The Na₂O-ZrO₂-SiO₂ and CaO-ZrO₂-SiO₂ Systems:

Theoretical Petrogenetic Grids and Synthesis Experiments

by

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Abstract

Fixed-slope P_{i} - μ_{H2O} diagrams have been generated for the pseudoternary systems SiO_2 -Na₂ZrO₃-H₂O and SiO_2 -CaZrO₃-H₂O as first approximations to P-T phase relations for the Na- and Ca-zirconosilicates, respectively. Two possible topologies were determined for each pseudoternary based on an interchange of stable and metastable invariant points. Although for the SiO₂-Na₂ZrO₃-H₂O system the correct topology cannol 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 mineral assemblage: elpidite + parakeldyshite.

The observed replacement of armstrongite by gittinsite + quartz in the Strange Lake peralkaline complex, Canada, suggests that the preferred topology for the S_1O_2 -CaZrO₃-H₂O system may be the one in which the calcium catapleiite-, quartz- and calciohilairite-absent invariant points are stable.

Synthesis experiments in the SiO_2 -CaZrO₃-H₂O system resulted in the formation of the compound Ca₂ZrSi₄O₁₂ as well as zircon, baddeleyite, xonotlite and wollastonite under various conditions, but synthesis of naturally-occurring Ca-zirconosilicates remained elusive.

Résumé

4

Des diagrammes de P_s - μ_{H2O} à pente fixé ont été produits pour les systèmes pseudoternaire SiO₂-Na₂ZrO₃-H₂O et SiO₂-CaZrO₃-H₂O comme première approximation des relations pour les zirconosilicates sodiques et calciques, respectivement. Deux topologies possibles ont été déterminées pour chaque pseudoternaires basées sur l'échange de points invariants stables et métastables. Quoi que la topologie correcte pour le système SiO₂-Na₂ZrO₃-H₂O n'est pas encore résolue, dû au manque de contraintes d'observations éxpérimentaux et de terrains, l'analyse chémographique révéle que l'observation critique serait la coexistence ou l'incompatibilité de l'assemblage minéral: elpidite + parakeldyshite.

Le remplacement observé de l'armstrongite par gittinsite + quartz dans le complexe hypercalin de Strange Lake (Lac Brisson), Canada, suggère que la topologie préferée pour le système SiO_2 -CaZrO₃-H₂O est possiblement celle dans laquelle les points invariants pour l'absence de la catapléite calcique, le quartz et la calciohilairite sont stables.

Des éxpériments de synthèse dans le système SiO_2 -Ca ZrO_3 -H₂O ont donné la formation de Ca₂ZrSi₄O₁₂ ainsi que zircon, baddeleyite, xonotlite et wollastonite sous différentes conditions; les zirconosilicates calciques naturelles n'ont pas été produites.

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I extend my sincere gratitude to Dr. Scott Wood, for his patience and guidance throughout this project. I found his tutelage most enriching and enlightening in a field of geology which most new graduate students (myself included) consider to be "rocket science". I would also like to thank NSERC, FCAR and the Department of Geological Sciences at McGill for providing financial support for this project. I am indebted to Dr. A.E. Williams-Jones and Dr. Robert Martin for the valuable advice which they provided throughout this project. Special thanks are also extended to Tariq Ahmedah, Dr. Steven Aja and Glenna Keating for their assistance in the XRD lab. Colleagues and friends at McGill deserving of special mention include Gary Nassif whose discussions of the petrology of Strange Lake and assistance in writing the résumé 15 greatly appreciated. Prokopis Kranidiotis, Steeve McCauley, Stefano Salvi, Bruce Mountain, Jim Mungall and Alex Kiddie each contributed in one way or another and deserve special thanks. Finally, I would like to acknowledge Vicky for her love and support which was essential to the completion of this project.

Table of Contents

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No.

Abstract 1
Résumé
Acknowledgements 3
Chapter 1: Introductory Statement
Chapter 2: Preliminary petrogenetic grids for sodium
and calcium zirconosilicate minerals in felsic peralkaline
rocks: The SiO_2 -Na ₂ ZrO ₃ and SiO_2 -CaZrO ₃ pseudobinary systems
Abstract
Introduction
World Occurrences 13
Theory 19
Mineralogy of Zirconosilicates
Experimental Data
Determination of Schematic P_s - μ_{1120} Diagrams
Discussion
Conclusions
Tables
Figures
Chapter 3: Synthesis Experiments in the CaO-ZrO ₂ -SiO ₂
system

E	Experime	ental A	Appr	oach	•			••	• •	• •	••	• •	••	••	•	•••	•	• •	•	•	•	٠	•	45
E	Experime	ental l	Resul	ts.	••			•••	••	•										•				47
Ľ	Discussio	on	•••		•••					•	••	•••	• •		•	• •	•			•	•			49
Т	ables .		•••		•••	•••	· 	• •	••	• •	•	••		•••	•	•••			•			•	•	51
F	igures .		•••	•••	•••				••		•••	• •	••	••	•	••		•••	•			•		52
Referenc	es	• • • •	•••		•••			•••		• •	••	•••	• •	••	•		•	•	•					53

۹۳ ۱

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Chapter 1

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Introductory Statement

Introductory Statement

Alkali and alkaline-earth zirconosilicates are common accessory minerals in felsic peralkaline rocks and can constitute several volume percent in some localities. This group of minerals could be useful petrogenetic indicators of P-T-f_{volatile} conditions of formation and subsolidus modification of peralkatine rocks. Unfortunately, the current body of data from reversed subsolidus phase equilibria experiments involving these minerals is quite limited, as is the available thermodynamic data for these phases. In order for zirconosilicate minerals to be useful petrogenetic indicators, phase diagrams based on reversed experiments must be generated. This thesis seeks to add to the currently available data in order to achieve this goal.

In the second chapter of this thesis, fixed-slope $P_s - \mu_{II20}$ diagrams have been generated for the pseudoternary systems SiO₂-Na₂ZrO₃-H₂O and SiO₂-CaZrO₃-H₂O. The value in this approach lies in the fact that fixed-slope diagrams yield only two possible topologies based on an exchange of stable and metastable invariant points Furthermore, if it is assumed that increasing temperature corresponds to decreasing μ_{II20} , $P_s - \mu_{II20}$ diagrams are topologically identical to P-T diagrams.

The correct topology for each system cannot be established with certainty owing to a lack of constraints from experimental and field relations. However, the key assemblage net field to make that determination in each case has been isolated, eipidite + parakeldyshite for the Na-zirconosilicate system and gittinsite + armstrongite for the Cazirconosilicate system. Observation of stability of either of these divariant assemblages in nature or in experiment would allow determination of the correct topology The third chapter of this thesis reports the results of the experimental component of this project. None of the naturally-occurring Ca-zirconosilicates could be synthesized and hence, the ultimate goal of constraining the reaction:

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armstrongite = gittinsite + quartz + water
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could not be achieved. However, many interesting results were obtained and have been reported.

Chapter 2

Petrogenetic Grids for the Ca and Na-zirconosilicate Minerals

The second chapter of this thesis is a modification of the following paper.

Marr, R.A. and Wood, S.A. (1992) Preliminary petrogenetic grids for sodium and calcium zirconosilicate minerals in felsic peralkaline rocks: The $SiO_2-Na_2ZrO_3$ and $SiO_2-CaZrO_3$ pseudobinary systems. American Mineralogist, (in press).

This paper comprises original research performed by the first author including generation of the petrogenetic grids, with assistance in the interpretation and writing of the manuscript provided by the second author. An expanded discussion of world occurrences of zirconosilicates and a summary of conclusions have been added.

Abstract

Although zircon is the most common zirconium-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 P₁-µ_{H2O} diagrams have been generated for the pseudoternary systems SiO₂-Na₂ZrO₃- H_2O and SiO_2 -CaZrO₃- H_2O as first approximations to P-T phase relations among the Na- and Cazirconosilicates, respectively. These two pseudotemary systems contain quartz, water and either, elpidite, vlasovite, catapleiite, gaidonnayite, 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 Na₂O-ZrO₂-SiO₂-H₂O and CaO- ZrO_2 -SiO₂-H₂O systems, serve as starting points for understanding the more complex phase relationships of the complete systems. The phase compositions in the two pseudotemary subsystems were projected through H_2O . Two possible $P_s - \mu_{H2O}$ topologies were determined for each pseudoternary based on an interchange of stable and metastable invariant points Although for the SiO_2 -Na₂ZrO₃-H₂O 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 SiO_2 -CaZrO₃-H₂O 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.

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Introduction

Alkali and alkaline-carth 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 zirconium. The alkali and alkaline-carth zirconosilicates could be useful petrogenetic indicators of P-T-f_{volatile} 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; Baussy 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 Cazirconosilicates, 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 Na zirconosilicates. Clearly, for zirconosilicate minerals to be useful petrogenetic indicators, phase diagrams based on reversed experiments must be determined. In order to provide a framework for future experiments on the Ca and Na zirconosilicate systems and for the interpretation of phase relations in nature, we present have preliminary schematic pressuretemperature 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.

