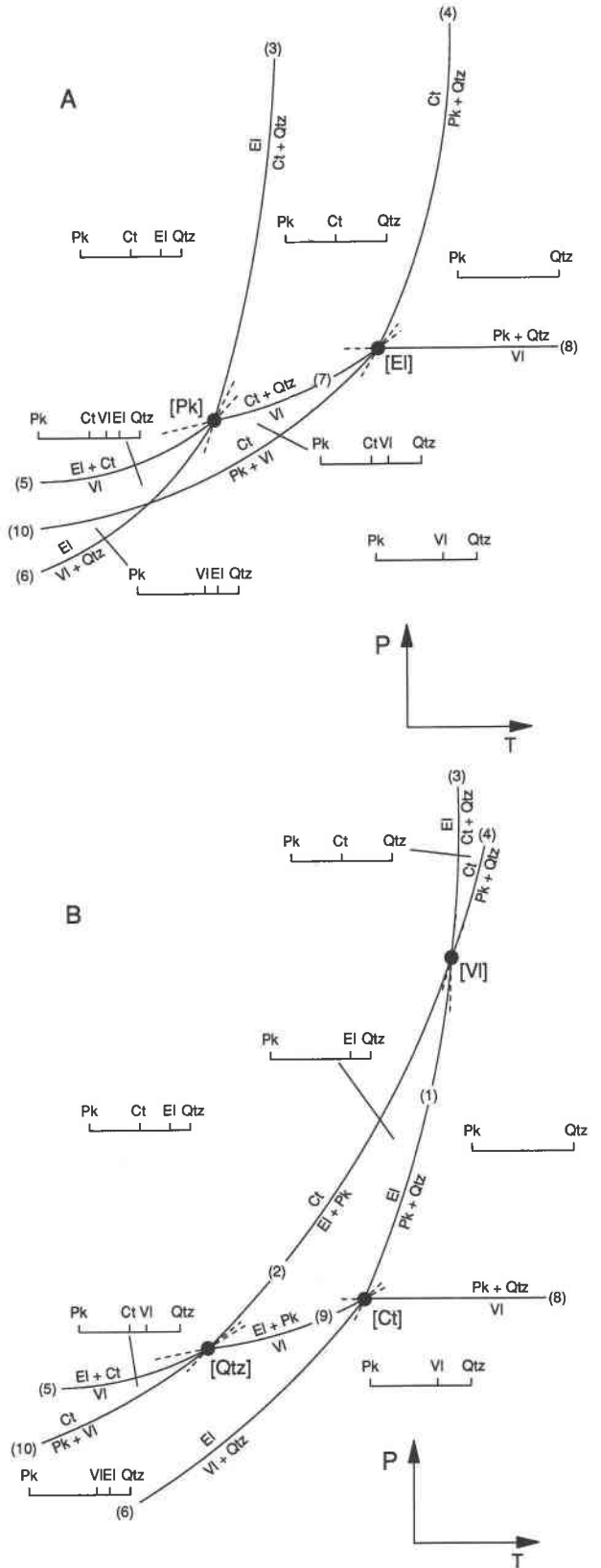


Fig. 6. Schematic *P-T* diagrams for the pseudoternary system $\text{Na}_2\text{O-ZrO}_2\text{-SiO}_2$ based on the topologies illustrated in Figure 3. Note: only stable invariant points are presented for clarity.

