

## Solution behavior of +4 cations in high silica melts: petrologic and geochemical implications

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**Abstract.** The saturation surfaces of rutile ( $\text{TiO}_2$ ), zircon ( $\text{ZrSiO}_4$ ), and hafnon ( $\text{HfSiO}_4$ ) were determined in anhydrous, peraluminous, high silica liquids of the system  $\text{SiO}_2\text{—Al}_2\text{O}_3\text{—Na}_2\text{O—K}_2\text{O}$  as functions of silica concentration at  $1,400^\circ\text{C}$  in air. The saturation concentrations of  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{HfO}_2$  in rutile, zircon, and hafnon-saturated liquids, respectively, decrease smoothly and gradually as functions of increasing silica concentration. Thermodynamic analyses of the data demonstrate that the activity coefficients of  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{HfO}_2$  increase smoothly and gradually as silica concentration is increased from 67 wt-% to 80 wt-%, and that changes in  $\text{SiO}_2$  of 1 or 2 wt-% result in small changes in the saturation concentrations and activity coefficients of +4 cations. Because the solution behavior of +4 cations in highly siliceous liquids (>75 wt-%  $\text{SiO}_2$ ) is predictably different than in less siliceous liquids (70 to 75 wt-%  $\text{SiO}_2$ ), classification of highly-siliceous igneous rocks on the basis of silica concentration alone should not be interpreted to mean that their solution chemistry differs significantly from that of less siliceous rocks. The results of this study are compared with other studies of +4 cation solution behavior. From this it is concluded that variations in liquid compositions observed in cogenetic suites of high silica rhyolites cannot cause the observed changes in +4 cation concentrations. Thus, even if a large change in solution behavior of +4 cations is inferred from the large variations in their concentrations, it cannot be due to changes in bulk composition of the parental liquid. In addition, the similarity in the solution behavior of Zr and Hf seen in this study suggests that their solution mechanisms are similar. It is thus unlikely that liquid-state processes can fractionate one with respect to another, and variations in Zr/Hf ratios in suites of extrusive rocks are likely due to crystal-liquid equilibria, e.g., zircon fractionation.

### Introduction

Though trace element abundances and distributions are routinely used to characterize the genesis and evolution of siliceous igneous rocks, little is known about the ways in which changes in bulk composition affect the solution properties of trace elements in siliceous magmas. Silica concentration is a useful compositional parameter because it in-

creases predictably with increasing differentiation of a magma. Numerous experimental studies in simple systems show that changes in silica concentration may significantly affect the properties of silicate liquids. This is particularly true of high silica liquids, which often show behavior quite different from that of less siliceous liquids. For example, some simple systems exhibit liquid immiscibility only in high silica compositions (e.g., Hess 1977), while in others the redox states of polyvalent cations change dramatically as a function of silica concentration (Paul and Douglas 1965a, 1965b; Nath and Douglas 1965; Douglas et al. 1965). It is timely to examine whether changes in silica concentration can have large, unanticipated effects upon the solution behavior of highly-charged cations in highly siliceous systems with natural analogs.

In order to investigate such effects, the solution behaviors of the +4 cations Ti, Zr, and Hf were determined as functions of the substitution of  $\text{SiO}_2$  for  $\text{MAlO}_2$  (where  $\text{M}=\text{Na, K}$ ). Knowledge of the changes in their solution behaviors can be used to examine the changes in the solution properties of the polymerized silicate melt. Specifically, if charge-balanced aluminum ( $\text{MAlO}_2$ ) behaves as a network-forming (T) cation (e.g., Navrotsky et al. 1985), the substitution of  $\text{SiO}_2$  for  $\text{MAlO}_2$  does not result in a change in the ratio of the number of bridging (T—O—T) bonds to non-bridging (M—O—T) bonds; in other words, the substitution does not change the *degree* of polymerization of a silicate liquid. The *nature* of the polymerization of the silicate liquid — the identity and relative abundance of polymerized species and their solution behavior — does change. Simple electrostatic arguments show that Si—O bonds are stronger than Al—O bonds. Spectroscopic studies and molecular orbital calculations show that Si—O bond lengths are shorter than Al—O bond lengths (Navrotsky et al. 1985). The substitution of  $\text{SiO}_2$  for  $\text{MAlO}_2$ , then, results in a more compact and less polarizable silicate liquid network structure, which must affect the solution behavior of highly-charged cations in the liquid.

To examine these changes, the saturation surfaces of rutile ( $\text{TiO}_2$ ), zircon ( $\text{ZrSiO}_4$ ), and hafnon ( $\text{HfSiO}_4$ ) were examined in peraluminous liquids of the system  $\text{SiO}_2\text{—Al}_2\text{O}_3\text{—Na}_2\text{O—K}_2\text{O}$  as functions of silica concentration at fixed temperature and pressure. The data from these experiments are used to determine the changes in the activity coefficients of the oxides of the +4 cations as silica concentration is increased. The activity coefficient of a component contains all the information about its solution behavior in

a liquid. Knowledge of the activity coefficient of a component in a liquid permits its solution behavior in that liquid to be compared with all other liquids in which its activity coefficient is known. Thus, changes in the values of activity coefficients sensitively measure changes in the solution properties of the high silica solvent, as well as the solution behaviors of the cations themselves. Determining the activity coefficients of the cations in this study is straight-forward because at fixed temperature and pressure, the chemical potentials and activities of  $\text{TiO}_2$ ,  $\text{ZrSiO}_4$ , and  $\text{HfSiO}_4$  are fixed by the saturation of rutile, zircon, and hafnon, respectively. The activity coefficients of  $\text{TiO}_2$ ,  $\text{ZrSiO}_4$ , and  $\text{HfSiO}_4$  (also  $\text{ZrO}_2$ , and  $\text{HfO}_2$ : see later discussion) are determined, therefore, as functions of silica concentration.

The most important conclusion of this study is that small changes in silica concentration in highly siliceous liquids do not produce large changes in the solution properties of the melt. Specifically, the results show that (1) changes in silica concentration on the order of 1 to 2 weight-percent cause small changes in the saturation concentrations of the oxides of +4 cations, (2) small changes in silica concentration do not strongly affect the activity coefficients of +4 cation oxides, and (3) changes in both the saturation concentrations and activity coefficients of +4 cation oxides are smooth, gradual functions of increasing silica concentration. Since the cations in this study show very similar behavior despite, for example, large differences in ionic radii, it is predicted that these conclusions are generally applicable to other highly-charged cations.

## Experimental methods

### Preparation of samples

Bulk compositions were in the system  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Na}_2\text{O--K}_2\text{O}$ , which mimics the anhydrous bulk compositions of many highly-siliceous rocks, yet simplifies thermodynamic interpretation by limiting the number of compositional variables that must be controlled. Starting materials were reagent grade except for  $\text{ZrO}_2$  (spectroscopic grade) and  $\text{HfO}_2$  (97+ % pure). Though the presence of sodium complicated electron microprobe analyses of experimental compositions, two alkalis were used to more closely approximate natural compositions.