World Occurrences

Alkali and alkaline-earth zirconosilicates have been identified at many localities worldwide, primarily as accessory minerals in peralkaline granitoids and nepheline synites. Some of the most important occurrences will be discussed in this section.

Strange Lake Complex, Canada

The Strange Lake complex of northern Québec and Labrador, comprises a small, Late-Proterozoic peraikaline granitic pluton intruded into high-grade quartzo-feldspathic, calc-silicate, graphitic, dioritic, gabbroic and anorthositic gneisses (Bélanger, 1984). The complex comprises three distinct lithologies: (1) hypersolvus alkali granite, (2) melanocratic microgranite and (3) subsolvus alkali granite (Nassif and Martin, 1991; Nassif, personal communication, 1992). The hypersolvus granite and the melanocratic microgranite are believed to be coeval and predate the geochemically more-evolved subsolvus granite. Elevated concentrations of Zr, Y, Be, Nb and REE occur in a highly-altered region of the subsolvus granite represented by a suite of exotic minerals including several zirconosilicates.

Dalyite $(K_2ZrSi_6O_{15})$ has been identified in the hypersolvus granite, commonly rimmed by elpidite and less commonly by vlasovite (Birkett et al., 1992). Vlasovite has also been observed as an independent mineral in both the hypersolvus and subsolvus granite. Elpidite and armstrongite have also been observed in both the hypersolvus and subsolvus granite, both as independent minerals and related by replacement of elpidite with armstrongite. An increase in the proportion of elpidite with respect to armstrongite has been observed as a function of depth in drill core studies (Birkett et al., 1992).

The most important zirconosilicate at Strange Lake is gittinsite. Gittinsite occurs primarily in the subsolvus granite as a replacement product of elpidite and armstrongite. In this occurrence, fine clusters of gittinsite are found intermixed with quartz occupying the onginal volume of the precursor mineral. A second and much less common mode of occurrence of gittinsite is as bladed crystals in association with allanite and quartz. This occurrence may represent a late-stage primary assemblage (Birkett et al., 1992) and is only found in rocks that also contain secondary gittinsite.

Minor amounts of catapleiite, calcium catapleiite and calciohilairite have also been reported at Strange Lake (Birkett et al., 1992).

Zircon is a common accessory mineral at Strange Lake. Early subhedral zircon crystals are commonly observed in the hypersolvus granite, often embayed by dalyite, vlasovite or elpidite. Late-stage zircon has also been reported as radiating needles partially or completely replacing earlier zirconosilicates (Birkett et al., 1992).

Lovozero Massif, Russia

One of the most important occurrences of zirconosilicates in the world is the Lovozero massif. Covering an area of approximately 650km² on the Kola peninsula of northern Russia, the Lovozero nepheline syenite massif is a layered intrusion of Devono-Carboniferous age (Gerling et al., 1941). The massif consists of four complexes: (1) a eudialytic lujavrite complex, (2) a differentiated complex consisting of alternating foyaites, urtites and lujavntes, (3) a poikilitic syenite complex and (4) dyke rocks (Vlasov et al., 1966). The eudialytic lujavrites and the

differentiated complex together comprise about 95% of the total known extent of the massit

Pegmatites are found throughout the massif and contain many of the exotic minerals identified at Lovozero. Vlasov et al. (1966) grouped these pegmatites into six paragenetic associations:

(1) nepheline-aegirine I-microcline-cudialyte;

(2) nepheline-aegirine I-microcline with accessory eudialyte;

(3) sodalite-nepheline-aegirine I-microcline-cudialyte with Zr, Ti, Nb and REE minerals;

(4) feldspar-aegirine II with Zr, Ti, and Nb minerals;

(5) hackmanite-natrolite with REE and Th minerals;

(6) natrolite-analcite-ussingite-albite with late microcline and Li and Be minerals.

The first three pegmatite types correspond mineralogically and geochemically to the eudialytic lujavrites, the rocks of the differentiated complex and the pork-litic syenites, respectively. The other associations represent more-evolved pegmatites and form separate zones within other pegmatites or independent complexes (Vlasov et al., 1966).

Several zirconosilicates occur at Lovozero, the most important being minerals of the eudialyte-eucolite group. Although eudialyte generally displays a considerable variability in composition from one occurrence to another, at Lovozero this group forms an isomorphous series conforming to the formula: $(Na,Ca)_3$ ZrSi₆O₁₇, eudialyte being the more sodic member and eucolite the more calcic. An intermediate member named mesodialyte has also been distinguished (Vlasov et al., 1966). No end member compositions have yet been reported.

Eudialyte-mesodialyte represents a rock-forming mineral in the cudialytic lujavrite, crystallizing early with nepheline, microcline, aegirine, sohene and apatite (Vlasov et al., 1966). Late-stage hydrothermal alteration of eudialyte-mesodialyte resulted in crystallization of lovozente In the differentiated and poikilitic syenite complexes, eudialyte-mesodialyte is a much less important phase and crystallizes later than in the eudialytic lujavrite. Again, hydrothermal alteration results in replacement of eudialyte by lovozerite and catapleiite.

Occurrence of zirconosilicates in the various pegmatite bodies at Lovozero is rather more complex, but generally follows a pattern of early crystallization of minerals from the eudialyteeucolite series replaced by late elpidite, lovozerite and catapleiite. Occasionally, the more sodic eudialyte and mesodialyte are replaced by eucolite. As with the main rock units, late-stage crystallization of pegmatites is believed to occur in a hydrothermal environment (Vlasov et al., 1966).

In contrast to Strange Lake, zircon is not an accessory mineral in rocks of the Lovozero massif. The only reported occurrences of zircon are in hybrid pegmatites formed by contamination of pegmatite melts by country rocks. The formation of zircon instead of eudialyte in these pegmatites was unaffected by composition of the contaminating host rock. This suggests that the physico-chemical conditions for stability of eudialyte are quite limited and easily disturbed (Vlasov et al., 1966).

Ilimaussaq Intrusion, Greenland

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, r . The Ilimaussaq intrusion is a stratified peralkaline complex with an age of approximately 1020 Ma (Bridgwater, 1965). Four intrusive stages have contributed to the formation of the Ilimaussaq complex (Larsen and Sørensen, 1987): (1) early alkali granite, (2) early augite syenite, (3) agpaitic nepheline syenite and (4) late lujavrite. Field relations of the alkali granite are unclear, but along with the augite syenite, is believed to predate the nepheline syenites.

Zirconium mineralogy is somewhat simpler at Ilimaussaq than at Lovozero or Strange Lake. Eudialyte occurs in all nepheline syenite horizons including the lujavrite, sometimes as a major phase (Sørensen, 1970). Lovozerite appears as an accessory mineral in the lujavrite, while zircon and elpidite occur in minor amounts in the alkali granite. It is interesting to note that, once again, zircon is limited to silica-saturated rocks.

Mont Saint-Hilaire, Canada

Mont Saint-Hilaire displays one of the mos' varied suites of zirconosilicates to be found anywhere in the world. The complex consists of three intrusions of Cretaceous age penetrating Ordovician shales and limestones. Using the designations of Curric (1989), the oldest of these intrusions is the Sunrise suite comprising melagabbros and pyroxenites Intruding the Sunrise suite as a ring dyke was the Pain du Sucre suite of nepheline diorites, gabbros and monzonites. Approximately coeval with the Pain du Sucre suite was the East Hill suite which consists of nepheline and sodalite syenites, porphyries and breccias. Extensive quarrying of the northern part of the East Hill suite has revealed most of the unusual mineralogy of Mont Saint-Hilaire

Many of the unusual minerals at Mont Saint-Hilaire are found in sychitic pegmatites. The pegmatite mineralogy commonly consists of microcline and aegirine with local concentrations of serandite, catapleiite and analcime. Other zirconosilicates that have been identified in unaltered pegmatites are elpidite, gaidonnayite and eudialyte. Some altered pegmatites have been found to contain zircon and petarasite as well (Horvath and Gault, 1990).

Exotic mineralogy has also been observed in miarolitic cavities in the nepheline syenite of the East Hill suite. These small (<10cm) cavities have been found to contain catapleiite, elpidite, eudialyte, gaidonnayite, hilairite and zircon as well as numerous rare-carth silicates and carbonates (Horvath and Gault, 1990). The presence of zircon without quartz is interesting as it defies the tendency of zircon to occur only in saturated peralkaline rocks

It should be noted that it is unlikely that all the zirconosilicate phases at Mont Saint-Hilaire coexist in equilibrium, in as much as the Gibb's phase rule would appear to be grossly violated.