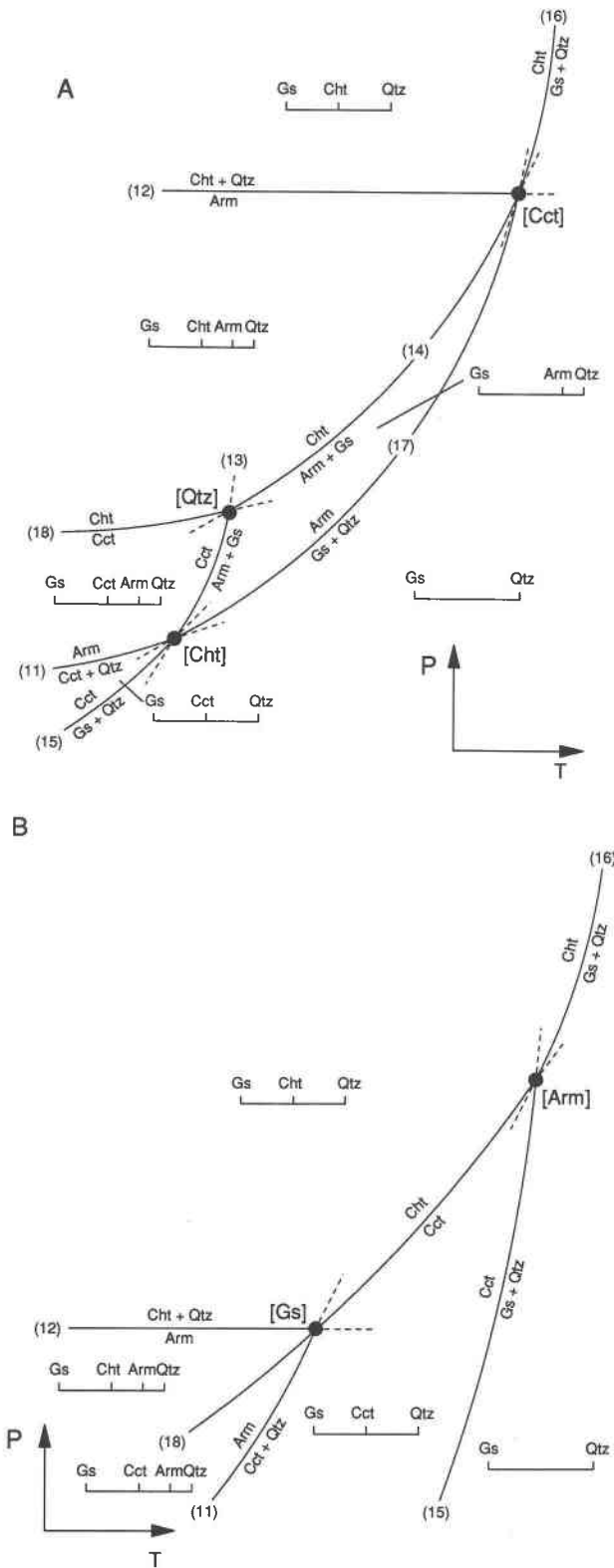


Fig. 7. Schematic P - T diagrams for the pseudoternary system $\text{CaO-ZrO}_2\text{-SiO}_2$ based on the topologies illustrated in Figure 4. Note: only stable invariant points are presented for clarity.

any other parakeldyshite breakdown reaction. (In the present system, the stability of parakeldyshite alone is unrestricted with respect to temperature and pressure because it is a chemographically external phase. This would be true even if other phases such as lovozerite and terskite were added to the system.) However, these experimental data do suggest that, at low pressure at least, none of the possible reactions (e.g., vlasovite = terskite + lovozerite + zircon or vlasovite = quartz + terskite + zircon; Fig. 1a) involving phases omitted from this study limits the high-temperature stabilities of vlasovite.

Both topologies are consistent with the fact that Baussy et al. (1974) and Currie and Zaleski (1985) found parakeldyshite + quartz and vlasovite + quartz to be the high-temperature phases relative to catapleiite and elpidite, respectively; these studies also serve to fix the location of the univariant curve for Reaction 6 in the P - T plane. However, in addition to the breakdown with increasing temperature of elpidite and catapleiite to vlasovite and parakeldyshite, respectively, Figure 6A predicts the occurrence of a stable reaction between catapleiite + quartz and vlasovite, and Figure 6B predicts the occurrence of a stable reaction between elpidite and parakeldyshite + quartz, neither of which was studied by Baussy et al. (1974) or Currie and Zaleski (1985).

Either topology for the $\text{Na}_2\text{O-SiO}_2\text{-ZrO}_2\text{-H}_2\text{O}$ system predicts that parakeldyshite + quartz is a high-pressure assemblage compared to vlasovite. However, given the presently available data, we cannot determine which of these assemblages has the higher entropy, and therefore, the higher temperature. Thus, in both Figures 6A and 6B, the slope of Reaction 8 (Table 2) has been assigned a value of zero.

Note that only the topology shown in Figure 6B possesses a divariant field of stability for the assemblage of parakeldyshite + elpidite. This is in accordance with the rule discussed by Burt (1978) and mentioned above, that the labels of the metastable invariant points in a given $P_s\text{-}\mu_{\text{H}_2\text{O}}$ topology correspond to an assemblage that is uniquely stable in that topology. As already mentioned, available experimental data and information from natural occurrences do not permit an unambiguous choice to be made between the two topologies in the $\text{Na}_2\text{O-SiO}_2\text{-ZrO}_2\text{-H}_2\text{O}$ system. Conclusive identification of the assemblage parakeldyshite + elpidite from natural occurrences or experimental demonstration of a stability field for this assemblage would require that the topology shown in Figure 6B be the correct one. Attempts to demonstrate the validity of the topology in Figure 6A directly from petrographic observations would be more difficult owing to the fact that the unique assemblage for this topology is univariant, thus requiring the good fortune of encountering the exact P - T conditions for this univariant assemblage in nature.