Starting materials were prepared as follows. Amorphous silica was obtained by heating silicic acid ( $\text{H}_4\text{SiO}_4$ ) in air at  $1,000^\circ\text{C}$  for 24 h.  $\gamma$ -Alumina was prepared by heating  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  in air at  $750^\circ\text{C}$  for 6 h, following the method of Rutherford (1967). Alkali carbonates and  $\gamma$ -alumina were premixed in a fixed ratio (referred to as ALK/AL) and used in all experiments.

Experimental compositions were prepared on a weight-percent (wt-%) basis, so in the following description of the experimental procedure the compositions represent a fixed wt-%  $\text{SiO}_2$  and a fixed value of alkali/aluminium (0.96 in moles). Two sets of starting compositions were prepared, one containing  $\text{SiO}_2$ , ALK/AL, and an amount of  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , or  $\text{HfO}_2$  greater than was needed to saturate a phase, and one in which an adjusted equivalent weight of ALK/AL was substituted for  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , or  $\text{HfO}_2$ . Both sets were combined in various ratios with an alumina mortar and pestle (under ethanol) for at least one hour to insure homogeneity. The ratios were varied until a phase saturated during normal experimental procedures that satisfied the criteria of reversibility (see below).

### Experimental procedure

Experiments were performed at  $1,400^\circ\text{C}$  in air in a vertical Deltech drop furnace for 24–72 h. Temperature was monitored with a Pt/Pt

10% Rh thermocouple. Observed variations in temperature during any experiment were less than  $2^\circ\text{C}$ .

Sample containers were 2 cm Pt tubes with one end welded shut and covered on the other end by a tightly fitting lid of Pt foil. A sample was packed into a container and suspended by a heavy gauge Pt 10% Rh wire in the Deltech drop furnace. Mixtures that had not been melted previously were heated for 30 min at  $900^\circ\text{C}$  to drive off  $\text{CO}_2$  from the carbonates before being heated in a single step to the run temperature ( $1,400^\circ\text{C}$ ). Previously-melted samples were heated only at  $1,400^\circ\text{C}$ .

After 12 h, samples were drop-quenched in cold water (roughly 1 s) and dried, and a grain mount was prepared for optical examination. If crystals of the expected phase were found, or if undissolved oxide remained in the glass, the sample was re-ground and reheated at  $1,400^\circ\text{C}$  for 12 h. This procedure was repeated until all oxide was dissolved. In  $\text{TiO}_2$ -bearing experiments a single re-grinding was sufficient to homogenize the sample.  $\text{ZrO}_2$  and  $\text{HfO}_2$ -bearing experiments were subjected to two cycles of grinding and melting, and subsequent cycles did not change the saturation concentrations.

### Analysis

Samples were analyzed using a Cameca electron microprobe operating at 10 kV accelerating potential and 10 nanoamp beam current. Between ten and twenty spots were analyzed in each sample, and all samples were analyzed in several sessions to check the reproducibility of the results. A wide beam (20  $\mu\text{m}$ ) and short counting times (10 to 20 s) were used to reduce loss of alkalis. The high totals and low standard deviations indicate minimal alkali loss. A volcanic glass, KN-18 (Devine et al. 1984), kindly supplied by the Graduate School of Oceanography, University of Rhode Island, was used as a microprobe standard for Si, Al, Na, and K. Ilmenite was used as a Ti standard. Zr and Hf standards were Corning Glass Works glasses X and V, respectively. Glass compositions obtained using these standards agreed well with the values expected from starting compositions for zircon and hafnon experiments. Rutile experiments, however, had lower  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  concentrations than expected from starting compositions. Because the totals from the microprobe analyses are close to 100%, the alkali loss probably occurred during the experimental runs.

The saturated phases were also analyzed to determine their compositions. The saturated phase in  $\text{TiO}_2$ -bearing glasses was compared with a synthetic rutile and found to be pure  $\text{TiO}_2$ , and was identified as rutile using powder X-ray analysis of saturated glasses. The phase in  $\text{ZrO}_2$ -bearing glasses was analyzed using a natural zircon as a standard (assumed to be pure  $\text{ZrSiO}_4$ ) and found to have the stoichiometry of zircon. The absence of a suitable hafnium standard hampered the analysis of the crystals that saturated in  $\text{HfO}_2$ -bearing glasses. Because the concentration of  $\text{HfO}_2$  in Corning Glass Works "V" is much lower than the saturated phase, analyses of the saturated phase yielded totals greater than 100%, and  $\text{HfO}_2$  concentrations were in excess of 80 wt-%. However, the silica concentration (24 wt-%) and the low alkali + alumina concentrations (less than 1 wt-%) are consistent with the expected composition of  $\text{HfSiO}_4$  (roughly 78 wt-%  $\text{HfO}_2$  and 22 wt-%  $\text{SiO}_2$ ).

### The criterion of reversibility

The process of re-grinding and re-melting the samples eliminated diffusion gradients near the crystals, which were present in electron back-scatter images of non-equilibrium glasses. Saturation concentrations showed no time-dependence after re-grinding, suggesting that all samples at least approached equilibrium during normal experimental procedures.

Two methods were used to establish the reversibility of rutile saturation experiments. Samples were prepared with  $\text{TiO}_2$  concentrations slightly above and slightly below the measured saturation concentration. The samples were then run according to the above

**Table 1.** Compositions of rutile-saturated liquids, in weight-%. Errors represent one standard deviation

SiO <sub>2</sub>	66.06 ± 0.72	70.69 ± 0.46	73.48 ± 0.30	76.56 ± 0.50	78.84 ± 0.39	80.17 ± 0.21
TiO <sub>2</sub>	9.27 ± 0.28	8.50 ± 0.27	8.18 ± 0.21	8.03 ± 0.21	7.33 ± 0.17	6.84 ± 0.26
Al <sub>2</sub> O <sub>3</sub>	14.88 ± 0.29	13.22 ± 0.29	11.77 ± 0.08	9.81 ± 0.22	8.73 ± 0.30	8.26 ± 0.26
Na <sub>2</sub> O	4.10 ± 0.10	3.28 ± 0.14	2.69 ± 0.19	2.43 ± 0.11	2.01 ± 0.12	1.61 ± 0.09
K <sub>2</sub> O	5.16 ± 0.08	4.34 ± 0.21	3.37 ± 0.13	3.05 ± 0.11	2.97 ± 0.18	2.61 ± 0.07
Total	99.47	100.03	99.49	99.88	99.88	99.49
$\sqrt{\sum \sigma_i^2}$	0.84	0.66	0.44	0.61	0.56	0.44
Alk/Al <sup>a</sup>	0.83	0.76	0.69	0.74	0.75	0.66

<sup>a</sup> (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub>, expressed as a ratio of mole-%

