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LETTER

The solubility of H_2O in peralkaline and peraluminous granitic melts

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ABSTRACT

The solubility of H_2O in a series of 13 melts based on a haplogranitic composition (HPG8) have been determined for the conditions of 500–5000 bar pressure and 800–1000 °C. The compositions represent the additions of individual components (Cs_2O, Rb_2O, K_2O, Na_2O, Li_2O, and Al_2O_3) to HPG8 (in wt% 78.6 SiO_2, 12.5 Al_2O_3, 4.6 Na_2O, 4.2 K_2O; see Knoche et al. 1995) to generate peralkaline and peraluminous compositions, respectively. The H_2O-saturated melts were generated by hydrothermal fusion of dry glassy starting materials in an internally heated pressure vessel. The quenched products of the hydration experiments were analyzed by Karl-Fischer titration for bulk H_2O contents.

H_2O solubility increases with added excess alkali oxide. Compared on a weight percent basis, the solubility of H_2O for a given degree of peralkalinity increases in the order Cs, Rb $<$K $<$ Na $<$ Li. On a molar equivalent basis the effects of excess Cs, Rb, K, and Na on increasing the solubility of H_2O are the same, whereas the effect of Li_2O is somewhat lower. This contrasts with the relatively high solubility of H_2O in $LiAlSi_3O_8$ melt relative to albite and orthoclase melts and implies that excess Li_2O is not contributing to the content of nonbridging O atoms in the melt as efficiently as the other alkalies.

For the peraluminous compositions, the solubility of H_2O decreases with the addition of 2 wt% Al_2O_3 to the HPG8 composition, then increases strongly with the further addition of excess Al_2O_3, so that a solubility minimum exists not at the 1:1 alkali-Al ratio of melt composition but at a slightly peraluminous melt composition. The solubility of H_2O in the melt with 5 wt% excess Al_2O_3 is significantly larger than that in HPG8. If the peraluminous composition with the minimum solubility of H_2O is taken as a basis for estimating the influence of nonbridging O atoms associated with ‘‘excess’’ alkalies or Al in the melt structure then the effects of excess Al and alkalies (Cs, Rb, K, Na) are comparable on the basis of the number of nonbridging O atoms added to the slightly peraluminous base.

The addition of Na_2O up to levels of peralkalinity commonly encountered in glassy magmatic eruptive rocks of peralkaline volcanic provinces leads to an almost doubling of the low pressure (500 bar) solubility of H_2O in the melt. Evidence for an H_2O-rich history of glassy peralkaline obsidians from melt inclusions or from stable isotopes may indicate much shallower depths of saturation than previously thought possible.

INTRODUCTION

The alkali-Al ratio of alkali aluminosilicate melts is a compositional parameter influencing several melt properties, including viscosity, density, diffusivities, and gas solubilities. The influence of the alkali-Al ratio on the solubility of H_2O in granitic melts is a subject of considerable interest regarding the evolution of H_2O-rich granitic magmas from undersaturated to saturated conditions during the late stages of igneous fractionation. Preliminary evaluation of the effect of the alkali-Al ratio on the solubility of H_2O in such melts is available from several previous studies. The early phase-equilibrium studies of Morey and coworkers (Morey and Fenner 1917; Morey and Ingerson 1938; Morey and Hesselgesser 1952) in Al-free alkali silicate systems indicates that solubility of alkali silicate phases is very high in H_2O. Clear chemographic indication of enhanced solubility of H_2O in peralkaline melts is also available from Mustart (1972) and this general trend was confirmed by analytical determination of H_2O solubility by Dingwell et al. (1984). The present experimental study was conducted to evaluate systematically the influence of the alkali-Al ratio on the solubility of H_2O in granitic melts.

METHODS

Several experimental and analytical procedures were used in the last decades to determine H_2O solubilities in silicate melts (see discussions in Ihinger et al. 1994, Behrens 1995). In this study, the experimental technique consisted of using anhydrous, bubble-free blocks of glass, sealed in a noble-metal capsule with an amount of water sufficient to reach H_2O saturation. After hydration of the samples at high *P* and *T*, H_2O contents in the quenched glasses were determined by Karl Fischer titration. A detailed description of both experimental and analytical procedures used to determine H_2O solubilities in this study has been given already by Behrens (1995) and Holtz et. al. (1995). It is emphasized that these procedures can be used successfully to determine H_2O solubilities in aluminosilicate melts containing 1 to 10–14 wt% H_2O (Behrens 1995).