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Ascension Island, South Atlantic

Peralkaline granitic blocks occurring in trachytic breccias on Ascension Island have been studied for many years. The blocks, which are interpreted as having been torn from the walls of a conduit during an explosive eruption, can be described in terms of three intergradational petrographic types: (1) hornblende non-perthitic granite, (2) arfvedsonite/ aegirine \pm oligoclase non-perthitic granite and (3) arfvedsonite/aegirine perthitic granite (Roedder and Coombs, 1967). It is this last petrographic type that has been observed to contain zirconosilicates.

The most common zirconosilicate in the peralkaline granite blocks of Ascension Island is vlasovite. Fleet and Cann (1967) reported vlasovite occurring as interstitial grains in contact with quartz and feldspar and projecting into miarolitic cavities. Associated minerals include arfvedsonite, aegirine, aenigmatite, fayalite and pyrochlore.

Dalyite is much less common than vlasovite, but occurs in similar rocks. Harris et al. (1982) reported that blocks containing dalyite are somewhat more miarolitic than those containing vlasovite, but are petrographically identical. It is interesting to note that dalyite and vlasovite have not yet been observed together in the same block.

A rare-earth- and iron-rich eudialyte has been reported in a dalyite-bearing block (Harris et al., 1982). The eudialyte is quite rare, occurring as an interstitial phase in contact with all major phases as well as dalyite, although it is not apparently in reaction with the latter mineral.

Finally, minor amounts of zircon have been reported both in blocks containing vlasovite and dalyite, although no intimate association has been reported.

The list of zirconosilicate occurrences described in this section is by no means exhaustive.

Other peralkaline complexes displaying zirconosilicate mineralogy include the Khibina massif in Russia, several localities in the Langesundfjord region of Norway, Isle de Rouma, Guinea and the Kipawa intrusion in Canada. Those complexes described do represent a good cross-section, however, since most other agaitic peralkaline rocks display similar parageneses.

Theory

As will be shown below, we will be dealing primarily with phase relationships in (n+3)phase multisystems, where n is the number of components. In general, there are (n+2)(n+3) + 2alternate pressure-temperature nets possible in a non-degenerate (n+3)-phase multisystem that are consistent with the rules of Schreinemakers (Zen, 1966; Zen and Roseboom, 1972; Mohr an ; 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 dat \cdot are usually insufficient to identify an 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-µ₁₁₂₀ diagram (Korzhinskii, 1959; Burt, 1978), where P_s represents the pressure on the solid phases and µ₁₁₂₀ represents the chemical potential of water. According to the thermodynamic relation:

$$\left(\frac{\partial P_s}{\partial \mu_{H2O}}\right)_T = -\frac{\Delta n H_2 O}{\Delta V_s}$$

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 water involved. The univariant reactions on such a diagram should approximate straight lines (i.e., constant slopes) assuming that there is no solid solution and the compressibilities of the solid phases are negligible

The main advantage of a fixed-slope diagram is that an (n+3)-phase multisystem 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 between 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.

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Once the appropriate choice of alternative P_s - μ_{H20} diagrams is made, the topology of the corresponding P-T diagram is also determined, because decreasing μ_{H20} 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.

Mineralogy 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 $NaCa_3Zr_4Si_{16}O_{40}(OH)_{11}.8H_2O$ and eudialyte $Na_3Ca_2ZrSi_6O_{17}(OH)_2$. This quinary system represents an unmanageable (n+16)-phase multisystem which we do not consider in this paper. It should be noted that phases in the K₂O-CaO-Na₂O-SiO₂-ZrO₂-H₂O system, including wadeite (K₂ZrSi₃O₉), dalyite (K₂ZrSi₆O₁₅), umbite (K₂(Zr,Ti)Si₃O₉.H₂O), khibinskite (K₂ZrSi₂O₇), georgechaoite (NaKZrSi₃O₉.2H₂O) and kostylevite (K₄Zr₂Si₆O₁₈.2H₂O), also occur in peralkaline rocks. Because

of the overwhelming complexity of the complete K_2O -CaO-Na₂O-SiO₂-ZrO₂-H₂O system, and the relative paucity of hydrated phases in the subsystem K_2O -SiO₂-ZrO₂-H₂O, for which it is impossible to construct meaningful P_s - μ_{H2O} diagrams, these phases are also not treated in this preliminary investigation. It should also be noted that the K-zirconosilicates are often spatially and temporally separated from the Na- and Ca-zirconosilicates in a given paragenesis (Harris et al., 1982; Birker; et al., 1992).

Sodium Zirconosilicates

The chemography of part of the Na₂O-SiO₂-ZrO₂-H₂O system is depicted in Figure 1a We make t¹⁺2 simplifying assumption that water 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 H₂O onto the Na₂O-SiO₂-ZrO₂ plane. The probable presence of a separate water phase during the formation of most Na zirconosilicates can be inferred from the fact that these are often latecrystallizing, 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 two-fold: first, the complexity of the system is reduced by one component and one phase, and second, it eliminates the need to consider the water-absent invariant point, which is difficult to represent in P₁-µ₁₂₀ space, because all associated univariant water-absent reactions have zero slopes. The drawback to projection from H₂O is that the schematic P-T nets that we will ultimately derive are not applicable to those situations where the activity of water is not fixed either externally or by the presence of a vapor phase.

In addition to the Na zirconosilicate minerals whose compositions are plotted in Figure 1a, a variety of Na 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

have 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 an (n+9)-phase multisystem, which is still too complicated to represent graphically. It is necessary to further simplify this system by systematically excluding phases until an (n+3)-phase multisystem, which can be handled by established methods, has been obtained. Criteria for initial exclusion of phases include rarity and exhibition of substantial solid solution, which could potentially invalidate the assumptions required to use P_{a} - μ_{H2D} 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 (n+3)-phase multisystem are well understood, the excluded phases may be reintroduced into the system in a stepwise fashion.

As a first step in simplifying the (n+9)-phase multisystem 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 pseudotemary depicted in Fig. 1a). Baddeleyite is rare in felsic peralkaline rocks and is stable relative to zircon and the zirconosilicates only under extremely silicaundersaturated conditions. Terskite is also quite rare. Lovozerite, although more common, exhibits considerable isomorphic 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

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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, catapleiite, gaidonnayite, hilairite, and parakeldyshite) in Figure 1a, such as lovozerite, terskite, baddelyite 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, catapleiite, hilarite and gaidonnayite all have the same Na-Zr ratio and plot along a pseudobinary Na_2ZrO_3 -SiO₂, together with quartz. We have thus reduced the ternary system to a pseudobinary and an (n+5)-phase multisystem remains. The best-known and most widespread of the Na-zirconosilicates, catapleiite 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 Na-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 cataplente, hilarrite and gaidonnayite all plot at the same point when projected through water. The P-T diagram for the pseudobinary will therefore be split into three parts by the three degenerate reactions among catapleiite, 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 an (n+3)-phase multisystem, and the phase relations can be hand'ed and depicted using standard methods.

As noted above, an implicit assumption in using P_{a} - μ_{H2O} diagrams to discern phase relationships is the absence of significant solid solution in the phases considered. Published chemical analyses of elpidite, vlasovite, parakeldyshite, catapleiite, 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 to 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 11 the formula $(Na,H)_2$ ZrSi₂O₇. 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 Na_2 ZrSi₂O₇, is now known as parakeldyshite, and the other, with the formula $(Na,H_3O)_2$ ZrSi₂O₇, is apparently as yet unnamed. Evidently, the latter mineral is a lowtemperature alteration product of parakeldyshite, related to it solely by the exchange of hydronium for sodium ion (Raade and Mladeck, 1977); we therefore do not consider it further in this paper.

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Calcium zirconosilicates

Compositional relationships in the CaO-SiO₂-ZrO₂-H₂O 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 Na-zirconosilicates above. The system as shown is an (n+6)-phase multisystem. Baghdadite is a rare mineral that apparently does not occur in the same types of environments as the other Ca-zirconosilicates. The sole occurrence of baghdadite known to the authors is in a mellitte skam in Iraq (Al-Hermezi et al., 1986): it has not yet been reported from felsic peralkaline rocks Similarly, other phases in the CaO-SiO₂-ZrO₂-H₂O system not shown in Figure 1b, such as wollastonite (CaSiO₃), lamite (Ca₂SiO₄), rankinite (Ca₃Si₂O₂), 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 Na-zirconosilicates This leaves the phases calcium catapleiite, gittinsite, armstrongite, calciohilairite, and quartz which constitute an (n+3)phase multisystem along the CaZrO₃-SiO₂ 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 CaZrSi₆O₁₅.2.5H₂O. However, Jambor et al. (1987), based on electron microprobe studies, suggested that the number of H₂O 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_{e} - μ_{H2O} 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 Ca zirconosilicate minerals listed in Table 1, a phase with the formula Ca₂ZrSi₄O₁₂ 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 Na-zirconosilicates, the extent of natural compositional variation

of armstrongite, gittinsite, Ca-catapleiite and calciohiliarite appears to be relatively small. Total impurities, including Na₂O, K₂O, Al₂O₃, TiO₂, P₂O₅, MgO and Fe₂O₃, 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 one atmosphere pressure (Gardinier, 1980). In this investigation, it was found that parakeldyshite melts incongruently to ZrO_2 + 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 cutectic mixture of albite + nepheline + Na₂SiO₅ and ZrO₂, Lazutkina et al. (1980) determined that parakeldyshite melted incongruently to ZrO₂ + 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 a gel of bulk composition equivalent to pure elpidite as a reactant. 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 NaHCO₃, elpidite or vlasovite + quartz was the product. Currie and Zaleski (1985) attribute this curious finding to an effect of the chloride ion on the activity of either silica or water. 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 synthesized successfully 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 catapleiite to parakeldyshite + quartz at 700 bars.