**Table 2.** Compositions of zircon-saturated liquids, in weight-%. Errors represent one standard deviation

SiO <sub>2</sub>	67.89 ± 0.41	69.86 ± 0.50	71.34 ± 0.36	72.55 ± 0.64	75.81 ± 0.40	77.39 ± 1.10	81.13 ± 0.61
ZrO <sub>2</sub>	1.49 ± 0.09	1.37 ± 0.07	1.17 ± 0.18	1.14 ± 0.11	1.10 ± 0.10	1.08 ± 0.09	0.97 ± 0.09
Al <sub>2</sub> O <sub>3</sub>	18.61 ± 0.49	16.38 ± 0.80	16.01 ± 0.20	15.81 ± 0.31	13.53 ± 0.20	12.45 ± 0.80	10.06 ± 0.40
Na <sub>2</sub> O	5.90 ± 0.17	5.62 ± 0.43	5.30 ± 0.20	4.84 ± 0.05	4.56 ± 0.17	4.18 ± 0.20	3.48 ± 0.17
K <sub>2</sub> O	6.28 ± 0.10	5.91 ± 0.13	5.75 ± 0.12	5.64 ± 0.22	5.01 ± 0.22	4.51 ± 0.20	3.85 ± 0.07
Total	100.17	99.14	99.57	99.98	100.01	99.61	99.49
$\sqrt{\sum \sigma_i^2}$	0.67	1.05	0.51	0.75	0.54	1.39	0.76
Alk/Al <sup>a</sup>	0.89	0.96	0.93	0.89	0.96	0.94	0.98
M <sup>b</sup>	1.43	1.47	1.41	1.32	1.35	1.29	1.27

<sup>a</sup> (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub>, expressed as a ratio of mole-%

<sup>b</sup> (Na + K)/(Al + Si), expressed as a ratio of cation-percents (Watson and Harrison 1983)

procedure. The sample with the ratio below that needed to saturate rutile was a clear glass, while the sample with the high ratio saturated rutile and had a TiO<sub>2</sub> saturation concentration identical to that of the reference glass. In a second series, a glass saturated with rutile at 1,400° C was either run at 1,500° C for 24 h, or run at 1,500° C for 12 h, cooled in a single step to 1,400° C, and run for another 12 h. No rutile was present in liquids run only at 1,500° C. The saturation concentration of TiO<sub>2</sub> in liquids with a final run temperature of 1,400° were identical to those of glasses run only at 1,400° C.

Saturation concentrations of both ZrO<sub>2</sub> and HfO<sub>2</sub> invariably increased after a single re-grinding. This illustrates that run times of 12 h were insufficient for equilibration. It is nonetheless possible to establish that equilibrium was approached. For instance, there was no observed time-dependence of the saturation concentration of zircon or hafnon after samples had been reground once and heated for a total of 24 h. Second, glasses that did not saturate zircon or hafnon always had concentrations of ZrO<sub>2</sub> or HfO<sub>2</sub> that were lower than those measured in comparable zircon or hafnon-saturated glasses. Finally, experiments run at 1,450° C and 1,350° C had saturation concentrations that bracket the observed values at 1,400° C. These observations do not establish the reversibility of the experiments, but shows that the procedure results in an approach to equilibrium.

The approach to equilibrium in these liquids was tested by subjecting them to three meltings, the last of which was at 1,400° C. In one set of liquids the first melting was at 1,400° C and the second at 1,500° C, while in the other the first melting was at 1,500° C and the second was at 1,400° C. If zircon is completely inert, the zircon formed at 1,400° C will not dissolve when reheated at 1,500° C. The liquid will approach the "real" value of the saturation concentration from "below". By contrast, liquids heated initially at 1,500° C will dissolve all of the ZrO<sub>2</sub> in the melt. A second heating at 1,400° C will result in an approach to the "real" value of the saturation concentration from above. Thus, if zircon is truly inert, the liquids produced in these experiments should have ZrO<sub>2</sub>

saturation concentrations that bracket the real value. Not only was it found that the ZrO<sub>2</sub> saturation concentrations of these liquids were identical, but they also were identical to equivalent liquids run only at 1,400° C. The same results were found for HfO<sub>2</sub>-bearing glasses. These results demonstrate that (1) normal experimental procedures result in saturation concentrations that closely reflect the equilibrium concentration, and (2) zircon and hafnon were not inert in the experiments. This last conclusion is consistent with the results of Harrison and Watson (1983), who found that the diffusivity of Zr in dry obsidian melts at 8 kb increases by roughly an order of magnitude from 1,400° C to 1,500° C, suggesting that zircon is not inert at high temperatures.

## Results

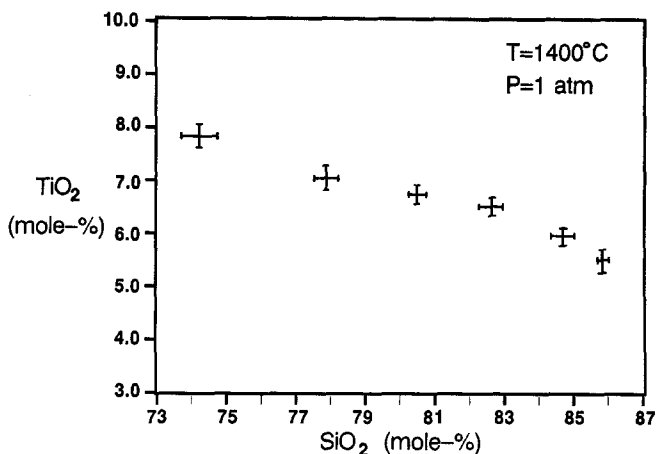
The experimental results show systematic decreases in the solubilities of the oxides of +4 cations with increasing silica concentration. The TiO<sub>2</sub> concentration of rutile-saturated liquids decreases smoothly as a function of increasing silica concentration, from 9.3 wt-% at 66 wt-% SiO<sub>2</sub> to 6.8 wt-% at 80 wt-% SiO<sub>2</sub> (Table 1). The ZrO<sub>2</sub> concentration in zircon-saturated glasses decreases from 1.5 wt-% at 68 wt-% SiO<sub>2</sub> to 1.0 wt-% at 81 wt-% SiO<sub>2</sub> (Table 2). Over the same range of silica concentration, the HfO<sub>2</sub> concentration in hafnon-saturated glasses decreases from 2.7 wt-% to 1.8 wt-% (Table 3).