The starting compositions were synthesized to represent the additions of individual components to a haplogranitic base composition near the 2 kbar H_2O-saturated ternary minimum composition in the $KAlSi_3O_8$-$NaAlSi_3O_8$-SiO_2 system, labelled HPG8 (see composition above). These glasses were used in several studies to determine the physical properties of melts (Hess et al. 1995, Knoche et al. 1995) and were prepared from powders of carbonates (Li, Na, K, Rb, Cs) and oxides (Al, Si) placed in platinum crucibles inside a $MoSi_2$ box furnace. The partially fused products were transferred to a viscometer furnace, fused again, and stirred from hours to days until melts were bubble-free (see procedure in Knoche et al. 1995). The compositions of the dry glasses were determined by ICP-AES methods and have been presented by Knoche et al. (1995).

Glass cylinders of 40–70 mg were sealed together with doubly distilled water in gold capsules. The proportions of H_2O were 5–6, 10–12, and 15–17 wt% for experiments carried out at 0.5, 2, and 5 kbar, respectively. Experiments were conducted in internally heated pressure vessels working horizontally (0.5 kbar) or vertically (2–5 kbar, see Roux and Lefèvre 1992 for descriptions). Experimental durations were 12–17 d at 0.5 kbar (1000 °C), 7–9 d at 2, 4, and 5 kbar (800–900 °C). These durations were long enough to allow compete homogenization of H_2O through the sample (for diffusion coefficients of H_2O in haplogranitic or feldspar melts, see review in Watson 1994). Isobaric quenching was performed for 0.5 and 2 kbar experiments, but not for the 4 and 5 kbar experiments (for technical reasons). Most quenched experimental glasses were clear and bubble free. Two peraluminous glasses (+5Al) contained mullite needles (Table 1) after the quench. Some glasses synthesized at 5 kbar were cloudy as a result of the formation of bubbles during the quench. However, because we used a bulk analytical technique (Karl-Fischer titration) for the determination of H_2O in the glasses, the presence of bubbles containing H_2O is not expected to affect the determined H_2O solubility, as demonstrated by Holtz et al. (1995, see table p. 98).

TABLE 1. Experimental data for water solubility

Sample	*P* (kbar)	*T* (°C)	Water analysis (KFT)	Solubility
HPG8	0.5	1000	2.28, (2.35–2.45)*	2.44
	2	800	5.94*	6.04
	5	900	9.34, 9.38	9.46
+2Al	0.5	1000	2.11, 2.13	2.22
	2	800	6.07	6.17
	5	900	9.71	9.81
+5Al	0.5	1000	2.70 (cr)	
	2	800	6.12 (cr)	
	5	900	(9.91–9.82)	9.96
−2Al	0.5	1000	2.44, 2.48	2.56
	2	800	6.10, 6.18	6.24
	5	900	10.21	10.31
−5Al	0.5	900	2.89, 2.93	3.01
	2	800	6.67, 6.77	6.82
	4	800	11.22	11.32
	5	900	11.91, 12.19	12.15
5Li	0.5	1000	3.31	3.41
	2	800	8.12	8.22
	4	800	12.15	12.25
10Li	0.5	1000	3.70	3.80
5Na	0.5	1000	3.08	3.18
10Na	0.5	1000	3.57	3.67
5K	0.5	1000	2.83	2.93
5Rb	0.5	1000	2.54	2.64
	2	800	6.56	6.66
10Rb	0.5	1000	2.76	2.86
5Cs	0.5	1000	2.45	2.55

Note: The different water contents determined by Karl-Fischer titration (KFT) for a given composition and given *P-T* conditions are obtained from samples synthesized in different experiments. Analyses given in parentheses were duplicated for the same sample. Water solubilities were calculated from average values obtained by KFT and by adding 0.1 wt% H_2O (see Behrens 1995).