In the case of the $\text{CaZrO}_3\text{-SiO}_2\text{-H}_2\text{O}$ system, in both topologies (Fig. 7) the stability field for gittinsite + quartz is unrestricted at low pressures and high temperatures. In

the topology shown in Figure 7A, upon decreasing T or increasing P , gittinsite + quartz first breaks down to calcium catapleite at low T and P , to armstrongite at intermediate T and P , and to calcohilairite at high T and P . In Figure 7B, upon decreasing T or increasing P , gittinsite + quartz cannot break down to armstrongite by means of a stable reaction, but rather hydrates to form either calcium catapleite or calcohilairite, depending on the P - T conditions. In either topology, the stability of gittinsite alone is unrestricted, as required by the chemography shown in Figure 1b. Both topologies have stability fields for calcohilairite alone restricted to low temperatures or high pressures or both, and the calcohilairite + quartz field opens to high pressures and temperatures. Both topologies also have the armstrongite stability field opening up toward lower pressures and temperatures.

The topology shown in Figure 7A is the only one that has a divariant stability field for the assemblage armstrongite + gittinsite, again in agreement with the rules laid out above. Furthermore, only the topology in Figure 7A has the stable univariant reaction armstrongite = gittinsite + quartz. As pointed out above, this reaction may have occurred stably at Strange Lake. The critical experimental or petrographic observation required to verify the validity of Figure 7A is the unequivocal demonstration of a divariant field of stability for armstrongite + gittinsite. Alternatively, demonstration of the stable existence of the univariant assemblage quartz + calcium catapleite + calcohilairite (potentially a more difficult determination to make), would indicate that Figure 7B is the correct topology.

Unlike for the sodium zirconosilicate system, we have no experimental constraints whatsoever on any of the potential reactions in the calcium zirconosilicate system. Furthermore, we are aware of only one study where an attempt has been made to determine the pressure-temperature conditions of formation of any of the zirconosilicates. Salvi and Williams-Jones (1990) present evidence that much of the gittinsite + quartz at Strange Lake is a metasomatic replacement product of elpidite. These authors have studied primary fluid inclusions in quartz in gittinsite + quartz pseudomorphs after elpidite and have thus estimated the temperature and pressure of formation of gittinsite + quartz to be in the range 150–200 °C and <500 bars, respectively. This is consistent with the prediction of either P - T topology that gittinsite + quartz is a low-pressure assemblage. Furthermore, if the P - T topology depicted in Figure 7A is correct, then the fluid inclusion data of Salvi and Williams-Jones (1990) may provide a lower pressure limit of 500 bars for the reaction armstrongite = gittinsite + quartz + H₂O over the temperature range 150–200 °C.