Bulk compositions reported in Tables 1, 2, and 3 were recalculated in mole-% (oxide basis) normalized to 100%. The changes in the mole-% of TiO<sub>2</sub>, ZrO<sub>2</sub>, and HfO<sub>2</sub> in saturated glasses are plotted against increasing silica concentration in Figs. 1, 2, and 3, respectively. These figures illustrate several important points. First, the saturation concentrations decrease smoothly as silica concentration in-

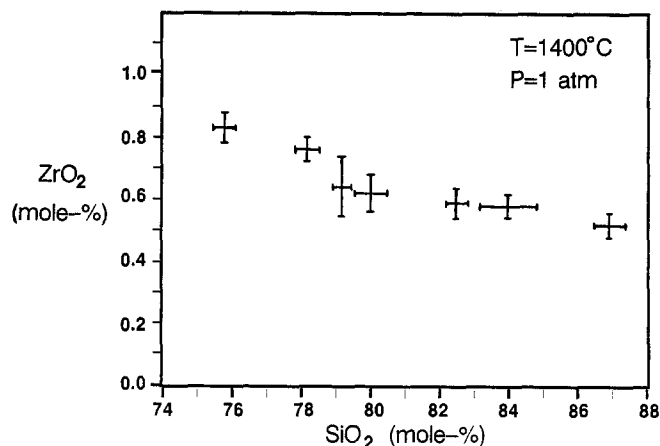
**Table 3.** Compositions of hafnon (HfSiO<sub>4</sub>)-saturated liquids, in weight-%. Errors represent one standard deviation

SiO <sub>2</sub>	66.89 ± 0.27	68.85 ± 0.41	71.12 ± 0.20	75.66 ± 0.17	77.88 ± 0.70	80.02 ± 0.50
HfO <sub>2</sub>	2.65 ± 0.14	2.43 ± 0.09	2.15 ± 0.11	2.01 ± 0.07	1.80 ± 0.07	1.85 ± 0.12
Al <sub>2</sub> O <sub>3</sub>	17.94 ± 0.17	16.81 ± 0.22	15.71 ± 0.16	13.08 ± 0.13	11.97 ± 0.30	10.98 ± 0.17
Na <sub>2</sub> O	6.00 ± 0.19	5.64 ± 0.16	5.32 ± 0.14	4.30 ± 0.05	3.92 ± 0.13	3.02 ± 0.07
K <sub>2</sub> O	6.24 ± 0.10	5.91 ± 0.21	5.48 ± 0.08	4.57 ± 0.10	4.29 ± 0.15	3.32 ± 0.13
Total	99.72	99.64	99.78	99.62	99.86	99.19
$\sqrt{\sum \sigma_i^2}$	0.41	0.54	0.32	0.25	0.79	0.56
Alk/Al <sup>a</sup>	0.93	0.93	0.93	0.92	0.93	0.78

<sup>a</sup> (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub>, expressed as a ratio of mole-%



**Fig. 1.** Harker diagram showing the decrease in TiO<sub>2</sub> concentration of rutile-saturated glasses plotted as a function of increasing silica concentration, plotted in mole-% (oxide basis). Points correspond to compositions listed in Table 1. Error bars represent one standard deviation. The solubility of rutile decreases by roughly 35% over the range of compositions examined



**Fig. 2.** Harker diagram showing the decrease in ZrO<sub>2</sub> concentrations in zircon-saturated glasses plotted as a function of increasing silica concentration, plotted in mole-% (oxide basis). Points correspond to compositions listed in Table 2. Error bars represent one standard deviation. The solubility of zircon decreases by roughly 40% over the range of compositions examined

creases. Second, the percentage-decrease in the saturation concentrations of all three oxides are very similar, despite large differences in their concentrations in their respective liquids.

Figure 4 shows the variations in the saturation concentrations of both ZrO<sub>2</sub> and HfO<sub>2</sub> as a function of silica concentration. It is apparent that the saturation concentrations of both are very similar over the range in experimental compositions. An additional interesting feature of Fig. 4 is that the saturation concentrations of ZrO<sub>2</sub> and HfO<sub>2</sub> appear to flatten for silica concentrations greater than about 80 mole-%. It is unlikely that this is an artifact of errors in the determinations because the same trends are seen for zircon and hafnon-saturated glasses alone (see Figs. 2 and 3). The data of Watson (1979) also seem to show that ZrO<sub>2</sub> saturation concentrations flatten in water-saturated peralkaline liquids in the neighborhood of 80 mole-% SiO<sub>2</sub>. Explanation of these effects requires further experiments.

#### Thermodynamic analysis of rutile saturation experiments

The thermodynamic definition of equilibrium requires that the chemical potentials of all components are equal in co-existing phases. Saturation of rutile fixes the chemical potential of TiO<sub>2</sub> in the liquid, regardless of the composition

of the liquid. The chemical potential of TiO<sub>2</sub> in the liquid ( $\mu_{\text{TiO}_2}(l)$ ) is therefore equal to the chemical potential of TiO<sub>2</sub> in rutile ( $\mu_{\text{TiO}_2}(\text{rut})$ ). This may be expressed as

$$\mu_{\text{TiO}_2}(\text{rut}) = \mu_{\text{TiO}_2}(l) = \mu_{\text{TiO}_2}^{\circ} + RT \ln(a_{\text{TiO}_2}), \quad (1)$$

where  $\mu_{\text{TiO}_2}^{\circ}$  is the chemical potential of a reference state of pure TiO<sub>2</sub> at  $T$  and  $P$ ,  $a_{\text{TiO}_2}$  is the activity of TiO<sub>2</sub> in the liquid, and  $R$  is the gas constant. If rutile at 1,400°C is chosen as the standard state, the activity of TiO<sub>2</sub> must equal unity.

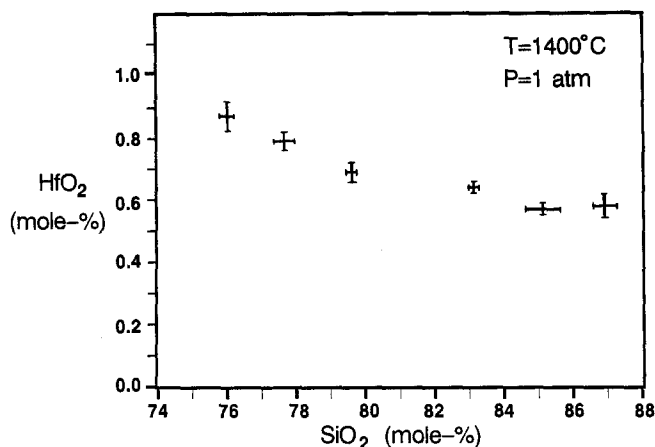
The activity of TiO<sub>2</sub> may be written as

$$a_{\text{TiO}_2} = \gamma_{\text{TiO}_2} X_{\text{TiO}_2}, \quad (2)$$

where  $\gamma_{\text{TiO}_2}$  is the activity coefficient of TiO<sub>2</sub> and  $X_{\text{TiO}_2}$  is its mole fraction in the liquid. Since the activity of TiO<sub>2</sub> is equal to unity,

$$\gamma_{\text{TiO}_2} = 1/X_{\text{TiO}_2}. \quad (3)$$

(The choice of a standard state is arbitrary. If any other pure form of TiO<sub>2</sub> is picked as a standard state, the chemical potential and activity of TiO<sub>2</sub> are still fixed by rutile saturation; however, the value of the activity, and, therefore, the activity coefficient, will change.) The ratio of the activity coefficients of TiO<sub>2</sub> in two liquids,  $r$  and  $s$ , thus varies inver-