* Data are taken from Holtz et al. (1995, 1992). The presence of mullite is indicated by (cr).

H_2O contents were determined by Karl Fischer titration with the use of an extraction line coupled with a high-frequency generator (Behrens et al. 1996). H_2O is extracted from the hydrous glass sample by heating the sample placed in an induction coil up to 1300 °C. The H_2O is carried toward the titration cell by a flow of dry argon. Typical heating rates are given by Behrens (1995) and Holtz et al. (1995). For glass samples of 10 mg or more (weight of the samples analyzed in this study), these authors have calculated a precision of the determined H_2O contents of ± 0.15 wt% H_2O.

RESULTS

The results are presented in Table 1 as a function of the amount of oxide added to HPG8. A trend of increasing H_2O solubility with increasing alkali oxide content is clearly evident. Also clear is that the solubility of H_2O in the peralkaline melts, compared at a constant weight percent of added alkali oxide, increases in the order Cs, Rb $<$ K $<$ Na $<$ Li. Most of the results presented in Table 1 were obtained at 0.5 kbar. Although few data are avail-

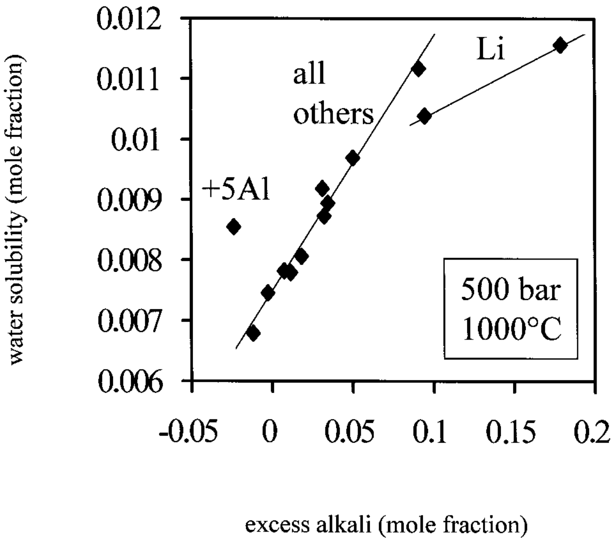

FIGURE 1. The effect of excess alkalies on the solubility of H_2O in granitic melts at 500 bar and 1000 °C. The excess alkali content is defined as the difference between the total mole fraction of alkalies and that of Al. The solubility data for H_2O in melts with excess alkalies all lie on a single curve with the exception of the two data points for excess Li on the right and one for excess Al on the left. The line defining the bulk trend does not pass through a minimum at 0 but rather at a slightly peraluminous composition. See text for a discussion of the relevance of these trends.

able at higher pressure, the comparison of data obtained for 5Li, −2Al and −5Al compositions indicates that the same behavior can be expected at pressures up to 5 kbar. Clearly a small weight percent addition of excess Li_2O in a peralkaline melt can generate a significant increase in H_2O solubility. Similarly, the maximum geologically reasonable levels of excess Na_2O in peralkaline volcanics can lead to large increases in the solubility of H_2O in such melts.

The effect of excess Al_2O_3 on H_2O solubility is also included in Table 1. Starting from peralkaline compositions, increasing the Al_2O_3 content of the melts produces a decrease of the H_2O solubility down to a minimum and then an increase of the H_2O solubility in strongly peraluminous compositions. The minimum is close to the subaluminous composition (HPG8) at 2 and 5 kbar. However, at 0.5 kbar the H_2O solubility minimum is shifted toward the peraluminous compositions.