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REFERENCES CITED

- Al-Hermezi, H.M., McKie, D., and Hall, A.J. (1986) Baghdadite, a new calcium zirconium mineral from Iraq. *Mineralogical Magazine*, 50, 119–123.
- Ansell, H.G., Roberts, A.C., Plant, A.G., and Sturman, B.D. (1980) Gittinsite, a new calcium zirconium silicate from the Kipawa apatitic syenite complex, Quebec. *Canadian Mineralogist*, 18, 201–203.
- Baussy, G., Caruba, R., Baumer, A., and Turco, G. (1974) Minéralogie expérimentale dans le système ZrO₂-SiO₂-Na₂O-H₂O. *Corrélations pétrogénétiques*. *Bulletin de la Société française de la Minéralogie et la Cristallographie*, 97, 433–444.
- Birkett, T.C., Miller, R.R., Roberts, A.C., and Mariano, A.N. (1992) Zirconium-bearing minerals of the Strange Lake intrusive complex, Quebec-Labrador. *Canadian Mineralogist*, 30, 191–205.
- Boggs, R.C. (1988) Calcohilairite: CaZrSi₃O₉·3H₂O, the calcium analogue of hilairite from the Golden Horn batholith, northern Cascades, Washington. *American Mineralogist*, 73, 1191–1194.
- Burt, D.M. (1978) Multisystems analysis of beryllium mineral stabilities: The system BeO-Al₂O₃-SiO₂-H₂O. *American Mineralogist*, 63, 664–676.
- Cannillo, E., Rossi, G., and Ungaretti, L. (1973) The crystal structure of elpidite. *American Mineralogist*, 58, 106–109.
- Caruba, R. (1975) Étude expérimentale de la cristallographie, de la morphologie, de la stabilité et de la génèse du zircon et des zirconosilicates en vue d'applications pétrogénétiques, 324 p. Ph.D. thesis, University of Nice, Nice, France.
- Chao, G.Y. (1985) The crystal structure of gaidonnayite Na₂ZrSi₃O₉·2H₂O. *Canadian Mineralogist*, 23, 11–15.
- Chao, G.Y., and Watkinson, D.H. (1974) Gaidonnayite, Na₂ZrSi₃O₉·2H₂O, a new mineral from Mont St. Hilaire, Quebec. *Canadian Mineralogist*, 12, 316–319.
- Chao, G.Y., Rowland, J.F., and Chen, T.T. (1973) The crystal structure of catapleite. *Geological Society of America Abstracts with Programs, Annual Meeting*, 572.
- Chao, G.Y., Watkinson, D.H., and Chen, T.T. (1974) Hilairite, Na₂ZrSi₃O₉·3H₂O, a new mineral from Mont St. Hilaire, Quebec. *Canadian Mineralogist*, 12, 237–240.
- Christophe-Michel-Lévy, M. (1961) Reproduction artificielle de quelques minéraux riches en zirconium (zircon, eudialyte, catapleite, elpidite); comparaison avec leurs conditions naturelles de formation. *Bulletin de la Société française de la Minéralogie et Cristallographie*, 84, 265–269.
- Currie, K.L., and Zaleski, E. (1985) The relative stability of elpidite and vlasovite: A P-T indicator for peralkaline rocks. *Canadian Mineralogist*, 23, 577–582.
- Fleet, S.G., and Cann, J.R. (1967) Vlasovite: A second occurrence and a triclinic to monoclinic inversion. *Mineralogical Magazine*, 36, 233–241.
- Fyfe, W.S. (1960) Hydrothermal synthesis and determination of equilibrium between minerals in the subliquidus region. *Journal of Geology*, 68, 553–566.
- Gardinier, C.F. (1980) Phase relations in the systems alkali oxide (Li₂O, Na₂O)-ZrO₂-SiO₂ and Na₂ZrO₃-NaAlO₂-SiO₂, 156 p. Ph.D. thesis, Miami University, Oxford, Ohio.
- Gerasimovskii, V.I. (1962) Keldyshite—a new mineral. *Proceedings of the Academy of Science of the USSR*, 142, 123–125.
- Ghose, S., Wan, C., and Chao, G.Y. (1980) Petarosite, Na₂Zr₂Si₆O₁₈(Cl,OH)·2H₂O, a zeolite-type zirconosilicate. *Canadian Mineralogist*, 18, 503–509.
- Gittins, J., Gasparrini, E.L., and Fleet, S.G. (1973) The occurrence of vlasovite in Canada. *Canadian Mineralogist*, 12, 211–214.
- Harris, C., Cressey, G., Bell, J.D., Atkins, F.B., and Beswetherick, S.