In the case of the Ca 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 have been synthesized, in spite of several attempts (Caruba, 1975; Morgan et al., 1987). As mentioned above, to our knowledge, the only other Ca zirconosilicate to have been synthesized is $Ca_2ZrSi_4O_{12}$.

Determination of Schematic P,-µ_{H20} 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-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 phases catapleiite, gaidonnayite and hilairite, which effectively splits the

phase diagram into three portions without affecting the overall topology. A P_s - μ_{H2O} 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 μ_{H2O}), whereas catapleiite has the lowest molar volume and is stable at high pressures.

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We next derived the two alternative topologies for the (n+3)-phase multisystem involving quartz, catapleiite, elpidite, vlasovite and parakeldyshite. The two alternative P_s - μ_{H20} nets for this system are shown in Figure 3. Catapleiite 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 (catapleiite, 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 b, that turns out to be the correct one, in such a way that univariant reactions involving catapleiite (gaidonnayite, hilairite) are refracted as they cross the univariant reactions in Figure 2, and univariant reactions not involving catapleiite (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.

It is evident that the assemblage vlasovite + catapleiite + quartz is stable only in the topology depicted in Figure 3a, whereas the assemblage clpidite + 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.

CaZrO₃-SiO₂-H₂O

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The two alternative topologies of the P_{a} - μ_{HZO} diagram for the Ca zirconosilicate system are presented in Figure 4. The two key assemblages for selecting the correct topology in this system are gittinsite + armstrongite and calcium catapleiite + calciohilairite + 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 (Figure 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 + water 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} - μ_{H2O} diagram Each of the alternative topologies in P-T space for the two systems are shown schematically in Figures 6 and 7. Experiments and further careful petrographic observations will ultimately 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 Na_2ZrO_3 -SiO₂-H₂O system (Figure 6) predict that viasovite 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(±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 Na₂O-ZrO₂-S₁O₂-H₂O system could potentially lead to limitations in the higher temperature stability of parakeldyshite + quartz and/or vlasovite(±quartz). In this regard it is interesting to recall that the few experimental data available (Gardinier, 1980; Lazutkina et al., 1980) suggest that, at 1 bar at least, vlasovite and parakeldyshite remain the stable phases until incongruent melting occurs at comparatively high temperatures (>1200°C). This is not surprising for parakeldyshite alone because the chemography of the system Na₂O-ZrO₂-SiO₂-H₂O does not permit 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; Figure 1a) involving phases omitted from this study limit 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 of elpidite and catapleiite to vlasovite and parakeldyshite, respectively, with increasing temperature, 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 Na₂O-SiO₂-ZrO₂-H₂O 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 is the higher-entropy, and therefore, the highertemperature one. Thus, in both Figures 6a and b, 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_1 - μ_{1120} 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 Na₂O-SiO₂-ZrO₂-H₂O 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 CaZrO₃-SiO₂-H₂O system, in both topologies (Figure 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 Ca-catapleiite at low T and P, to armstrongite at intermediate T and P, and to calciohilairite at high T and P. In Figure 7b, upon decreasing T or increasing P, gittinsite + quartz cannot break down to armstrongite via a stable reaction, but rather hydrates to form either Ca-catapleiite or calciohiliarite 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 calciohiliarite alone restricted to low temperatures or high pressures or both and the calciohiliarite + 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 catapleiite + calciohilairite (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 pressuretemperature 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

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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 $150^{\circ}-200^{\circ}$ 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° to 200°C.

Conclusions

We have derived the two alternative topologies of the P-T diagrams for portions of each of the systems $Na_2O-SiO_2-ZrO_2-H_2O$ and $CaO-SiO_2-ZrO_2-H_2O$ using the techniques of Burt (1978) The diagrams so generated are applicable to phase relationships among zirconosilicates in peralkaline felsic rocks. This work has resulted in the following conclusions:

1) Available petrographic descriptions of natural occurrences and experimental data are insufficient to discriminate between alternative topologies in the Na-zirconosilicate subsystem studied A tentative choice of topologies has been made for the Ca-zirconosilicate subsystem studied, based on the observed replacement of armstrongite by gittinsite + quartz at Strange Lake.

2) Vlasovite and parakeldyshite are high-temperature phases limited in upper thermal stability only by their incongruent melting at temperatures in excess of 1200°C. Because parakeldyshite is a chemographically external phase, its stability is unrestricted at low temperatures as well, whereas vlasovite breaks down at low temperature to assemblages involving various hydrous sodium zirconosilicates, depending on which P-T topology is the correct one. Parakeldyshite + quartz is apparently stable only at pressures in excess of 2kbars and temperatures greater than 650°C.

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3) Whether or not a field of stability exists for the assemblage parakeldyshite + elpidite in the P-T plane constitutes the critical observation required to choose between alternative topologies in the Na₂ZrO₃-SiO₂-H₂O system.

4) In the system $CaZrO_3$ -SiO₂-H₂O, both P-T topologies have the stability field of the assemblage gittinsite + quartz increasing to high temperatures and low pressures and the assemblage calciohilairite + quartz to high pressures and high temperatures.

Mineral	Formula	V (J/bar-mole)	Abbrev.	
NSZH system				
catapleiite	Na,ZrSi,O.2H20	14.385 ¹	Ci	
elpidite	NazZrSi O, s. 3H2O	23.118 ²	El	
gaidonnayite	Na, ZrSi, O., 2H, O	15.161 ³	Gdn	
hilairite	Na ₂ ZrSi ₃ O ₆ .3H ₂ O	15.3524	Ht	
lovozerite	Na ₂ Ca(Zr,Ti)Si ₆ (O,OH) ₁₁	23.570 ⁵	Lv	
parakeldyshite	$Na_2ZrSi_2O_7$	8.973 ⁶	Pk	
petarasite	Na ₅ Zr ₂ Si ₆ O ₁₂ (Cl,OH).2H ₂ O	28.67 6 ⁷	Ptr	
terskite	Na, ZrSi, O15 (OH), H2O	23.520 ⁴	Tk	
vlasovite	Na ₂ ZrSi ₄ O ₁₁	13.853	VI	
CSZH system				
armstrongite	CaZrSi ₆ O ₁₅ .3H ₂ O	22.017 ¹⁰	Arm	
baghdadite	Ca ₃ (Zr,Ti)Si ₂ O ₄	11.729 ¹¹	Bg	
calciohilairite	CaZrSi ₁ O ₉ .3H ₂ O	15.145 ¹²	Cht	
calcium catapleiite	$CaZrSi_{1}O_{9}.2H_{2}O$	14.385 ¹³	Cct	
gittinsite	$CaZrSi_2O_7$	8.198 ¹⁴	Gs	
(1) artz	SiO-	2.26715	Otz	
zircon	7rSiO	3.93116	7m	
baddeleyite	ZrO ₂	2.18717	Bd	

TABLE ONE: FORMULAE AND MOLAR VOLUMES OF SODIUM AND CALCIUM ZIRCONOSILICATES AND RELATED MINERALS

Cell dimensions used in calculation of molar volume data obtained from following sources: 1.Chao et al. (1973), 2.Canillo et al. (1973), 3.Chao and Watkinson (1974), Chao (1985), 4.Chao et al. (1974), 5.II'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.Hiemstra (1955).