It should be noted that the minimum H_2O solubility that is found in this study near Al/(Na + K) = 1 is in good agreement with the data of Dingwell et al. (1984) at 1 kbar and 800 °C. An excellent agreement is also observed with the data of Linnen et al. (1996) obtained at 850 °C and 2 kbar (in this study, data are obtained at 800 °C and 2 kbar). In these two previous studies, the compositions investigated are haplogranitic or correspond to the peralkaline and peraluminous equivalents of haplogranitic compositions (compositions belong to the system SiO_2-Al_2O_3-Na_2O-K_2O). Qualitatively, a good agreement with the H_2O solubilities determined by Oxtoby and Hamilton (1978) at $P < 2$ kbar and Behrens (1995) between 0.5 and 5 kbar for a subaluminous albite composition and equivalent peralkaline compositions is observed (the H_2O-solubility data determined are higher than in this study, as a result of changing normative feldspar and quartz proportions). At higher pressures, Oxtoby and Hamilton (1978) observe a crossover of the solubility curves (higher solubility in albite melts than in the equivalent peralkaline composition) but it has been shown that the analytical procedure used to determine the H_2O contents dissolved in the glasses used by Oxtoby and Hamilton (1978) is not suited for glasses with high H_2O contents (Behrens 1995). At pressures higher than 1 kbar, the minimum H_2O solubility is clearly at Al/(Na + K) = 1, which contrasts with our results obtained at low pressure (0.5 kbar).

Figure 1 compares the influence of the individual alkali oxides on the solubility of H_2O on the basis of moles of added oxide. This molar comparison reveals that the molar effect of peralkalinity is identical for all the alkali oxides with the exception of Li_2O. The lower enhancement of H_2O solubility with the addition of Li_2O can be taken to imply that excess Li_2O does not generate nonbridging O atoms in the peralkaline melt structure that are accessible for coordination by hydrous species. This contrasts with the enhancement of solubility in $LiAlSi_3O_8$ melt compared with albite and orthoclase melts at 2 kbar and 800 °C. Whether the inference can be drawn that the coordination of Li deviates from the rest of the alkalies to a lower value of mean coordination number remains open.

DISCUSSION

If the minimum in H_2O solubility shifts in position from 0.5 kbar (in melts with approximately 2 wt% H_2O) to 2 and 5 kbar, this might imply that the other properties of hydrous subaluminous and peraluminous melts change at low pressure (at low melt-H_2O content) when compared with high pressure (high melt-H_2O content). In particular, it might reflect an change in Al activity in these melts and the stability of aluminosilicate phases as well as phase relationships. For example, the effects of excess Al_2O_3 on phase relationships in the Qz-Ab-Or system at low pressure may be qualitatively different from those determined by Holtz et al. (1992) and Joyce and Voigt (1994) at 2 kbar.

From Figure 1, increasing Na, K, or Na + K produces the same increase in H_2O solubility. This suggests that the effect of the exchange of these two alkalis on H_2O solubility is very low at 0.5 kbar. At 0.5 kbar, Holtz et al. (1995) also observed a very weak change in H_2O solubility for changing Na/K in haplogranitic melts (subaluminous compositions). Thus, our data confirm that the Na/K ratio in melts at 0.5 kbar has very little effect on the H_2O solubility mechanisms, in subaluminous melts as well as in peralkaline to peraluminous compositions. This contrasts with the data of Oxtoby and Hamilton (1978, at $P < 2$ kbar), Holtz et al. (1992, 1995), Behrens (1995), and Romano et al. (1996) showing a significant effect of the alkalies at 1–5 kbar in alkali feldspar melts. Unfortunately, we have no data at higher pressure to confirm that the alkali effect also exists in peraluminous to peralkaline melts, but it is emphasized that the thermodynamic and empirical models proposed to calculate H_2O solubilities (e.g., Burnham and Nekvasil 1986, Burnham 1994, Moore et al. 1995) do not account for that effect. Although this alkali effect observed at $P > 1$ kbar becomes less important (but not negligible) if solubilities are calculated for natural compositions, it should be taken into account in future models for the incorporation and solubility mechanisms of H_2O in aluminosilicate melts.

The simplest considerations of the implications for the solubility minimum in the petrogenesis of granitic magmas involves the variations in the timing of boiling in such systems because of crystallization of liquidus phases with an alkali-Al ratio different from that of the melt composition. Crystallization of feldspars from slightly peraluminous melts can be expected to drive the liquid composition more rapidly toward boiling as the H_2O solubility drops significantly with increasing peraluminosity. This could act as a potential barrier to developing peraluminous melts in nature with more than a few percent normative corundum. Such melts are indeed not very common.

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