**Fig. 3.** Harker diagram showing the decrease in HfO<sub>2</sub> concentration of hafnon-saturated glasses as a function of increasing silica concentration, plotted in mole-% (oxide basis). Points correspond to compositions listed in Table 3. Error bars represent one standard deviation. The solubility of hafnon decreases by roughly 40% over the range of compositions examined

sely with the ratio of the mole fraction of TiO<sub>2</sub> in the liquids, or

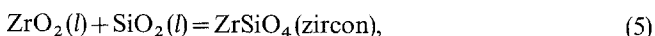
$$\gamma_{\text{TiO}_2, r} / \gamma_{\text{TiO}_2, s} = X_{\text{TiO}_2, s} / X_{\text{TiO}_2, r} \quad (4)$$

Since the changes in the saturation concentration are small (Figure 1), the changes in the activity coefficient of TiO<sub>2</sub> must also be small.

#### Zircon and hafnon saturation experiments

The derivation of the activity coefficients of ZrO<sub>2</sub> and HfO<sub>2</sub> is more complex because ZrO<sub>2</sub> and HfO<sub>2</sub> do not saturate as simple oxides in these experiments, but as silicates. ZrO<sub>2</sub> will be used as an example in what follows, but the analysis of HfO<sub>2</sub>-bearing liquids is identical.

The equilibrium for the formation of zircon from silicate liquids is



where ZrO<sub>2</sub>(*l*) and SiO<sub>2</sub>(*l*) are the oxide components of zircon in the liquid. At equilibrium the reaction may be written in terms of the chemical potentials of ZrO<sub>2</sub>, SiO<sub>2</sub>, and zircon (Gibbs 1948), or

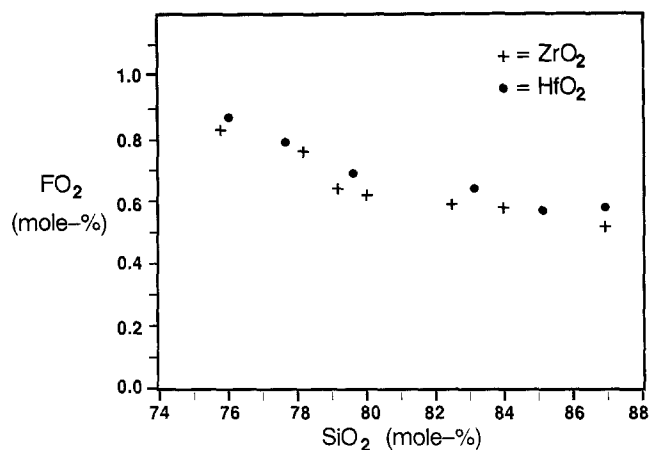
$$\mu_{\text{ZrO}_2}(l) + \mu_{\text{SiO}_2}(l) = \mu_{\text{ZrSiO}_4}(\text{zircon}). \quad (6)$$

The saturation of zircon fixes the chemical potential of ZrSiO<sub>4</sub> at a specific value, regardless of the composition of the liquid. The derivative of Eq. (6) with respect to the mole fraction of silica is

$$\left( \frac{\partial \mu_{\text{ZrO}_2}}{\partial X_{\text{SiO}_2}} \right)_{P, T} + \left( \frac{\partial \mu_{\text{SiO}_2}}{\partial X_{\text{SiO}_2}} \right)_{P, T} = 0 \quad (7)$$

The chemical potential of SiO<sub>2</sub> in a stable liquid must increase as its mole fraction increases, because increasing silica concentration pushes liquid compositions towards pure silica, where the chemical potential of silica is a maximum. Therefore, the chemical potential of ZrO<sub>2</sub> decreases with increasing silica concentration at constant *P* and *T*, i.e.

$$\left( \frac{\partial \mu_{\text{ZrO}_2}}{\partial X_{\text{SiO}_2}} \right)_{P, T} < 0. \quad (8)$$



**Fig. 4.** A Harker diagram showing the decreases in FO<sub>2</sub> solubilities (F = Zr, Hf) as a function of silica concentration, plotted in mole-%. Data is from Figures 2 and 3. Error bars are omitted. Note the very similar solubilities of Zr and Hf. Note also that FO<sub>2</sub> saturation concentrations flatten for SiO<sub>2</sub> concentrations greater than about 80 mole-%

The chemical potential of ZrO<sub>2</sub> is written

$$\mu_{\text{ZrO}_2} = \mu_{\text{ZrO}_2}^{\circ} + RT \ln(a_{\text{ZrO}_2}) \quad (9)$$

where  $\mu_{\text{ZrO}_2}^{\circ}$  is the chemical potential of ZrO<sub>2</sub> in the pure state at 1,400° C and 1 atm and  $a_{\text{ZrO}_2}$  is the activity of ZrO<sub>2</sub> in the liquid. Zircon saturation does not fix the chemical potential of ZrO<sub>2</sub> at any particular value. To further evaluate Eq. (9) it is useful to eliminate the standard state term. The difference in the chemical potential of ZrO<sub>2</sub> in two liquids,  $\alpha$  and  $\beta$ , that have saturated zircon at *T* and *P* but which differ in silica concentrations is

$$\Delta \mu_{\text{ZrO}_2} = RT (\ln a_{\text{ZrO}_2, \alpha} - \ln a_{\text{ZrO}_2, \beta}). \quad (10)$$

Substituting

$$a_{\text{ZrO}_2} = \gamma_{\text{ZrO}_2} X_{\text{ZrO}_2} \quad (11)$$

into Eq. (10) and rearranging,

$$\Delta \mu_{\text{ZrO}_2} = RT (\ln \gamma_{\alpha} / \gamma_{\beta} - \ln X_{\beta} / X_{\alpha})_{\text{ZrO}_2}. \quad (12)$$

Similarly, the change in the chemical potential of silica between these liquids is

$$\Delta \mu_{\text{SiO}_2} = RT (\ln a_{\text{SiO}_2, \alpha} - \ln a_{\text{SiO}_2, \beta}). \quad (13)$$

The changes in the chemical potentials of ZrO<sub>2</sub> and SiO<sub>2</sub> are opposite in magnitude [e.g., Eq. (7)], or

$$\Delta \mu_{\text{ZrO}_2} = -\Delta \mu_{\text{SiO}_2}. \quad (14)$$

Substituting Eq. (12) and Eq. (13) into Eq. (14) and rearranging,

$$(\gamma_{\alpha} / \gamma_{\beta})_{\text{ZrO}_2} = (X_{\beta} / X_{\alpha})_{\text{ZrO}_2} (a_{\beta} / a_{\alpha})_{\text{SiO}_2}. \quad (15)$$

This relationship shows that the ratio of the activity coefficients of ZrO<sub>2</sub> varies inversely with the product of the ratios of the activities of silica and the mole fractions of ZrO<sub>2</sub> in the liquids. If the concentration of silica increases from liquid  $\alpha$  to  $\beta$  then the ratio of the activities of silica in Eq. (15) is *greater* than unity. Since the mole fraction of ZrO<sub>2</sub> in zircon-saturated glasses decreases with increasing SiO<sub>2</sub>, the ratio of the mole fractions ZrO<sub>2</sub> must be *less* than unity. The magnitude of the variation in the ratio

of the activity coefficients of  $ZrO_2$  is therefore less than the magnitude of the variation of the ratio of its mole fractions.