- (1982) An occurrence of rare-earth-rich eudialyte from Ascension Island, South Atlantic. *Mineralogical Magazine*, 46, 421–425.
- Hiemstra, S.A. (1955) Baddeleyite from Phalaborwa, eastern Transvaal. *American Mineralogist*, 40, 275–282.
- Horvath, L., and Gault, R.A. (1990) The mineralogy of Mont Saint-Hilaire, Quebec. *Mineralogical Record*, 21, 284–359.
- Hurlbut, C.S., Jr., and Klein, C. (1977) *Manual of mineralogy* (19th edition) 532 p. Wiley, New York.
- Il'yukhin, V.V., and Belov, N.V. (1960) The crystal structure of lovozerite. *Proceedings of the Academy of Science of the USSR*, 131, 379–382.
- Jambor, J.L., Roberts, A.C., and Grice, J.D. (1987) Armstrongite from the Strange Lake alkalic complex, on the Quebec-Labrador boundary, Canada. *Powder Diffraction*, 2, 2–4.
- Kapustin, Y.L. (1966) A new occurrence of elpidite in the USSR. *Proceedings of the Academy of Science of the USSR*, 171, 157–160.
- Khomyakov, A.P., Voronkov, A.A., Kazakova, M.E., Vlasova, E.V., and Smolyaninova, N.N. (1975) Investigation on minerals of the keldyshite group. *Trudy-Akademiya Nauk SSSR, Mineralogicheskii Muzei im A.E. Fersmana*, 24, 120–131 (in Russian).
- Khomyakov, A.P., Semenov, E.I., Voronkov, A.A., and Nechelyustov, G.N. (1983) Terskite, $\text{Na}_2\text{ZrSi}_2\text{O}_{15} \cdot 2\text{H}_2\text{O}$, a new mineral. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, 112, 226–232 (in Russian).
- Kordyuk, R.A., and Gul'ko, N.V. (1962) Subsolidus structure and ternary compounds in the system $\text{CaO-ZrO}_2\text{-SiO}_2$. *Proceedings of the Academy of Science of the USSR*, 142, 6–8.
- Korzhinskii, D.S. (1959) Physicochemical basis of the analysis of the paragenesis of minerals, 142 p. Consultants Bureau, Inc., New York.
- Lazutkina, L.N., Kogarko, L.N., and Krigman, L.D. (1980) Stability of zirconium minerals in alkali agpaitic magmas. *Geochemistry International*, 17 (4), 83–86.
- Linthout, K. (1984) Alkali-zirconosilicates in peralkaline rocks. *Contributions to Mineralogy and Petrology*, 86, 155–158.
- Maurice, O.D. (1949) Transport and deposition of the non-sulphide vein minerals. V. Zirconium minerals. *Economic Geology*, 44, 721–731.
- Miller, R.R. (1986) Geology of the Strange Lake alkalic complex and the associated Zr-Y-Nb-Bc-REE mineralization. Current Research, Newfoundland Department of Mines and Energy, Mineral Development Division, Report 86-1, 11–19.
- Mohr, R.E., and Stout, J.H. (1980) Multisystem nets for systems of $n + 3$ phases. *American Journal of Science*, 280, 143–172.
- Morgan, P.E.D., Hicks, J.L., Bump, H.A., and Koutsoutis, M.S. (1987) Unit cells and indexed X-ray powder patterns of two calcium zirconium silicates. *Journal of Materials Science Letters*, 6, 559–561.
- Portnov, A.M. (1964) Calcic catapleiite, a new variety of catapleiite. *Proceedings of the Academy of Science of the USSR*, 154, 98–100.
- Portnov, A.M., and Rastsvetayeva, R.K. (1966) Vlasovite and manganoastrophyllite in alkalic syenite-pegmatite of the north Baikal region. *Proceedings of the Academy of Science of the USSR*, 166, 128–131.
- Raade, G., and Mladeck, M.H. (1977) Parakeldyshite from Norway. *Canadian Mineralogist*, 15, 102–107.
- Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) The structure of zircon: A comparison with garnet. *American Mineralogist*, 56, 782–790.
- Roelofsen-Ahl, J.N., and Peterson, R.C. (1989) Gittinsite: A modification of the thortveitite structure. *Canadian Mineralogist*, 27, 703–708.
- Salvi, S., and Williams-Jones, A.E. (1990) The role of hydrothermal processes in the granite-hosted Zr, Y, REE deposit at Strange Lake, Quebec/Labrador. Evidence from fluid inclusions. *Geochimica et Cosmochimica Acta*, 54, 2403–2418.
- Stout, J.H. (1990) Phase chemographies in quaternary systems of seven phases. I: The five convex polytopes. *American Journal of Science*, 290, 719–738.
- Tikhonenkova, R.P., and Kazakova, M.Y. (1962) Vlasovite—a new zirconium silicate from the Lovozero massif. *Proceedings of the Academy of Science of the USSR*, 137, 451–542.
- Vladhikin, N.V., Kovalenko, V.I., Kashaev, A.A., Sapozhnikov, A.N., and Pisarskaya, V.A. (1973) A new silicate of calcium and zirconium-armstrongite. *Doklady Akademii Nauk SSSR*, 209, 1185–1188 (in Russian).
- Vlasov, K.A., Kuz'menko, M.Z., and Es'kova, E.M. (1966) The Lovozero alkali massif. Oliver and Boyd, Edinburgh.
- Zen, E-An (1966) Some topological relations of P-T diagrams for multi-systems of $n + 3$ phases: I. General theory; unary and binary systems. *American Journal of Science*, 264, 401–427.
- Zen, E-An, and Roseboom, E.H., Jr. (1972) Some topological relationships in multisystems of $n + 3$ phases, III. Ternary systems. *American Journal of Science*, 272, 677–710.

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