$\begin{split} \text{Na}_2\text{O-SiO}_2\text{-ZrO}_2\text{-H}_2\text{O} \\ 1) & \text{El} = Pk + 4\text{Ql}z + 3\text{H}_2\text{O} & -5.077 & -0.591 \\ 2) & 4\text{Ct} = \text{El} + 3\text{Pk} + 5\text{H}_2\text{O} & -7.503 & -0.666 \\ 3) & \text{El} = \text{Ct} + 3\text{Ql}z + \text{H}_2\text{O} & -1.932 & -0.518 \\ 4) & \text{Ct} = \text{Pk} + \text{Qt}z + 2\text{H}_2\text{O} & -3.145 & -0.636 \\ 5) & \text{El} + 2\text{Ct} = 3\text{Vl} + 7\text{H}_2\text{O} & -4.731 & -0.634 \\ 7) & \text{Ct} + \text{Qt}z = \text{Vl} + 2\text{H}_2\text{O} & -4.731 & -0.634 \\ 7) & \text{Ct} + \text{Qt}z = \text{Vl} + 2\text{H}_2\text{O} & -2.799 & -0.715 \\ 8) & \text{Vl} = \text{Pk} + 2\text{Qt}z & -0.346 & 0 \\ 9) & \text{El} + \text{Pk} = 2\text{Vl} + 3\text{H}_2\text{O} & -4.385 & -0.684 \\ 10) & 2\text{Ct} = \text{Pk} + \text{Vl} + 4\text{H}_2\text{O} & -5.944 & -0.673 \\ * & \text{Ht} = \text{Ct} + \text{H}_2\text{O} & -0.967 & -1.034 \\ * & \text{Ht} = \text{Gdn} + \text{H}_2\text{O} & -0.967 & -1.034 \\ * & \text{Ht} = \text{Gdn} + \text{H}_2\text{O} & -0.776 & 0 \\ \hline & \text{CaO-SiO}_2\text{-ZrO}_2\text{-H}_2\text{O} \\ 11) & \text{Arm} = \text{Cct} + 3\text{Qtz} + \text{H}_2\text{O} & -10.93 & -0.457 \\ 14) & 4\text{Ctt} = \text{Arm} + 3\text{Gs} + 5\text{H}_2\text{O} & -13.97 & -0.644 \\ 15) & \text{Cct} = \text{Gs} + \text{Qtz} + 2\text{H}_2\text{O} & -3.9220 & -0.510 \\ 16) & \text{Cht} = \text{Gs} + \text{Qtz} + 3\text{H}_2\text{O} & -4.680 & -0.641 \\ 17) & \text{Arm} = \text{Gs} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 18) & \text{Cht} = \text{Ct} + 4\text{Qt} & -3.920 & -0.510 \\ 19) & \text{CaO-SiO}_2 + 3\text{H}_2\text{O} & -3.920 & -0.510 \\ 10) & \text{Cht} = \text{Gs} + \text{Qtz} + 3\text{H}_2\text{O} & -3.920 & -0.510 \\ 10) & \text{Cht} = \text{Gs} + \text{Qtz} + 3\text{H}_2\text{O} & -4.680 & -0.641 \\ 17) & \text{Arm} = \text{Gs} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 18) & \text{Cht} = \text{Ct} + 4\text{Qt} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 13) & \text{Cct} = \text{Ct} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 13) & \text{Cht} = \text{Ct} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 13) & \text{Cht} = \text{Ct} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 13) & \text{Cht} = \text{Ct} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 13) & \text{Cht} = \text{Ct} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 13) & \text{Cht} = \text{Ct} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 13) & \text{Cht} = \text{Ct} + 4\text{Qtz} + 3\text{H}_2\text{O} & -4.751 & -0.631 \\ 13) & \text{Cht} = \text{Ct} + 4\text{Qtz} + 3\text{H}_2\text{O} & -1.30 \\ 13) & \text{Cht} = $	REACTION	ΔV _s (J/bar-mole)	-dP, /dµ _{H20} (bar-mole/J)
1) El = Pk + 4Qtz + 3H_2O-5.077-0.5912) 4Ct = El + 3Pk + 5H_2O-7.503-0.6663) El = Ct + 3Qtz + H_2O-1.932-0.5184) Ct = Pk + Qtz + 2H_2O-3.145-0.6365) El + 2Ct = 3Vl + 7H_2O-10.33-0.6786) El = Vl + 2Qtz + 3H_2O-4.731-0.6347) Ct + Qtz = Vl + 2H_2O-2.799-0.7158) Vl = Pk + 2Qtz-0.34609) El + Pk = 2Vl + 3H_2O-4.385-0.68410) 2Ct = Pk + Vl + 4H_2O-5.944-0.673* Ht = Ct + H_2O-0.967-1.034* Ht = Gdn + H_2O-0.191-5.236* Gdn = Ct-0.7760CaO-SiO ₂ -ZrO ₂ -H ₂ O-10.93-0.45711) Arm = Cct + 3Qtz + H_2O-10.93-0.45714) 4Ctt = Arm + 3Gs + 5H_2O-13.97-0.64415) Cct = Gs + Qtz + 2H_2O-3.920-0.51016) Cht = Gs + Qtz + 3H_2O-4.751-0.63117) Arm = Cst + 4Qtz + 3H_2O-4.751-0.631	Na2O-SiO2-ZrO2-H2O		
2) $4Ct = El + 3Pk + 5H_2O$ 3) $El = Ct + 3Qtz + H_2O$ 4) $Ct = Pk + Qtz + 2H_2O$ 5) $El + 2Ct = 3Vl + 7H_2O$ 6) $El = Vl + 2Qtz + 3H_2O$ 7) $Ct + Qtz = Vl + 2H_2O$ 7) $Ct + Qtz = Vl + 3H_2O$ 7) $Ct + Qtz = Vl + 3Qtz + H_2O$ 7) $Ct = Ct + 3Qtz + 2H_2O$ 7) $Ct = Ct + 3H_2O$ 7) $Ct = Ct$	1) $EI = Pk + 4Qtz + 3H_2O$	-5.077	-0.591
3) El = Ct + $3Qtz + H_2O$ -1.932 -0.518 4) Ct = Pk + Qtz + $2H_2O$ -3.145 -0.636 5) El + 2Ct = $3Vl + 7H_2O$ -10.33 -0.678 6) El = Vl + $2Qtz + 3H_2O$ -4.731 -0.634 7) Ct + Qtz = Vl + $2H_2O$ -2.799 -0.715 8) Vl = Pk + $2Qtz$ -0.346 0 9) El + Pk = $2Vl + 3H_2O$ -4.385 -0.684 10) 2Ct = Pk + Vl + 4H_2O -5.944 -0.673 * Ht = Ct + H_2O -0.967 -1.034 * Ht = Gdn + H_2O -0.191 -5.236 * Gdn = Ct -0.776 0 CaO-SiO ₂ -ZrO ₂ -H ₂ O -0.831 -1.203 11) Arm = Cct + $3Qtz + H_2O$ -0.831 -1.203 12) Arm = Cht + $3Qtz$ -0.0711 0 13) 4Cct = Arm + 3Gs + 5H_2O -10.93 -0.457 14) 4Cht = Arm + 3Gs + 9H_2O -13.97 -0.644 15) Cct = Gs + Qtz + 2H_2O -3.920 -0.510 16) Cht = Gs + Qtz + 3H_2O -4.680 -0.641 17) Arm = Gs + 4Qtz + 3H_2O -4.751 -0.631 18) Cht = Cct + H_0O -0.760 -13.16	2) $4Ct = El + 3Pk + 5H_2O$	-7.503	-0.666
4) $Ct = Pk + Qtz + 2H_2O$ -3.145 -0.636 5) $El + 2Ct = 3Vl + 7H_2O$ -10.33 -0.678 6) $El = Vl + 2Qtz + 3H_2O$ -4.731 -0.634 7) $Ct + Qtz = Vl + 2H_2O$ -2.799 -0.715 8) $Vl = Pk + 2Qtz$ -0.346 0 9) $El + Pk = 2Vl + 3H_2O$ -4.385 -0.684 10) $2Ct = Pk + Vl + 4H_2O$ -5.944 -0.673 * $Ht = Ct + H_2O$ -0.967 -1.034 * $Ht = Gdn + H_2O$ -0.191 -5.236 * $Gdn = Ct$ -0.776 0 CaO-SiO ₂ -ZrO ₂ -H ₂ O 11) Arm = Cct + 3Qtz + H_2O -0.831 -1.203 12) Arm = Cht + 3Qtz -0.071 0 13) $4Cct = Arm + 3Gs + 5H_2O$ -10.93 -0.457 14) $4Cht = Arm + 3Gs + 9H_2O$ -13.97 -0.644 15) $Cct = Gs + Qtz + 2H_2O$ -3.920 -0.510 16) Cht = Gs + Qtz + 3H_2O -4.680 -0.641 17) Arm = Gs + 4Qtz + 3H_2O -4.751 -0.631 18) Cht = Cct + H_0 -0.760 -1.316	3) $EI = Ct + 3Qtz + H_2O$	-1.932	-0.518
5) $El + 2Ct = 3Vl + 7H_2O$ -10.33 -0.678 6) $El = Vl + 2Qtz + 3H_2O$ -4.731 -0.634 7) $Ct + Qtz = Vl + 2H_2O$ -2.799 -0.715 8) $Vl = Pk + 2Qtz$ -0.346 0 9) $El + Pk = 2Vl + 3H_2O$ -4.385 -0.684 10) $2Ct = Pk + Vl + 4H_2O$ -5.944 -0.673 * Ht = Ct + H_2O -0.967 -1.034 * Ht = Gdn + H_2O -0.967 -1.034 * Ht = Gdn + H_2O -0.776 0 CaO-SiO_2-ZrO_2-H_2O -0.071 0 11) Arm = Cct + 3Qtz + H_2O -0.831 -1.203 12) Arm = Cht + 3Qtz -0.071 0 13) 4Cct = Arm + 3Gs + 5H_2O -10.93 -0.457 14) 4Cht = Arm + 3Gs + 9H_2O -13.97 -0.644 15) Cct = Gs + Qtz + 2H_2O -3.920 -0.510 16) Cht = Gs + Qtz + 3H_2O -4.680 -0.641 17) Arm = Gs + 4Qtz + 3H_2O -4.751 -0.631 18) Cht = Cct + H_0 -0.760 -1.316	4) $Ct = Pk + Qtz + 2H_2O$	-3.145	-0.636
6) $EI = VI + 2Qtz + 3H_2O$ -4.731-0.6347) $Ct + Qtz = VI + 2H_2O$ -2.799-0.7158) $VI = Pk + 2Qtz$ -0.34609) $EI + Pk = 2VI + 3H_2O$ -4.385-0.68410) $2Ct = Pk + VI + 4H_2O$ -5.944-0.673* $Ht = Ct + H_2O$ -0.967-1.034* $Ht = Gdn + H_2O$ -0.191-5.236* $Gdn = Ct$ -0.7760CaO-SiO_2-ZrO_2-H_2O-0.831-1.20311) $Arm = Cct + 3Qtz + H_2O$ -0.831-1.20312) $Arm = Cht + 3Qtz$ -0.071013) $4Cct = Arm + 3Gs + 5H_2O$ -10.93-0.45714) $4Cht = Arm + 3Gs + 9H_2O$ -13.97-0.64415) $Cct = Gs + Qtz + 2H_2O$ -3.920-0.51016) $Cht = Gs + Qtz + 3H_2O$ -4.680-0.64117) $Arm = Gs + 4Qtz + 3H_2O$ -4.751-0.63118) $Cht = Cct + H_0O$ -0.760-1.316	5) $El + 2Ct = 3Vl + 7H_2O$	-10.33	-0.678
