The Canadian Mineralogist
Vol. 36, pp. 1001-1008 (1998)

CHEMICAL CONTROLS ON THE SOLUBILITY OF Zr-BEARING PHASES IN SIMPLIFIED PERALKALINE MELTS AND APPLICATION TO THE STRANGE LAKE INTRUSION, QUEBEC – LABRADOR

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ABSTRACT

The solubility of Zr-bearing minerals was measured in H_2O-saturated, peralkaline haplobasaltic, haplosyenitic and haplogranitic melts ± Cl ± F at 800°C and 1 kbar. In halogen-free and F-bearing melts, the solubility of Zr-bearing phases reached a maximum of 4 and 3.5 wt.% ZrO_2, respectively, in melts with 57 to 60 wt.% silica. No such maximum was observed for Cl-bearing compositions, which became saturated in a Zr-bearing phase at ZrO_2^{melt} concentrations of 2 to 2.2 wt.%. A silica concentration of 57 to 60 wt.% represents a threshold above which zircon is the saturating Zr-bearing phase for all compositions. For compositions with SiO_2 content below this range, wadeite ($K_2ZrSi_3O_9$) crystallizes in the halogen-free experiments, whereas ZrO_2 is the saturating phase in the F- and Cl-bearing experiments. The positive slope of the wadeite saturation curve on $X(ZrO_2) - X(SiO_2)$ plots suggests that increasing activity of silica increases the solubility of wadeite. Since this behavior of wadeite is not expected based on a simple dissolution mechanism, a more complex equilibrium involving different structural units is proposed. Observations that zircon is scarce, whereas elpidite ($Na_2ZrSi_6O_{15}$•$3H_2O$) and other alkali and alkaline-earth zirconosilicates are abundant in the Strange Lake peralkaline intrusive complex in northern Quebec – Labrador, indicate that the parent magma did not saturate with a Zr-bearing mineral until it cooled to a low temperature, probably less than 600°C.

Keywords: zircon, wadeite, solubility, peralkaline magmas, Strange Lake granite, Quebec – Labrador.

SOMMAIRE

La solubilité des minéraux porteurs de Zr a été établie par expériences impliquant des magmas hyperalcalins saturés en H_2O de composition haplobasaltique, haplosyénitique et haplogranitique ± Cl ± F à 800°C et 1 kbar. Dans un liquide dépourvu de halogènes ou contenant du fluor, la solubilité des phases contenant du Zr a donné jusqu'à 4 et 3.5% de ZrO_2, en poids, dans un liquide contenant 57 et 60% de SiO_2, respectivement. Un tel maximum n'est pas atteint dans les compositions de liquide contenant du chlor, qui deviennent saturées avec une phase contenant du Zr à une teneur de ZrO_2 dans le liquide silicaté entre 2 et 2.2% (poids). Une teneur en silice entre 57 et 60% représente un seuil au delà duquel c'est le zircon qui devient le zirconosilicate saturant pour toutes compositions. Pour des teneurs en SiO_2 inférieures à ce seuil, la wadéite ($K_2ZrSi_3O_9$) cristallise dans les compositions sans halogènes, tandis que le ZrO_2 est la phase saturante dans les liquides porteurs de F et de Cl. La pente positive de la courbe de saturation de la wadéite, en termes des variables $X(ZrO_2) - X(SiO_2)$, fait penser qu'une augmentation de l'activité de la silice augmente la solubilité de la wadéite. On ne s'attendait pas à ce comportement de la wadéite suite à une dissolution simple; il s'agit donc d'un équilibre plus complexe impliquant des modules structuraux différents. Dans le complexe intrusif hyperalcalin de Strange Lake (Québec – Labrador), le zircon est rare, tandis que l'elpidite ($Na_2ZrSi_6O_{15}$•$3H_2O$) et autres zirconosilicates alcalins et alcalino-terreux sont abondants. Le magma responsable n'aurait donc pas atteint la saturation avec une phase zirconosilicatée avant son refroidissement, probablement en dessous de 600°C.

(Traduit par la Rédaction)

Mots-clés: zircon, wadéite, solubilité, magmas hyperalcalins, granite de Strange Lake, Québec – Labrador.