The variations in the activity coefficients of  $ZrO_2$  may be obtained directly using Eq. (15), provided that the activities of silica are known. Calorimetric studies of the  $NaAl-Si_3O_8-Si_4O_8$  binary (Navrotsky et al. 1982) and the  $KAl-Si_3O_8-Si_4O_8$  binary (Hervig and Navrotsky 1984) suggest that they are approximately ideal mixtures. Ryerson (1985) demonstrated that the activity coefficients of silica in  $MAO_2-SiO_2$  liquids (where  $M=Na, K$ ) are very close to unity at high silica concentrations. Thus, to a good approximation, the ratio of the activities of silica is equal to the ratio of its mole fractions in these high  $SiO_2$  liquids (where moles are calculated on an equal oxygen basis). Eq. 15 becomes

$$(\gamma_a/\gamma_\beta)_{ZrO_2} = (X_\beta/X_a)_{ZrO_2} (X_\beta/X_a)_{SiO_2}. \quad (16)$$

In this study, a 15% increase in silica concentration results in a 40% decrease in the saturation concentration of  $ZrO_2$ . The activity coefficient of  $ZrO_2$  therefore increases by roughly 30%. Larger changes in the activity of silica result in smaller increases in the activity coefficients of  $ZrO_2$  and  $HfO_2$ . Thus, as argued above, the value of the ratio of the activity coefficients of  $ZrO_2$  and  $HfO_2$  in Eq. (15) cannot exceed the ratio of their mole fractions in the liquids. More generally, it is seen that the chemical potential, and thus the activity, of  $ZrO_2$  must decrease with increasing silica concentration [Eq. (8)].

### Interpretation of experimental results

The results of this study may now be compared with other studies of the solution behavior of +4 cations. Knowledge of the solution behavior of these cations may then be used to understand the ways in which their distributions in igneous rocks are affected by melt composition. In addition, the importance of liquid state processes in controlling +4 cation solution behavior may be critically evaluated.

The thermodynamic analysis of rutile saturation experiments shows that variations in the activity coefficient of  $TiO_2$  between two liquids are inversely proportional to variations in its mole fraction [Eq. (4)]. Since the saturation concentration of  $TiO_2$  decreases smoothly and gradually with increasing silica concentration, the activity coefficient of  $TiO_2$  must increase smoothly and gradually with increasing silica concentration. Because the changes are gradual (Table 1; Fig. 1), small changes in silica concentration can only cause small changes in the saturation concentration and activity coefficient of  $TiO_2$ .

It was shown [Eq. (15)] that the ratio of the activity coefficients of  $ZrO_2$  (or  $HfO_2$ ) vary inversely with the product of the ratios of the mole fractions of  $ZrO_2$  and the activities of  $SiO_2$  between two liquids. It was further demonstrated that the change in the ratio of the activity coefficients of  $ZrO_2$  and  $HfO_2$  cannot exceed the change in the ratio of their mole fractions in zircon and hafnon-saturated liquids (see above). From Tables 2 and 3 and Figs. 2 and 3 it is seen that the saturation concentrations of  $ZrO_2$  and  $HfO_2$  decrease smoothly and gradually with increasing silica concentration. As is the case in rutile-saturated liquids, the activity coefficients of  $ZrO_2$  and  $HfO_2$  increase smoothly and gradually with increasing  $SiO_2$ . Indeed, thermodynamic calculations (see above) indicate a maximum of a 40% in-

crease in the activity coefficient of  $ZrO_2$  and  $HfO_2$  over an interval of silica concentrations from 75 to 86 mole-%. Small changes in silica concentration thus do not cause large changes in the solution behavior of these cations.

The results of this study can be compared with the study of Watson and Harrison (1983), who determined zircon solubility in a variety of magmas over a range of temperatures, and in both water-saturated and water-undersaturated magmas. The authors derived an empirical relationship to describe zircon solubility in these experiments:

$$\ln D_{Zr}^{zircon/melt} = -3.80 - (0.85(M-1)) + 12,900/T,$$

where  $D_{Zr}^{zircon/melt}$  is the concentration ratio of Zr in stoichiometric zircon to that in the melt,  $M$  is the cation ratio  $(Na + K + 2Ca)/(Al \cdot Si)$ , and  $T$  is the absolute temperature.  $T$  is fixed and  $(Na + K)/Al$  is roughly constant in the liquids of this study. The model thus predicts that zircon saturation depends almost entirely on variations in  $1/Si$ . Since the silica concentration is so high, the change from 66.9 wt-% to 81.1 wt-%  $SiO_2$  results in only a small change in  $M$  values (see Table 2). When these values are used in the formula for zircon solubility the model predicts  $ZrO_2$  saturation concentrations of 1.9 wt-% in the 66.9 wt-%  $SiO_2$  liquid, and 1.7 wt-% for the liquid with 81.1 wt-%  $SiO_2$ , a total variation of about 10%. The observed variation is from 1.4 wt-% to roughly 1 wt-%, a change in  $ZrO_2$  solubility of 40%. The model calculates values for the saturation concentration of  $ZrO_2$  that are too high, and underestimates the magnitude of the variation observed experimentally in this study. In view of the vastly different experimental conditions between the study of Watson and Harrison and this study, however, the fact that the model comes so close to predicting the correct values is remarkable.

### Correlations with other experimental studies

Igneous rocks with 67 wt-%  $SiO_2$  typically contain 8 to 10 wt-% of components other than  $SiO_2$ ,  $Al_2O_3$ ,  $Na_2O$ , and  $K_2O$ , while in very siliceous rocks these other components are typically 3 to 4 wt-%. In addition, highly siliceous rocks are frequently not peraluminous, but metaluminous or peralkaline. Finally, anions such as  $F^{-1}$ ,  $Cl^{-1}$ ,  $PO_4^{-3}$ , and  $OH^{-1}$  are certainly present in the melt. It is thus necessary to evaluate the effects of these components upon the solution behavior of +4 cations.