7) $Ct + Qtz = Vl + 2H_2O$ -2.799 -0.715 8) $Vl = Pk + 2Qtz$ -0.346 0 9) $El + Pk = 2Vl + 3H_2O$ -4.385 -0.684 10) $2Ct = Pk + Vl + 4H_2O$ -5.944 -0.673 * $Ht = Ct + H_2O$ -0.967 -1.034 * $Ht = Gdn + H_2O$ -0.191 -5.236 * $Gdn = Ct$ -0.776 0 CaO-SiO_2-ZrO_2-H_2O -0.071 0 11) $Arm = Cct + 3Qtz + H_2O$ -0.831 -1.203 12) $Arm = Cht + 3Qtz$ -0.071 0 13) $4Cct = Arm + 3Gs + 5H_2O$ -10.93 -0.457 14) $4Cht = Arm + 3Gs + 9H_2O$ -13.97 -0.644 15) $Cct = Gs + Qtz + 2H_2O$ -3.920 -0.510 16) Cht = Gs + Qtz + 3H_2O -4.680 -0.641 17) $Arm = Gs + 4Qtz + 3H_2O$ -4.751 -0.631 18) Cht = Cct + H_0 -0.760 -1.316	6) $EI = VI + 2Quz + 3H_2O$	-4.731	-0.634
8) $VI = Pk + 2Qtz$ -0.346 0 9) $EI + Pk = 2VI + 3H_2O$ -4.385 -0.684 10) $2Ct = Pk + VI + 4H_2O$ -5.944 -0.673 * Ht = Ct + H_2O -0.967 -1.034 * Ht = Gdn + H_2O -0.191 -5.236 * Gdn = Ct -0.776 0 CaO-SiO_2-ZrO_2-H_2O -0.071 0 11) Arm = Cct + 3Qtz + H_2O -0.831 -1.203 12) Arm = Cht + 3Qtz -0.071 0 13) 4Cct = Arm + 3Gs + 5H_2O -10.93 -0.457 14) 4Cht = Arm + 3Gs + 9H_2O -13.97 -0.644 15) Cct = Gs + Qtz + 2H_2O -3.920 -0.510 16) Cht = Gs + Qtz + 3H_2O -4.680 -0.641 17) Arm = Gs + 4Qtz + 3H_2O -4.751 -0.631 18) Cht = Cct + H_0 -0.760 -1.316	7) $Ct + Qtz = Vl + 2H_2O$	-2.799	-0.715
9) El + Pk = $2Vl + 3H_2O$ 10) $2Ct = Pk + Vl + 4H_2O$ * Ht = $Ct + H_2O$ 6.967 * Ht = $Ct + H_2O$ * Gdn = Ct 11) Arm = $Cct + 3Qtz + H_2O$ 12) Arm = $Ct + 3Qtz + H_2O$ 13) $4Cct = Arm + 3Gs + 5H_2O$ 14) $4Cht = Arm + 3Gs + 9H_2O$ 15) $Ct = Gs + Qtz + 2H_2O$ 16) $Cht = Gs + Qtz + 3H_2O$ 17) Arm = $Gs + 4Qtz + 3H_2O$ 18) $Cht = Ct + 4Qtz + 3H_2O$ 19) -4680 10) -0.631 10) -0.631 10) -0.631 11) Arm = $Ct + 3Qtz + 100$ 12) -0.644 13) -0.644 14) -0.644 15) $Cct = Gs + Qtz + 2H_2O$ 16) $Cht = Gs + Qtz + 3H_2O$ 17) $Arm = Gs + 4Qtz + 3H_2O$ 18) $Cht = Cct + H_2O$ 19) -0.640 10) -0.660 10) -0.631 10) -0.631 11) -0.631 12) -0.631 13) -0.631 13) -0.631 14) -0.631 15) -0.631 16) -0.631 16) -0.631 17) -0.631 18) -0.64 17) -0.631 18) -0.64 17) -0.631 18) -0.64 17) -0.64 18) -0.64 10) -0.760 10) -0.760 11) -0.631 11) -0.631 11) -0.631 12) -0.631 13) -0.631 13) -0.64 13) -0.631 13) -0.631 13) -0.631 13) -0.631 13) -0.631 13) -0.631 14) -0.760 15) -0.631 15) -0.631 16) -0.631 17) -0.631 18) -0.631 18) -0.631 18) -0.631 18) -0.631 19) -0.760 10)	8) VI = Pk + 2Qtz	-0.346	0
10) $2Ct = Pk + Vl + 4H_2O$ -5.944-0.673* $Ht = Ct + H_2O$ -0.967-1.034* $Ht = Gdn + H_2O$ -0.191-5.236* $Gdn = Ct$ -0.7760CaO-SiO_2-ZrO_2-H_2O-0.831-1.20311) $Arm = Cct + 3Qtz + H_2O$ -0.831-1.20312) $Arm = Cht + 3Qtz$ -0.071013) $4Cct = Arm + 3Gs + 5H_2O$ -10.93-0.45714) $4Cht = Arm + 3Gs + 9H_2O$ -13.97-0.64415) $Cct = Gs + Qtz + 2H_2O$ -3.920-0.51016) $Cht = Gs + Qtz + 3H_2O$ -4.680-0.64117) $Arm = Gs + 4Qtz + 3H_2O$ -4.751-0.63118) $Cht = Cct + H_2O$ -0.760-1.316	9) El + Pk = $2Vl + 3H_2O$	-4.385	-0.684
* $Ht = Ct + H_2O$ * $Ht = Gdn + H_2O$ * $Gdn = Ct$ CaO-SiO ₂ -ZrO ₂ -H ₂ O 11) $Arm = Cct + 3Qtz + H_2O$ 20) -0.831 11) $Arm = Cct + 3Qtz + H_2O$ 20) -0.831 20) -1.203 20) -0.457 20) -1.397 20) -0.644 20) -0.641 20) -0.641 20) -0.641 20) -0.641 20) -0.641 20) -0.631 20) -0.760 20) -1.316	10) $2Ct = Pk + Vl + 4H_2O$	-5.944	-0.673
* $Ht = Gdn + H_20$ * $Gdn = Ct$ CaO-SiO ₂ -ZrO ₂ -H ₂ O 11) $Arm = Cct + 3Qtz + H_20$ 20) -0.831 11) $Arm = Cct + 3Qtz + H_20$ 20) -0.831 20) $Arm = Cht + 3Qtz$ 20) -0.071 20) -0.044 20) -0.044 20) -0.044 20) -0.0510 20) -0.0641 20) -0.0641 20) -0.0611 20) -0.06	* $Ht = Ct + H_2O$	-0.967	-1.034
* $Gdn = Ct$ $CaO-SiO_2-ZrO_2-H_2O$ 11) $Arm = Cct + 3Qtz + H_2O$ 22 Arm = Cht + 3Qtz $4Cct = Arm + 3Gs + 5H_2O$ $4Cct = Arm + 3Gs + 5H_2O$ $13) 4Cct = Arm + 3Gs + 9H_2O$ $14) 4Cht = Arm + 3Gs + 9H_2O$ $15) Cct = Gs + Qtz + 2H_2O$ $16) Cht = Gs + Qtz + 3H_2O$ $16) Cht = Gs + Qtz + 3H_2O$ $16) Cht = Gs + 4Qtz + 3H_2O$ $17) Arm = Gs + 4Qtz + 3H_2O$ 10,776 10,93 -0.644 10,93 -0.644 -0.641 10,93 -0.641 -0.631 10,93 -0.631 -0.631 -0.760 -1,316	* $Ht = Gdn + H_2O$	-0.191	-5.236
CaO-SiO_2-ZrO_2-H_2O11) Arm = Cct + $3Qtz + H_2O$ -0.831-1.20312) Arm = Cht + $3Qtz$ -0.071013) 4Cct = Arm + $3Gs + 5H_2O$ -10.93-0.45714) 4Cht = Arm + $3Gs + 9H_2O$ -13.97-0.64415) Cct = Gs + Qtz + $2H_2O$ -3.920-0.51016) Cht = Gs + Qtz + $3H_2O$ -4.680-0.64117) Arm = Gs + $4Qtz + 3H_2O$ -4.751-0.63118) Cht = Cct + H_0-0.760-1.316	* $Gdn = Ct$	-0.776	0
11) $Arm = Cct + 3Qtz + H_2O$ -0.831-1.20312) $Arm = Cht + 3Qtz$ -0.071013) $4Cct = Arm + 3Gs + 5H_2O$ -10.93-0.45714) $4Cht = Arm + 3Gs + 9H_2O$ -13.97-0.64415) $Cct = Gs + Qtz + 2H_2O$ -3.920-0.51016) $Cht = Gs + Qtz + 3H_2O$ -4.680-0.64117) $Arm = Gs + 4Qtz + 3H_2O$ -4.751-0.63118) $Cht = Cct + H_2O$ -0.760-1.316	CaO-SiO ₂ -ZrO ₂ -H ₂ O		
12) $Am = Cht + 3Qtz$ -0.071013) $4Cct = Arm + 3Gs + 5H_2O$ -10.93-0.45714) $4Cht = Arm + 3Gs + 9H_2O$ -13.97-0.64415) $Cct = Gs + Qtz + 2H_2O$ -3.920-0.51016) $Cht = Gs + Qtz + 3H_2O$ -4.680-0.64117) $Arm = Gs + 4Qtz + 3H_2O$ -4.751-0.63118) $Cht = Cct + H_2O$ -0.760-1.316	11) Arm = Cct + $3Qtz + H_2O$	-0.831	-1.203
13) $4Cct = Arm + 3Gs + 5H_2O$ -10.93-0.45714) $4Cht = Arm + 3Gs + 9H_2O$ -13.97-0.64415) $Cct = Gs + Qtz + 2H_2O$ -3.920-0.51016) $Cht = Gs + Qtz + 3H_2O$ -4.680-0.64117) $Arm = Gs + 4Qtz + 3H_2O$ -4.751-0.63118) $Cht = Cct + H_2O$ -0.760-1.316	12) $Am = Cht + 3Qtz$	-0.071	0
14) $4Cht = Arm + 3Gs + 9H_2O$ -13.97-0.64415) $Cct = Gs + Qtz + 2H_2O$ -3.920-0.51016) $Cht = Gs + Qtz + 3H_2O$ -4.680-0.64117) $Arm = Gs + 4Qtz + 3H_2O$ -4.751-0.63118) $Cht = Cct + H_2O$ -0.760-1.316	13) $4Cct = Arm + 3Gs + 5H_2O$	-10.93	-0.457
15) $Cct = Gs + Qtz + 2H_2O$ -3.920-0.51016) $Cht = Gs + Qtz + 3H_2O$ -4.680-0.64117) $Arm = Gs + 4Qtz + 3H_2O$ -4.751-0.63118) $Cht = Cct + H_2O$ -0.760-1.316	14) 4Cht = Arm + 3Gs + $9H_2O$	-13.97	-0.644
16) Cht = Gs + Qtz + $3H_2O$ -4.680-0.64117) Arm = Gs + $4Qtz + 3H_2O$ -4.751-0.63118) Cht = Cct + H_2O-0.760-1.316	15) Cct = Gs + Qtz + $2H_2O$	-3.920	-0.510
17) $Arm = Gs + 4Qtz + 3H_2O$ -4.751-0.63118) $Cht = Cct + H_2O$ -0.760-1.316	16) Cht = Gs + Qtz + $3H_2O$	-4.680	-0.641
18) Cht = Cct + H ₀ -0.760 -1.316	17) $Arm = Gs + 4Qtz + 3H_2O$	-4.751	-0.631
	$18) \text{Cht} = \text{Cct} + \text{H}_2\text{O}$	-0.760	-1.316