INTRODUCTION

Peralkaline felsic rocks have been a focus of study because of the exotic minerals they commonly contain and because of their potential as ore deposits of rare metals such Zr, Y, Nb and the rare-earth elements (*REE*). The unusual mineralogy of these rocks has long held promise of providing a means for constraining the pressure, temperature and chemical environment of crystallization. The wide array of alkali and alkaline-earth zirconosilicates reported in peralkaline intrusions (*e.g.*, Chao *et al.* 1967, Semenov 1972, Harris 1983, Currie 1985, Birkett *et al.* 1992, Marr & Wood 1992, Salvi & Williams-Jones 1995) is particularly promising in this respect.

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Currie & Zaleski (1985) published the first reversed phase-equilibrium results involving alkali zirconosilicates and constrained the reaction:

$Na_2ZrSi_6O_{15}{\bullet}3H_2O$ (elpidite) $\Leftrightarrow$ $Na_2ZrSi_4O_{11}$
(vlasovite) + $2SiO_2$ + $3H_2O$

at 0.5, 1.0, 1.5 and 2.0 kbars. These experiments were limited to the system $Na_2O–SiO_2–ZrO_2–H_2O \pm Cl$. Marr & Wood (1992) later produced $P–\mu(H_2O)$ petrogenetic grids (as an analogue for P–T reactions involving hydrated phases) for the systems $SiO_2–Na_2ZrO_3–H_2O$ and $SiO_2–CaZrO_3–H_2O$. To our knowledge, however, no attempt has been made to utilize phase equilibria of alkali zirconosilicates to constrain petrogenetic conditions in systems more closely approximating those of natural peralkaline magmas.

The solubility of Zr-bearing minerals in peralkaline melts is much greater than in peraluminous or metaluminous melts. Watson (1979) conducted the earliest systematic study of zircon solubility in such melts. For peralkaline felsic melts, he suggested a solution mechanism involving the formation of alkali zirconosilicate complexes of the form: $A_4ZrSi_nO_{2n+4}$, in which A represents an alkali metal. The existence of such complexes was supported by Raman spectroscopic analyses (Ellison & Hess 1994), which indicate the presence of SiO_4 tetrahedra with one non-bridging oxygen atom shared by one Zr and two K ions in anhydrous, Zr-bearing, K-aluminosilicate glasses. The purpose of our study is to extend the work of Watson (1979) by including SiO_2-undersaturated peralkaline compositions, such as are found in well-known localities as Mont Saint-Hilaire, and Lovozero, Kola Peninsula, Russia. The effects of Cl and F on the solubility of Zr also were investigated, and the results applied to the petrogenesis of the Strange Lake granitic intrusion, Quebec–Labrador.

EXPERIMENTAL AND ANALYTICAL PROCEDURES

We chose as starting materials glasses with compositions ranging from 50 to 70 wt.% SiO_2, and with (Na + K)/Al and Na/K values of about 1.4. These compositions span the range commonly found in peralkaline intrusions. In addition, results on the more SiO_2-rich samples can be compared with the results of Watson (1979), who performed similar experiments on compositions ranging from 68 to 79 wt.% SiO_2. Glasses were prepared using reagent-grade SiO_2, Al_2O_3, Na_2CO_3, K_2CO_3, NaCl, NaF and ZrO_2. The carbonates and oxides were ground together and decarbonated at 750°C for 24 hours, then reground and fused in air at 1450°C for only one hour to avoid volatilization of Na. The resulting glasses were then ground a third time, with NaF or NaCl added as appropriate.

For each experiment, 0.01 g of sample was sealed in a 0.2 × 1.2 cm gold capsule with 2 μL of distilled water. The experiments were held for 2 weeks at 800°C and 1 kbar in cold-seal pressure vessels, utilizing Ar as a pressure medium. The pressure vessels were air-quenched, achieving subsolidus temperatures in approximately 20 s. After the experiments, the capsules were reweighed to ensure that there was no loss of volatiles. Only those samples that had excess water upon opening were retained.

The samples were analyzed using a JEOL 8900 electron microprobe (Table 1). Crystalline phases were analyzed with a beam current of 20 nA and a beam width of 5 μm to minimize damage to standards and samples. The instrument was calibrated using zircon (Zr), albite (Na,Si,Al), orthoclase (K), fluorite (F), and scapolite (Cl) standards. The beam width was increased to 20 μm for glasses. Glass standards with Na/Si values similar to the samples were used to calibrate the instrument for alkalis, Al and Si where analyses of glass were performed. This was done to account for the effects of Na loss during analysis.