#### Alkali/aluminum ratio

The studies of Watson (1979), Dickinson and Hess (1985), and Naski and Hess (1985) have shown that the alkali/aluminum ratio is one of the most important chemical factors affecting the solubility of +4 cations in silica-rich peralkaline liquids. The solubilities of Zr, Ti, and Sn increase strongly and linearly as functions of increasing alkali/aluminum ratio in peralkaline liquids. The change in the solubility of a given +4 cation varies in a fixed stoichiometry with the number of alkalis in excess of those needed to charge-balance Al. This stoichiometry does not vary with changes in temperature. It is concluded that alkali cations act directly to stabilize +4 cations in peralkaline silicate liquids. It is therefore expected that changes in the alkali/aluminum ratio over the course of differentiation of peralkaline magmas will have a much more pronounced effect upon the

solubility of +4 cations than small changes in silica concentration.

In contrast, the solubility of Ti and Sn are only weakly affected by changes in the alkali/aluminum ratio in peraluminous liquids. Variations in the alkali/aluminum ratio in the liquids reported here do not appear to significantly affect the trends seen in the solubility data. It is concluded, then, that neither changes in the alkali/aluminum ratio nor changes in the silica concentration will strongly affect +4 cation solubility in peraluminous liquids.

#### *Divalent cation concentration*

Dickinson and Hess (1985) show that rutile solubility increases upon the substitution of CaO for K<sub>2</sub>O in peraluminous liquids, but that it decreases with substitution of CaO for K<sub>2</sub>O in peralkaline liquids. Watson (1979) found that the addition of CaO lowers the solubility of zircon in peralkaline liquids. Thus the ratio of CaO/(Na<sub>2</sub>O + K<sub>2</sub>O), and most likely the ratio of MO/(Na<sub>2</sub>O + K<sub>2</sub>O) (where M = divalent cations such as Fe<sup>+2</sup> and Mg<sup>+2</sup>), affects the solution properties of Ti, Zr, and other +4 cations. Increases in the MO/(Na<sub>2</sub>O + K<sub>2</sub>O) ratio will increase the solubility of these cations in peraluminous liquids, but decrease their solubility in peralkaline liquids; however, small changes in the abundances of divalent cations will not strongly influence the solution behavior of +4, and other highly-charged cations in highly siliceous magmas.

#### *Na<sub>2</sub>O/K<sub>2</sub>O ratio*

The rutile-saturation experiments in this study incorporated Na<sub>2</sub>O in order to mimic natural compositions, whereas those of Dickinson and Hess (1985) used only K<sub>2</sub>O. The saturation concentration of TiO<sub>2</sub> in comparable liquids of both studies are very similar (within the uncertainties of measurement) suggesting that the Na/K ratio does not significantly affect rutile solubility. This interpretation is generally consistent with the lack of dependence of Ti solubility upon the Na/K ratio in liquids of this study, and is also consistent with the results of Watson (1979) for zircon saturation experiments. Changes in the Na/K ratio in magmas, then, are unlikely to significantly affect the solution behavior of highly-charged cations.

#### *The effects of water*

The experiments of this study, the rutile-saturation study of Dickinson and Hess (1985) and the cassiterite-saturation study of Naski and Hess (1985) are anhydrous experiments run at high temperature, whereas the zircon-saturation experiments of Watson (1979) are water-saturated, at much lower temperatures (700° to 800° C), and higher pressure (2 kb). Despite the considerable differences in experimental conditions, the behavior of the +4 cations in both water-saturated and anhydrous experiments have many similarities. For example, it was found that the saturation concentrations of all these +4 cations increase sharply and linearly with increasing alkali/aluminum ratio in peralkaline melts. The +4 cations are inferred to be stabilized in peralkaline liquids by forming +4 cation-alkali complexes, and the stoichiometries of these complexes are not affected by changes in temperature. Watson (1979) found that zircon solubility decreases slightly with increasing silica concentration in per-

alkaline liquids, much as was found for peraluminous liquids in this study. The correlations between the anhydrous experiments and those of Watson (1979) strongly suggest that water primarily lowers liquidus and solidus temperatures, and does not strongly affect the solution mechanisms of these cations. This conclusion is further supported by experiments of Watson and Ryerson (1986), who found that rutile solubility at 15 to 30 kb shows no apparent dependence upon H<sub>2</sub>O or CO<sub>2</sub> contents in liquids from basaltic to rhyodacitic compositions. Experiments in progress will determine the saturation surface of zircon as a function of the alkali/alumina ratio in dry, siliceous liquids to further investigate this question.

While the high TiO<sub>2</sub> concentration of rutile-saturated liquids makes them quite unlike natural compositions, the bulk compositions of highly-siliceous zircon and hafnon-saturated liquids are very similar to the anhydrous compositions of high silica magmas, which may contain only 3 wt-% of components other than SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O (see Mahood and Hildreth 1983, for excellent examples of high silica rhyolites). Since +4 cations show broadly similar behavior whether in water-saturated conditions (Watson 1979) or anhydrous conditions (e.g., Dickinson and Hess 1985), it is suggested that the conclusions of this study are generally applicable to highly siliceous magmas under a variety of crustal magma conditions. What is most interesting about this conclusion is that the +4 cations discussed above are very different. For example, while strongly metallic behavior is expected of Ti, Zr, and Hf, the position of Sn in the periodic table indicates Sn—O bonds should be less ionic than those of Ti, Zr, and Hf. The ionic radius of Ti is significantly smaller than that of Sn, which in turn is smaller than Zr and Hf, whose ionic radii are nearly identical (Shannon 1976). The broadly similar behavior of these cations in silicate liquids suggests that the solution behavior of other +4 – and probably +5 cations (Hess 1986) – will be only weakly affected by small changes in silica concentration.

#### *Substitution of SiO<sub>2</sub> for other cations*

It is important to note that the substitution of SiO<sub>2</sub> for MAIO<sub>2</sub> (where M = Na, K) does not change the polymerization of the liquid *sensu stricto* because aluminum is a network-forming cation when charge-balanced by alkali cations. In effect, one network-forming cation (Si<sup>+4</sup>) is substituted for another (M<sup>+1</sup>Al<sup>+3</sup>) in the silicate network structure. Therefore, changes in the solution behavior of the cations in this study are almost entirely due to changes in the *nature* of the polymerization of the silicate liquids, not the *degree* of polymerization. Changes in the degree of polymerization are caused by the formation of non-bridging bonds and the breakdown of the aluminosilicate network. Similarly, alkalis in excess of aluminum form non-bridging bonds and disrupt the aluminosilicate network.