TABLE TWO: REACTIONS IN THE Na AND Ca ZIRCONOSILICATE SYSTEMS WITH ΔV_{r} and Calculated slopes in P_{μ} - μ_{H20} space

* See Figure 2.

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FIGURE 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 water.



FIGURE 2: Topology of the P_s - μ_{H2O} phase diagram for the phases catapleiite, 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 - μ_{H2O} diagrams have been exaggerated for clarity of presentation.

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FIGURE 3: The two alternative topologies of the P_s - μ_{H2O} phase diagram for the pseudoternary system Na₂ZrO₃-SiO₂-H₂O. In diagram A, the elpidite- and parakeldyshite-absent invariant points are stable, whereas the catapleiite-, vlasovite- and quartz-absent invariant points are metastable. In diagram B, the catapleiite-, 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.



FIGURE 4: The two alternative topologies of the P_s - μ_{H2O} phase diagram for the pseudoternary system CaO-ZrO₂-SiO₂. In diagram A, the calcium catapleiite-, calciohilairite- and quartz-absent invariant points are stable, whereas the gittinsite- and armstrongite-absent invariant points are metastable. In diagram B, the gittinsite- and armstrongite-absent invariant points are stable, whereas the calcium catapleiite-, calciohilairite- and quartz-absent invariant points are metastable. See caption to Figure 2 for the significance of symbols employed.

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FIGURE 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



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FIGURE 6: Schematic P-T diagrams for the pseudoternary system Na_2O - ZrO_2 -SiO₂ based on the topologies illustrated in Figure 3. Note: only stable invariant points are presented for clarity.



FIGURE 7: Schematic P-T diagrams for the pseudoternary system $CaO-ZrO_2-SiO_2$ based on the topologies illustrated in Figure 4. Note: only stable invariant points are presented for clarity.

Chapter 3

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Synthesis Experiments in the CaO-ZrO₂-SiO₂ System

Experimental Approach

The initial thrust of the experimental component of this thesis was the generation of a univariant curve for the replacement of armstrongite by gittinsite + quartz in pressure-temperature space. It was hoped that establishing the lower stability limit of gittinsite would represent an important first step toward constraining the physicochemical conditions of a hypothetical Cametasomatic reaction involving the replacement of elpidite by gittinsite + quartz which has been proposed by Salvi and Williams-Jones (1991) as the mechanism for Zr, Be, Nb, Y and REE mineralization at Strange Lake.

Achieving this goal was predicated upon successful hydrothermal synthesis of gittinsite and armstrongite. The technique used to attempt these syntheses was modified from a method outlined by Currie and Zaleski (1985), with which they successfully synthesized the Nazirconosilicates, elpidite and vlasovite. Starting materials were dried gels prepared from reagentgrade zirconyl chloride octahydrate, silica gel and calcium hydroxide. An appropriate weight of zirconyl chloride was dissolved in 0.1M HCl. Silica gel was added while the solution was stirred. Stock solution NH₄OH was added to gel the material, which was then dried at 90°C for 12 hours and fired at 900°C to quantitatively drive off the chlorine as NH₄Cl. Ca(OH)₂ was added to the dried gel and the material was agitated for 30 minutes.

Approximately 0.2g of the starting material was placed in gold capsules along with 100-120µL of fluid. The fluid phase for most experiments was distilled water, although a few runs were performed using a $Ca(OH)_2$ solution which was saturated at 25°C The capsules were immediately sealed by welding. During this procedure, the capsules were wrapped in wet paper towel in order to keep them cool and prevent loss of volatiles. The sealed capsules were tested for leakage by weighing, heating at 150°C for 15 minutes and reweighing. One or two capsules were then placed in each cold-seal vessel along with a length of ceramic filler rod and pressurized to approximately 1kbar. The system was left overnight to check for leaks and then taken to the desired P-T conditions in less than an hour.