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF GLASSES DERIVED FROM MELTS SATURATED WITH A Zr-BEARING PHASE

RMG	1	1r	2	2r	3	4	5	6a	6c	6	7
SiO_2	49.42	49.99	51.41	51.39	52.86	53.97	55.25	56.86	56.86	56.60	69.20
Al_2O_3	20.82	20.80	19.89	20.14	19.05	18.47	17.83	17.00	17.02	17.12	11.10
Na_2O	10.50	10.46	9.99	9.89	9.65	9.32	9.06	8.51	8.56	8.71	5.38
K_2O	10.61	10.09	10.15	9.45	9.76	9.54	9.20	8.68	8.66	8.94	5.67
ZrO_2	2.74	2.43	2.97	2.44	3.30	3.39	3.44	3.59	3.41	3.31	2.60
σZrO_2	±0.07	±0.07	±0.05	±0.04	±0.08	±0.07	±0.17	±0.07	±0.23	±0.23	±0.08
F	1.15	1.11	1.11	0.93	1.29	1.03	1.03	1.04	1.03	1.06	0.68
=O	-0.48	-0.47	-0.47	-0.39	-0.54	-0.43	-0.43	-0.44	-0.43	-0.45	-0.29
Total	94.76	94.41	95.05	93.85	95.37	95.29	95.38	95.24	95.11	95.29	94.34
A.I.	1.38	1.35	1.38	1.32	1.39	1.39	1.39	1.38	1.38	1.40	1.35
RMH	1	2	3	4	5		RMJ	1	2	3	4
SiO_2	51.58	52.24	54.81	56.73	64.17			52.73	56.20	57.50	65.70
Al_2O_3	19.94	19.60	18.04	16.56	12.87			20.13	19.07	18.28	13.94
Na_2O	9.99	9.99	8.85	9.00	7.45			9.84	8.58	8.20	6.47
K_2O	10.23	9.61	9.43	8.35	6.41			9.69	9.09	8.77	6.38
ZrO_2	1.89	2.92	3.35	3.97	3.82			2.22	1.94	2.09	2.34
σZrO_2	±0.13	±0.09	±0.04	±0.08	±0.18			±0.12	±0.09	±0.11	±0.12
Cl								0.20	0.16	0.16	0.13
=O								-0.05	-0.04	-0.04	-0.03
Total	93.63	94.36	94.48	94.61	94.72			94.76	95.00	94.96	94.93
A.I.	1.38	1.37	1.37	1.44	1.49			1.33	1.26	1.26	1.26

Compositions are reported in weight %. A.I. represents (K + Na) /Al, the agpaitic index. Errors reported are for one standard deviation. Experiments denoted by "r" are reversed (see text). Samples RMG6a and RMG6c are run products of the variable-duration experiments shown in Figure 2. These experiments were performed for one and three weeks, respectively. Totals do not include loss of dissolved H_2O during analysis.

RESULTS OF SOLUBILITY EXPERIMENTS

Synthetic wadeite ($K_2ZrSi_3O_9$) saturated the melt in experiments employing low-silica glasses with no added halogens. Wadeite appeared as large (up to 50 μm in diameter), equant crystals, each with a well-defined boundary; it was accompanied by leucite and nepheline

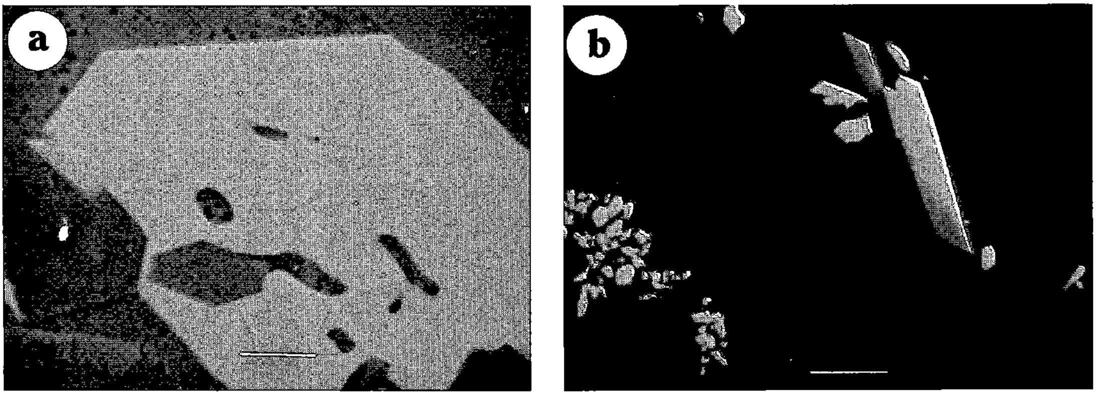

FIG. 1. Secondary electron images of a) wadeite crystal with nepheline from sample RMG1r at 650°C and 1 kbar after one week, and b) ZrO_2 crystal from the same sample at 800°C and 1 kbar after two weeks. Scale bars: 10 μm in both cases.