This study demonstrates that high silica concentration alone does not cause novel solution properties in silicate liquids, but does not address the effect of changes in the degree of polymerization. These effects are indirectly investigated in the studies of +4 cation solution behavior cited above in which the alkali/aluminum ratio is varied at fixed silica concentration. It is of interest to examine the solution behavior of +4 cations as both the *nature* and the degree of polymerization are changed. From the discussion above,

it is clear that this may be investigated experimentally simply by substituting  $\text{SiO}_2$  for an ALK/Al mixture that has an alkali/aluminum ratio greater than unity. In this way  $\text{SiO}_2$  is substituted not only for  $\text{MAIO}_2$ , but for  $\text{M}_2\text{O}$  as well – that is, the *nature* of T–O–T bonds is changed, and the *number* of M–O–T bonds is decreased. It is this type of substitution that occurs during the differentiation of silica-rich metaluminous and peralkaline magmas. Watson (1979) measured the silica-dependence of zircon saturation in water-saturated peralkaline liquids using essentially this method and observed no consistent dependence. Experiments are in progress using this method to investigate zircon saturation in anhydrous, siliceous, peralkaline liquids. Preliminary results show that small substitutions of  $\text{SiO}_2$  for  $\text{K}_2\text{O} + \text{KAlO}_2$  cause only small changes in the saturation concentrations of  $\text{ZrO}_2$ . The conclusions of this paper are therefore generally valid for high silica melts. A summary of these experiments and a model of cation solution behavior in siliceous silicate liquids that successfully describes the results of this and other studies of highly-charged cations will be published separately.

## Petrologic applications

### *Trace elements distributions in high silica rhyolites*

The results of this study contribute to the general understanding of the solution properties of minor and trace elements and how they are affected by changes in the bulk compositions of silicate melts. An example of the need for this information is seen in the study of so-called high silica rhyolites, defined by Mahood and Hildreth (1983) as having silica concentrations in excess of 75 wt-% (anhydrous). Trace element abundances and distributions in these and other cogenetic suites of highly-siliceous rocks often show large variations despite only small changes in the concentrations of major rock-forming elements. For instance, the silica concentration of the Bishop Tuff varies 2 wt-%, from 77.4 wt-% (anhydrous) in the “early” eruptive unit to 75.5 wt-% in the “late” eruptive unit (Hildreth 1979); yet there is a three-fold increase in Ti, a two-fold increase in Zr, and large changes in the concentrations of other highly-charged cations from the “early” to “late” eruptive units. The changes in the concentrations of trace elements can be very dramatic – a 22-fold increase in Sr, and a 50-fold increase in Ba from “early” to “late” units. The physical or chemical processes that produce rocks with such fractionated trace element trends are vigorously debated. Models range from liquid-state processes (Hildreth 1979; Bacon et al. 1981; Mahood 1981; Mahood and Hildreth 1983; and others) to crystal-liquid fractionation processes (Christiansen 1982; Michael 1982; Miller and Mittlefehldt 1982, 1984; Cameron, 1984; and others).

Mahood (1981) and Mahood and Hildreth (1983) suggest that small changes in the bulk composition of a high silica liquid may profoundly affect its structural properties, resulting in large changes in the solution properties of trace elements. Mahood (1981) discusses the bulk compositions and trace element distributions of the rhyolitic rocks of the Sierra La Primavera volcanic suite. The extrusive rocks of the ring domes (Older and Younger Ring Domes, or O.R.D. and Y.R.D., respectively), the southern arc lavas, and the Cerro El Colli dome rocks represent successive tappings

of the magma chamber. The Hf and Zr concentrations decrease markedly from the older to the younger rocks. Zr and Hf are three times and 1.5 times more abundant in the older rocks, respectively. The Zr/Hf ratios are very similar within single eruptive units, but decrease significantly as the rocks become younger. Ti concentration also decreases by nearly a factor of three from O.R.D. to the Cerro El Colli rocks.

The results of this study, as well as those of Watson (1979), show that changes in the solution behavior of +4 cations do not change dramatically with small changes in silica concentration, for liquids with silica concentrations below those of granites to concentrations far in excess of 75 wt-%. The thermodynamic analyses above show that the solution mechanisms of these cations change smoothly and gradually from low silica liquids to high silica liquids. The changes in solution behavior inferred from Sierra La Primavera cannot be produced by the observed changes in silica concentration. While useful as a means of distinguishing these rocks, liquids with 75 wt-% silica do not have solution behaviors that are significantly different than less siliceous liquids. Such a classification should not be interpreted as implying unique chemical properties.

It should be noted that changes in silica concentration are by no means the only compositional changes that are observed or inferred in high silica rhyolites. Using data from Mahood (1981), the alkali/aluminum ratio in the sequence of volcanics described above decreases from roughly 1.09 to 1.03, while the total weight-fraction of cation components other than  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  decreases from 2.6 wt-% to about 0.5 wt-%. Experimental studies discussed above suggest that these changes are much too small to have caused the observed changes in +4 cation distributions; however, the presence of other complicating factors cannot be disregarded. For example, large quantities of volatiles ( $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{F}_2$ ,  $\text{Cl}_2$ , etc.) have been lost as a result of eruption, and, with the exception of  $\text{H}_2\text{O}$ , their effects upon silicate melt structure and cation solution behavior are poorly known. Finally, it should be emphasized that the focus of this study is the solution behavior of highly-charged cations with small ionic radii. Larger cations with lower ionic charge may show somewhat larger variations (see Leshner 1986, for the special case of cation behavior during thermal diffusion). These observations, however, do not change the fact that small changes in silica concentration do not and cannot produce large changes in the solution behavior of highly-charged cations, and high silica concentrations by themselves do not imply unusual chemical properties.

### *Zr/Hf ratios*

Because of the similarities in the ionic radii, electronic structures, and other elemental properties of Zr and Hf, it is perhaps not surprising that both show nearly identical variations in saturation concentration with increasing silica concentration. Because both saturate at nearly the same molar concentrations in liquids with similar bulk compositions, their solution mechanisms in these liquids must be similar. This, in turn, implies that liquid-state processes are unlikely to fractionate one with respect to the other. Variations in the Zr/Hf ratio seen in cogenetic suites of igneous rocks, such as in Sierra La Primavera (Mahood 1981), are likely due to crystal-liquid fractionation, such as between



zircon and a liquid, or due to influxes of magma from geochemically distinct source regions.

## Conclusions

The conclusions from this study are as follows:

1. The saturation concentrations of the +4 cations Ti, Zr, and Hf decrease smoothly and gradually with increasing silica concentration.
2. The activity coefficients of Ti, Zr, and Hf increase smoothly, gradually, and continuously as functions of increasing silica concentration.
3. Small changes in silica concentration cannot produce large, unanticipated changes in the solution chemistry of highly-charged cations.
4. Silica concentration, in and of itself, does not serve as a useful means of distinguishing the chemical behavior of highly siliceous rocks from less siliceous rocks, because small changes in silica concentration in highly siliceous liquids do not result in large changes in cation solution behavior. The term "high silica rhyolite" thus does not imply unique solution chemistry.
5. The changes in silica concentration seen in the suites of highly siliceous rocks cannot produce the observed variations in the concentrations of +4 cations.
6. Liquid state processes alone cannot fractionate Zr and Hf with respect to one another. Variations in Zr/Hf ratios in cogenetic suites of rocks probably require either selective partitioning of Zr or Hf into growing phenocrysts, or influxes of magma with different Zr/Hf ratios than the resident magma.

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