Temperature measurement was facilitated using chromel-alumel thermocouples which were calibrated against the melting points of H_2O , Sb, Bi and NaCl. The thermocouples were placed in wells external to the central bore of the vessel. Temperature measurements are accurate to about $\pm 5^{\circ}C$, allowing for small thermal gradients along the length of the capsules as well as between the thermocouple and the capsule.

Pressure was continually monitored with Astra Bourdon-tube gauges periodically calibrated against a large dial Heise gauge, which was in turn periodically calibrated at the factory. Argon was employed as the pressure medium. Pressure measurements are considered accurate to ± 50 bars.

After an equilibration period of 1 or 2 weeks, the vessels were quenched in cold water while under pressure. Quenching to 20°C required less than three minutes. The capsules were then removed from the the vessels and cut open. The solid material is removed. Only material from capsules with excess water was retained.

Oxygen fugacity was not explicitly controlled as the reactions investigated involved recrystallization of calcium, zirconium and silicon solids with no change in valency. Hence, the reactions were independent of oxygen fugacity. However, the redox conditions of the experiments were probably held to within a log unit or two of the Ni/NiO buffer due to the buffering effect of the pressure vessel, which is made of a nickel-bearing alloy (Chou, 1987).

Analysis of run products was done using X-ray diffraction. The X-ray diffractometer in the Department of Geological Sciences at McGill utilizes $CuK\alpha$ radiation with an operating voltage of 40kV and a current of 20mA. Some analyses were also performed using a scanning electron microscope at an operating voltage of 15kV.

Experimental Results

The first set of synthesis experiments involved starting materials with cation ratios equivalent to gittinsite (i.e. Ca:Zr:2Si). Runs of one week duration were performed at temperatures of 650°C, 500°C, 350°C and 250°C at a pressure of 1kbar. A run at 350°C was also performed at 0.5kbar. The runs at 250°C yielded products which had not crystallized sufficiently to facilitate identification using X-ray diffraction analysis and will not be discussed further.

The runs performed at 650°C and 500°C yielded two phases, zircon and the compound $Ca_2ZrSi_4O_{12}$, which has been synthesized previously (Kordyuk and Gul'ko, 1962; Morgan et al., 1987), but only at significantly higher temperatures. Photographs of this material using a scanning electron microscope reveal zircon needles up to 1mm in length in the higher temperature runs Zircon growth was not as pronounced at 500°C, with needles rarely exceeding a few tens of microns (Figure 8). The Ca-zirconosilicate phase occurs as tabular crystals usually about 1 to 20µm in length with no significant difference in size as a function of temperature. SEM analysis of these tabular crystals indicates considerable variability in zirconium content with one crystal showing no significant zirconium at all. Furthermore, close inspection of the XRD patterns of these run products reveal several small peaks which cannot be attributed to either of the identified phases. This evidence suggests that the tabular crystals represent $Ca_2ZrSi_4O_{12}$ with a minor amount of an unidentified calcium silicate phase also present, possibly as a coating or filling in cracks and as rare crystals. It should also be noted that these experiments were repeated with a small amount of altered gittinsite from Strange Lake included in the capsules to serve as a seed. This measure had no effect on the run products produced.

The experiments performed at 350°C yielded similar results at 1 and 0.5kbar. Strong peaks of baddeleyite appeared in the XRD analysis, although several peaks which could not be attributed to baddeleyite were also present. Despite extensive examination of these XRD patterns, the other

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phase or phases could not be identified.

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In an attempt to overcome kinetic barriers to gittinsite formation, a second set of experiments using starting materials with cation ratios equivalent to gittinsite was also performed. These experiments were run for two weeks at 1.2kbars and temperatures of 500°C and 600°C. The lower temperature run yielded a complex XRD pattern with clear peaks for wollastonite and baddeleyitr as well as other peaks which could not be identified, although several complex calcium silicates matched the pattern closely including truscottite ($Ca_{14}Si_{24}O_{58}(OH)_2$), dellaite ($Ca_6(SiO_4)(Si_2O_7)(OH)_2$) and xonotlite ($Ca_6Si_6O_{17}(OH)_2$). At 600°C, The pattern was even more complex. Wollastonite was indicated once again, but neither it nor any other phase could be identified with certainty. Both analyses are presented in Table 3.

Another set of experiments was performed in which the cation ratio was equivalent to armstrongite (i.e. Ca:Zr:4Si). Synthesis experiments of one week at 1.5kbar of pressure and temperatures of 400°C and 550°C were run. XRD analysis of lower temperature run products revealed strong peaks of synthetic quartz. The remaining material apparently did not crystallize sufficiently to allow identification since only a few small peaks were present which were not due to quartz. The higher temperature experiments yielded the same run products as the high temperature gittinsite runs, namely zircon + $Ca_2ZrSi_4O_{12}$.

In an attempt to determine the effects of excess calcium on the synthesis of zirconosilicates, a series of experiments was performed at 1kbar using starting materials with cation molar ratios of 2Ca:Zr:2Si. These experiments were carried out at 400°C, 500°C and 700°C and indicated a preference for crystallization of calcium silicates and baddeleyite over zirconosilicates. XRD analysis of run products from experiments at 400°C revealed the presence of synthetic xonotlite, baddeleyite and possibly wollastonite. The presence of wollastonite could not be verified with absolute certainty due to the weakness of the peaks relative to background.

The products of the experiments at 500°C and 700°C both consisted of synthetic wollastonite and baddeleyite.

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Finally, synthesis of gittinsite was attempted by way of cation exchange. The replacement of elpidite by gittinsite + quartz proposed by Salvi and Williams-Jones (1990) at Strange Lake was recreated by placing synthetic elpidite + quartz in a capsule with Ca(OH)₂. Experiments were performed at 500°C and 1kbar with a molar ratio of two elpidite to one Ca. The run times of these experiments was one week. XRD analysis of the run products only revealed peaks of elpidite and quartz, indicating that the calcium did not crystallize a new phase or that cation exchange did not progress far enough to alter the elpidite.

Discussion

It is clear that calcium zirconosilicate mineral synthesis is impeded by kinetic barriers. Synthesis of the Na-zirconosilicates, elpidite and vlasovite using the technique of Currie and Zaleski (1985) proved to be routine, indicating that this difficulty is limited to the calcium zirconosilicate system. Caruba (1975) also encountered problems in his attempts to synthesize Cazirconosilicates. His experiments involved inclusion of ZrO₂ gel, SiO₂ gel and fluorite in a vessel at 375bars and 450°C for two days. These experiments yielded zircon and fluorite No Cazirconosilicates were detected. Unfortunately, the relatively short duration of Caruba's synthesis runs makes assessment of the kinetic effects difficult.

The kinetics of subsolidus mineral synthesis is dominated by the 'Ostwald Step Rule' (Fyfe, 1960). By this rule, a reaction involving a large decrease in Gibb's free energy will often result in a metastable product if the ΔG between the metastable product and the stable product is small. This is often the case in mineral synthesis experiments since highly-reactive starting materials such as dried gels or glasses are used to accelerate reaction. This impediment can

sometimes be overcome by a multi-stage process involving one or more intermediate metastable phases and this may be necessary if any naturally-occurring Ca-zirconosilicates are to be synthesized. Alternatively, materials could be run in the vessels, removed from the capsules, ground together and returned to the vessels for another run. This procedure could be repeated several times. Finally, it may be necessary to perform synthesis experiments with apparatus that are capable of attaining higher temperatures and pressures than are possible using cold-seal vessels, such as the piston cylinder or internally-heated vessels.

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TABLE THREE: XRD ANALYSES OF RUN PRODUCTS OF GITTINSITE SYNTHESIS EXPERIMENTS AT PRESSURE OF 1.2kbar AND TEMPERATURES AT 500°C AND 600°C

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2.825182.6392.649492.5822.475*162.3392.286*162.2072.217272.1172.151202.015	29
2.649492.5822.475*162.3392.286*162.2072.217272.1172.151202.015	47
2.475*162.3392.286*162.2072.217272.1172.151202.015	28
2.286*162.2072.217272.1172.151202.015	27
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1.932 20 1.665	31
1.920 10 1.649	26
1.887 22 1.643	23
1.854 18 1.346	21
1.738 15 1.294	18
1.732 12	
1.688 10	
1.679 11	
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1.375 9	
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Asterisk corresponds to peaks of wollastonite IT M RG (PDF 27-0088)



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FIGURE 8. SEM photograph of run products from Ca-zirconosilicate synthesis experiment at 1kbar and 500°C Prismatic crystals are zircon, while the tabular crystals consist of the synthetic phase $Ca_2ZrSi_4O_{12}$ possibly mixed with an unidentified calcium sili ate.

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