in some experiments. Small clusters of unreacted ZrO_2 were occasionally detected in the cores of wadeite crystals. Leucite was found to exhibit little solid-solution, with Na representing about 5 mol.% of total alkalis. Nepheline displays a very nearly ideal $(Na_3K)Al_4Si_4O_{16}$ composition. The addition of F or Cl destabilized wadeite at 800°C, and ZrO_2 crystallized instead, appearing as clusters of small, rounded grains. Since the source of Zr among the reactants was ZrO_2, the presence of this phase in the run products did not inspire confidence that equilibrium was achieved. Therefore, a series of experiments were performed using F-bearing glasses at 650°C and 1 kbar for one week. These experiments yielded synthetic wadeite, as observed in the halogen-free experiments (Fig. 1a). This material was then ground and used in experiments at 800°C for 2 weeks, and the results compared to the initial results at those conditions. Zirconia re-appeared as the saturating phase in the reversed experiments as elongate, euhedral crystals 10 to 15 μm in length (Fig. 1b). The Zr concentrations in melts formed in the reversed experiments (Table 1) were similar to those in the other experiments, but always slightly lower. The equilibrium concentration of Zr is presumed to be between measurements of the forward and reversed experiments. Disequilibrium concentrations of Zr in the melts are deemed to be much less likely for those experiments in which the starting Zr-bearing phase and the saturating phase were different. Reagent ZrO_2 would first have to dissolve into the melt and then crystallize the new phase. To further establish that the Zr content in the melts reached equilibrium, or at least a steady state after two weeks, one sample (RMG6) was selected for a series of variable-duration experiments at 800°C and 1 kbar. The results, presented in Figure 2, indicate that there is no change in ZrO_2 content in the melt from two to three weeks. Since Watson (1979) also found that two weeks was a sufficient duration for experiments on zircon solubility, we accept that these results represent good evidence that a steady state was achieved.

Zircon was the saturating phase in all experiments with SiO_2 contents above or approximately equal to 55 wt.%. Occasionally, small amounts of unreacted ZrO_2 were observed as clusters of rounded grains similar to those described above, each grain measuring about 1 or 2 μm in diameter. They do not comprise euhedral crystals like those observed in the reversed, F-bearing experiments.

Chemical analyses of run products (Table 1, Fig. 3) indicate a maximum solubility of ~4 wt.% ZrO_2 at 55 to 60 wt.% SiO_2 for the halogen-free and ~3.5 wt.% ZrO_2

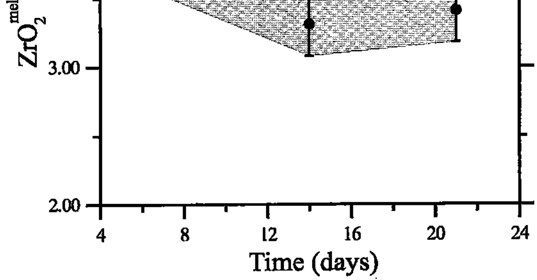

FIG. 2. Concentration of ZrO_2 in the melt as a function of run duration for sample RMG6, a F-bearing sample with approximately 56.7 wt.% SiO_2. Error bars represent one standard deviation.

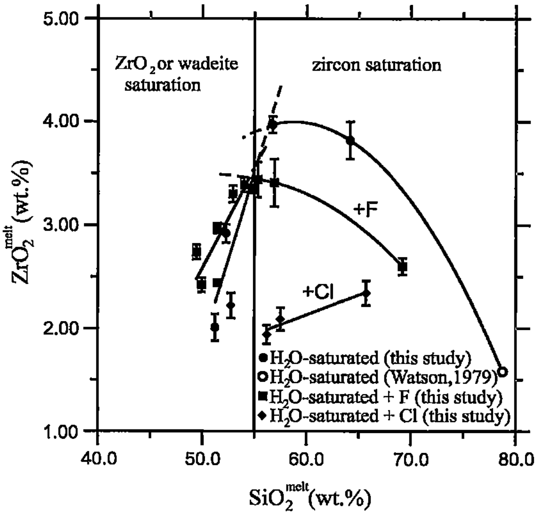

FIG. 3. Solubility of Zr-bearing phases as a function of silica concentration for peralkaline alkali aluminosilicate glasses with no added halogens (round symbols), with added F (square symbols), and with added Cl (triangular symbols). The hollow circle represents a datum from Watson (1979). A second-order polynomial was fitted to the data for zircon-saturated, F-bearing and halogen-free experiments. Linear fits have been applied to all other data. Dashed lines represent extrapolations of these regressions. Error bars represent one standard deviation.

in F-bearing experiments. As mentioned, this concentration of SiO_2 represents a threshold above which zircon is the saturating phase for all experiments (Fig. 3). The solubility of Zr-bearing phases in the Cl-bearing melts is much lower, near 2 wt.% ZrO_2^{melt}, and shows no such maximum across the entire range of SiO_2 content.

DISCUSSION

A model for wadeite crystallization

The positive slope of the curve representing the solubility of Zr in the low-silica region of the halogen-free experiments in Figure 3 is puzzling. It suggests that as the activity of silica in the melt increases, the precipitation of wadeite is suppressed. This cannot be reconciled with the reaction:

$$K_2O^{melt} + ZrO_2^{melt} + 3SiO_2^{melt} \Leftrightarrow K_2ZrSi_3O_9^{crystal} \quad (1)$$

because increased $a(SiO_2)$ should favor wadeite crystallization and lower concentrations of the component ZrO_2. Only with a strong decrease in the activity of the alkali would this reaction be compatible with our results. Given the relatively low enthalpy of mixing in the binary alkali – silica systems (*i.e.*, metastable liquid – liquid miscibility gap: Haller *et al.* 1974), this seems unlikely. Therefore, a more complicated explanation must be proposed. One possibility is the presence of a high-silica, alkali zirconosilicate complex in the melt. Such alkali zirconosilicate complexes have been proposed in previous investigations, with (Na,K)/Zr varying from 2 (Ellison & Hess 1994) to 4 (Watson 1979). Ellison & Hess (1994) attributed the difference in alkali/Zr ratio to the higher temperature at which their experiments were performed and possibly a different coordination geometry for Zr in the two studies as a result. Unfortunately, the approaches taken by Ellison & Hess (1994) and Watson (1979) did not allow the number of SiO_4 tetrahedra associated with these melt complexes to be determined. The Raman spectra of Ellison & Hess (1994) can only provide indirect information on the local environment around Zr ions in a glass or melt by detecting changes in the structure of the network of (Si,Al)-tetrahedra resulting from its presence, whereas solubility studies like those of Watson (1979) provide no information about melt structure. Thus the presence of a high-silica complex is speculative.

An alternative approach is to model a reaction in terms of structural units. Ellison & Hess (1994) concluded, on the basis of Raman spectra, that a Q^3 structure (a SiO_4 tetrahedron with one non-bridging oxygen atom) is involved in the alkali zirconosilicate melt complex. Assuming this to be the case, we have used $(Na,K)_2Zr[3Si_2O_5]^{melt}$ to represent the alkali zirconosilicate complex, based strictly on charge balance. For simplicity, we have also assumed ideal mixing among all species in the melt. Because the structure of wadeite is based upon three-membered rings of Q^2 SiO_4 tetrahedra (Henshaw 1955), we may write its formula as $(Na,K)_2Zr[3SiO_3]^{crystal}$. Using this notation, we can write an equation that schematically accounts for the increase in Zr concentrations in wadeite-saturated melts as silica concentration increases:

$$K_2Zr[3Si_2O_5]^{melt} \Leftrightarrow K_2Zr[3SiO_3]^{crystal} + 3[SiO_2]^{melt} \quad (2)$$

Written in this way, the reaction proceeds to the left as the SiO_2 concentration increases, which is consistent with the solubility data reported in this study.

The effect of halogens on solubility of Zr-bearing phases

The addition of halogens significantly affects on the solubility of Zr-bearing phases in peralkaline melts. As indicated in Figure 3, the saturation curves of Zr-bearing minerals in fluorinated and halogen-free, H_2O-saturated melts are similar, indicating that F and H_2O affect Zr in a similar manner in the melt. However, there are differences in the solubilities of Zr-bearing phases in the F-bearing and F-free melts that must be addressed. The solubility of Zr-bearing phases in F-bearing low-silica glasses is approximately equal to that in halogen-free compositions, whereas the solubility of zircon is decreased in the F-bearing glasses relative to the F-free glasses for the high-silica compositions. This observation must be related to the effect of F on melt structure and alkali activity because direct complexation of F with

Zr is unlikely (Farges 1996). Previous experiments have demonstrated that the addition of F to metaluminous haplogranitic melts increases the solubility of zircon (Keppler 1993). This increase results from the creation of additional non-bridging oxygen atoms as aluminofluoride complexes are formed (Mysen & Virgo 1985, Kohn *et al.* 1991, Schaller *et al.* 1992). It is not clear whether such a mechanism is applicable in peralkaline melts, however, as the presence of alkalis in excess of what is needed to charge-balance Al may favor direct alkali–F bonding. The observation in this study that the presence of F appears to decrease zircon solubility for the more SiO_2-rich compositions bears this out, suggesting that (Na,K)–F bonding may be involved.

As in the halogen-free experiments, a positive slope is also observed for the saturation curve of ZrO_2 in the F-bearing experiments below the threshold of zircon saturation (Fig. 2). As ZrO_2 is the saturating phase and given the reaction:

$$(Na,K)_2Zr(Si_2O_5)_3^{melt} \Leftrightarrow ZrO_2^{crystal} + (Na,K)_2SiO_3^{melt} + 5SiO_2^{melt} \quad (3),$$

it is clear that increasing the activity of SiO_2 or alkalis in the melt would favor an increase in the solubility of ZrO_2. The solubility of Zr-bearing phases increases with the addition of F in the low-silica melts, but the different saturating phases in the F-free (wadeite) and F-bearing (ZrO_2) experiments make the comparison less meaningful.

The reason for the difference in saturating phase between the low-silica F-free and F-bearing compositions is unclear. Wadeite crystallizes from the F-bearing melts at 650°C, but is replaced by ZrO_2 at 800°C, indicating that F lowers the upper stability-limit of wadeite. On the basis of the reaction:

$$K_2ZrSi_3O_9^{crystal} \Leftrightarrow ZrO_2^{crystal} + K_2SiO_3^{melt} + 2SiO_2^{melt} \quad (4),$$

the destabilization of wadeite in favor of ZrO_2 could be achieved by lowering the activity of either silica or alkalis. Although the results of this study do not indicate which of these mechanisms is responsible for the observed differences between the F-free and F-bearing experiments, the (Na,K)–F complex we propose should result in a decrease in the availability of alkalis to interact with the aluminosilicate network.

The addition of chlorine lowers the solubility of zircon and ZrO_2 across most of the compositional range investigated in this study. Furthermore, the solubility maximum observed in the halogen-free and F-bearing compositions is not present in the Cl-bearing experiments. It has been known for some time that Cl affects melt properties differently than F or H_2O. Viscosity studies of (Na,Ca)- and (K,Ba)-silicate melts by Hirayama & Camp (1969) indicate that the addition of F results in a decrease in viscosity, whereas Cl increased it. Since viscosity is a reflection of the degree of polymerization, the observed increase in viscosity means that Cl polymerizes a silicate melt, at least for alkali and alkaline-earth silicate compositions. A recent study of diffusion lends further support to this proposal. Activation energies for diffusion determined by Baker (1993) were lowered by the presence of fluorine, whereas the addition of chlorine increased the activation energy of diffusion. Baker (1993) proposed that these results are due to decreases and increases in the degree of melt polymerization produced by the presence of F and Cl, respectively. Solubility and partitioning experiments (Metrich & Rutherford 1992, Webster 1992) provide evidence of a solution mechanism for Cl that could account for this behavior: Cl forms melt complexes with network-modifying alkalis (at least for compositions with alkalis/Al ≥ 1) rather than with network-forming Al, as is the case with F (Mysen & Virgo 1985, Kohn *et al.* 1991, Schaller *et al.* 1992). This solution mechanism would lower the activity of alkalis and, therefore, be expected to reduce the solubility of Zr-bearing phases by destabilizing alkali zirconosilicate complexes in the melt. Given the significant decrease in solubility of Zr-bearing minerals in Cl-bearing melts, it is clear that more investigation is needed of the effect of Cl on the concentration of high-field-strength elements (HFSE) in peralkaline magmas.

Applications to the Strange Lake peralkaline granite

The mid-Proterozoic Strange Lake (Lac Brisson) peralkaline granitic pluton on the Quebec – Labrador border may represent the extension into Labrador of Gardar anorogenic igneous activity (Currie 1985). The pluton comprises two main rock types: a hypersolvus granite and a typically altered subsolvus granite that seems to have been emplaced as a volatile-saturated melt (Nassif 1993). The hypersolvus granite consists of mesoperthitic alkali feldspar, interstitial quartz and late-crystallizing arfvedsonite with accessory fluorite, zircon, thorite, aenigmatite and astrophyllite.

The subsolvus granite is either equigranular or porphyritic. It contains idiomorphic quartz, arfvedsonite (occurring as phenocrysts in the porphyritic granite) and coexisting sodic and potassic alkali feldspars. Accessory minerals in the subsolvus granite include late zircon, elpidite ($Na_2ZrSi_6O_{15}{\bullet}3H_2O$), armstrongite ($CaZrSi_6O_{15}{\bullet}2.5H_2O$), gittinsite ($CaZrSi_2O_7$), kainosite ($Ca_2[Ce,Y,\mathit{HREE}]_2Si_4O_{12}[CO_3]{\bullet}H_2O$) and calcite. Pegmatites and miarolitic cavities are associated with the subsolvus granite, indicating that it crystallized under H_2O-saturated conditions.

Elpidite has been identified as the primary, magmatic Zr-bearing mineral in the subsolvus granite (Salvi & Williams-Jones 1995). It appears as doubly terminated orthorhombic prisms up to 3 mm in length that may be flow-aligned (Miller 1996). It shows varying degrees of replacement by gittinsite or armstrongite. Anhedral elpidite also has been reported in the porphyritic granite, either as single crystals interstitial to quartz and feldspar or as large aggregates of small grains (<0.1 mm in diameter) (Salvi & Williams-Jones 1995).

Although elpidite was the primary, magmatic Zr-bearing mineral at Strange Lake, the experiments performed in this study, in some cases with compositions roughly similar to those of Strange Lake rocks, have yielded only zircon, ZrO_2 and $K_2ZrSi_3O_9$. This suggests that the upper stability limit of elpidite is exceeded at the P–T conditions of these experiments. This inference is consistent with the results of Currie & Zaleski (1985), which indicate that the transition from elpidite to vlasovite + quartz + H_2O at $P(H_2O) = 1$ kbar occurs at 595 ± 4°C. The inferred pressure of crystallization at Strange Lake, based on fluid-inclusion data (Salvi & Williams-Jones 1992), is 0.7 kbar, assuming $P_{fluid} = P_{total}$. At this pressure, the upper thermal stability limit of elpidite is about 575°C, a low temperature for a magma, but close to the approximate lower-temperature limit suggested by Nassif (1993) of 590°C for the subsolvus-granite-forming magma at Strange Lake. The solidus temperature proposed by Nassif (1993) is based on that reported for a topaz-bearing quartz keratophyre (ongonite) from Mongolia (Kovalenko *et al.* 1971), with a high F content similar to that in the Strange Lake magma. Thermometric studies of melt inclusions in topaz from this locality indicated a solidus between 550 and 600°C (Naumov *et al.* 1971), which Nassif (1993) estimated to be 575°C at 1 kbar and 590°C at 0.7 kbar. Thus, the solidus temperature is not well constrained. Furthermore, the Mongolian ongonite is not peralkaline. Experiments have indicated that peralkaline melts have solidi significantly lower than those of haplogranitic melts (McDowell & Wyllie 1972). Therefore, lowering the proposed solidus temperature for the Strange Lake subsolvus-granite-forming magma can be justified.

Since zircon is the saturating phase at 800°C and 1 kbar, granitic intrusions that contain elpidite as a magmatic phase must not have been saturated until late in the crystallization process or must have crystallized from a low-temperature magma. Textural evidence from the subsolvus granite (Salvi & Williams-Jones 1995) and related pegmatites (Miller 1996) indicates that in the case of Strange Lake, elpidite crystallized early. Based on the chemography of the common alkali zirconosilicate (AZS) minerals, which generally lie on the SiO_2–$(Na,K)_2ZrO_3$ pseudobinary (Marr & Wood 1992), zircon is an indifferent phase and is, therefore, stable at the same P–T conditions as elpidite, wadeite, vlasovite and other common AZS minerals. Consequently, if zircon crystallized from a magma at a temperature above the upper stability limit of elpidite, it would remain stable as the magma cooled to a temperature at which elpidite would also be stable. Indeed, small amounts of early zircon with a reaction rim of vlasovite or elpidite have been reported in the hypersolvus granite at Strange Lake (Birkett *et al.* 1992). Such early zircon may represent localized pockets of early saturation in zircon or it may be xenocrystic. Furthermore, vlasovite at Strange Lake commonly displays a reaction rim of elpidite in contact with quartz (Birkett *et al.* 1992). This sequence indicates a reaction series zircon → vlasovite → elpidite as the temperature decreases.

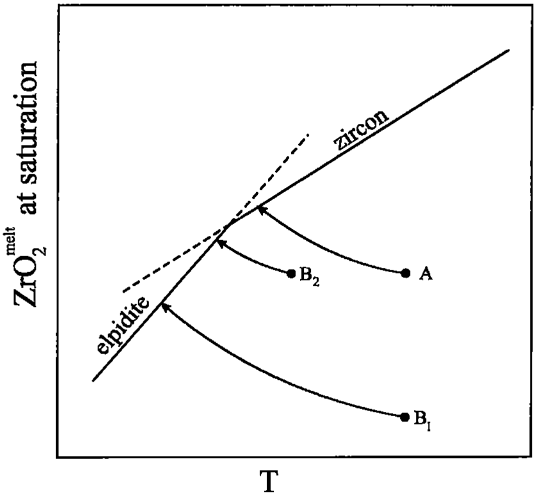

FIG. 4. Schematic representation of cooling paths for three peralkaline magmas on the assumption that Zr behaves as an incompatible element. Magma A represents a relatively high-temperature melt with high initial ZrO_2 content that becomes saturated in zircon. Magmas B_1 and B_2 represent melts at high T and low initial ZrO_2 content, and low T and high initial ZrO_2 content, respectively, which avoid early saturation in zircon and crystallize elpidite.

Thus, presence of magmatic alkali zirconosilicates in peralkaline granites implies either a lower initial Zr content in the melt or a lower temperature of the melt at the time of emplacement than if zircon is present. Three possible paths of melt evolution are indicated in Figure 4. Here, we assume that Zr behaves incompatibly until saturation of the melt in either zircon or elpidite. Path A illustrates the evolution of a relatively high-temperature magma with a relatively high initial content of Zr. As the magma cools, the concentration of Zr in the melt increases until zircon saturation is reached. Path B_1 indicates how a high-temperature magma with a low initial content of Zr would evolve differently from that illustrated by path A. Once again, the magma becomes enriched in Zr as it cools. However, saturation in zircon does not occur, and the melt continues to cool until saturation in elpidite is achieved. An alternative path that could lead to elpidite saturation is represented by B_2. A magma that has a high initial content of Zr, but is emplaced at a lower temperature, could avoid saturation in zircon and crystallize elpidite. It is this third alternative that is the most compatible with the textures observed at Strange Lake.

This model must be viewed as highly qualitative, since it does not take into account the effect of variable agpaitic index (alkali/Al); the index will increase in a fractionating peralkaline felsic melt. Nor does it consider pressure, which has a significant effect on the stability field of elpidite, especially for pressures below 1 kbar (Currie & Zaleski 1985). However, the model does provide some insight into the evolution of peralkaline felsic magmas. High concentrations of Zr can be reached in the late stages of magmatic crystallization from melts with relatively low initial Zr content. On the other hand, high initial concentrations of Zr may result in early saturation of zircon, which would be dispersed throughout the magma, yielding final contents of Zr comparable to those of magmas with low initial concentrations.

CONCLUSIONS

1) For H_2O-saturated, peralkaline, Zr-rich, alkali aluminosilicate melts with 55 wt.% SiO_2 or more, zircon is the saturating phase at 800°C and 1 kbar, whereas wadeite appears in melts with lower silica contents.

2) The addition of F lowers the upper thermal stability limit of wadeite in favor of ZrO_2 in low-silica melts, and decreases the solubility of zircon in high-silica melts.

3) There is a maximum in the solubility of Zr-bearing minerals between 55 and 60 wt.% SiO_2 for H_2O-saturated peralkaline melts with and without added F.

4) The addition of Cl serves to depress the solubility of Zr-bearing phases, particularly in the compositional range where a maximum is observed in Cl-free experiments. This may be the result of lower activity of alkalis due to alkali–Cl complexing.

5) Fluorine appears to destabilize alkali zirconosilicate melt complexes, possibly as a result of alkali fluoride complexation.

ACKNOWLEDGEMENTS

Technical assistance was provided by Glenn Poirier and Glenna Keating. The authors wish to thank R.F. Martin and the two anonymous referees for their invaluable comments. This project was funded by grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR).

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Received October 22, 1997, revised manuscript accepted May 12, 1998.