Water solubility in aluminosilicate melts of haplogranite composition at 2 kbar

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ABSTRACT

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The compositional dependence of H_2O solubility was investigated at 2 kbar and 800°C in haplogranite melts (system SiO_2–$NaAlSi_3O_8$–$KAlSi_3O_8$ or Qz–Ab–Or). The sixteen investigated compositions contained 25, 35 or 45 wt.% normative Qz and various Ab/(Ab+Or) ratios (0.15–0.92). Starting solid materials were anhydrous bubble-free glasses to which 10 wt.% H_2O was added. The H_2O contents of the isobarically quenched melts (glasses) were measured by Karl–Fischer titration.

The results show that H_2O solubility in aluminosilicate melts depends significantly upon anhydrous composition. The highest solubility values are obtained for the most Ab-rich melts. At a constant normative quartz content, the solubility of water decreases from 6.49 ± 0.20 wt.% H_2O for a composition $Qz_{35}Ab_{60}Or_{05}$ (normative composition expressed in wt.%) to 5.50 ± 0.15 wt.% H_2O for a composition $Qz_{35}Ab_{10}Or_{55}$. Along this join, the most significant changes are observed for Ab-rich melts whereas H_2O solubility in Or-rich melts remains almost constant.

The H_2O solubility data imply that H_2O is preferentially associated with the Ab component in aluminosilicate melts. Application of the results to natural granitic melts suggests that Na-rich, H_2O-saturated melts may be significantly less viscous than H_2O-saturated, K-rich melts.

The temperature dependence of H_2O solubility, investigated for composition $Qz_{28}Ab_{38}Or_{34}$ at 2 kbar, is low. Increasing temperature from 750° to 1150°C only causes a decrease in H_2O solubility from 6.00 to 5.41 wt.% H_2O. These data are in agreement with previous data obtained for albite melts.

1. Introduction

The solubility of H_2O in natural or synthetic granitic melts has been the subject of numerous studies (e.g., Goranson, 1931; Khitarov et al., 1959; Burnham and Jahns, 1962; Orlova, 1963; Oxtoby and Hamilton, 1978a, b; Dingwell et al., 1984). However, there are significant variations in the data for a given pressure (*P*), temperature (*T*) and composition. As a typical example, the reported H_2O solubility in albite melts varies from 7 to 10 wt.% at 3 kbar (e.g., Goranson, 1931; Burnham and Jahns, 1962; Orlova, 1963; Oxtoby and Hamilton, 1978a; Dingwell, 1987; Blamart et al., 1988). The variation of the data is due to the use of various starting materials (gel, powdered glass, pieces of glass, crystals) and various analytical techniques for the determination of the H_2O content (see reviews in Day and Fenn, 1982; Dingwell et al., 1984; McMillan and Holloway, 1987). In addition, quenching may not have been always performed under perfectly

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isobaric conditions, a factor which may influence significantly the solubility data. Thus, data obtained by different methods are not directly comparable and the absolute value of H_2O solubility is only known within a large uncertainty.

This study is an attempt to determine the effect of melt composition on the solubility of H_2O in the system $SiO_2(Qz)$–$NaAlSi_3O_8(Ab)$–$KAlSi_3O_8(Or)$ by using a single experimental and analytical method to obtain a consistent dataset at constant P and T (2 kbar, 800°C). In order to extend the compositional dependence to other temperatures, the effect of T on H_2O solubility has also been investigated for one composition close to the minimum melt composition (composition with the lowest liquidus temperature in the Qz–Ab–Or system or composition of the liquid participating in the solidus reactions). Most of the previous investigations of H_2O solubility in the system Qz–Ab–Or were carried out with one or with a limited number of compositions (mainly pure albite melts). One exception is the work of Voigt et al. (1981) in which H_2O solubility was investigated for several compositions in the binary system Ab–Or (however, data are only given for the Ab and Or end-member compositions). Clearly, there is a need for a coherent dataset of H_2O solubility values for compositions in the system Qz–Ab–Or, considering the important contribution of this system (e.g., Tuttle and Bowen, 1958) to the interpretation of granites and rhyolites. Although H_2O solubility has been measured for a variety of natural granitic and rhyolitic rocks (e.g., Khitarov et al., 1959; Burnham and Jahns, 1962; Oxtoby and Hamilton, 1978a) such data cannot be easily interpreted because they were obtained for a single multicomponent composition, in which additional elements, although present only in low concentrations may still influence significantly the solubility data (i.e. F, B, Li, Rb, excess Al). In addition, considering the current debate on solubility mechanisms of H_2O in aluminosilicate melts (e.g., Burnham, 1981; Stolper, 1982;

Mysen and Virgo, 1986; Kohn et al., 1989; Silver and Stolper, 1989; Silver et al., 1990), an internally consistent H_2O solubility dataset in the system Qz–Ab–Or may help to provide new insight into the solution mechanism(s) of H_2O in such systems.

2. Starting material and experimental technique

2.1. Starting glasses

The starting materials for preparation of the haplogranite glasses were powders of Na_2CO_3, K_2CO_3, Al_2O_3 and SiO_2 of p.a. quality. Sixteen compositions with three different normative Qz contents were synthesized (Qz_{45}, Qz_{35}, Qz_{25}). Along these sections at constant normative Qz content, five or six compositions with different Ab/(Ab+Or) ratios were prepared. The powders of the starting materials were dried at 120°C overnight prior to weighing. The powders were mixed in plastic bottles by agitation for ~5–10 min. The mixtures were melted stepwise into 75 cm³ thin-walled platinum crucibles and fused directly at 1600°C over a period of several hours. The products of the initial fusions were bubble-rich and inhomogeneous. To remove the bubbles and promote homogenization, the fused batches were loaded into a box furnace and reheated at 1700°C. At this temperature, the melts were stirred at 10–20 rpm with a $Pt_{80}Rh_{20}$ spindle for several days until virtually devoid of bubbles. The bubble content of the liquids was periodically checked by removing the stirrer from the melt and inspecting optically the adhered melt. Bubble-free melts were cooled slowly in the box furnace to <800°C, and then removed with their mullite cradles and allowed to cool slowly to room temperature in order to prevent excessive cracking during quenching.

The glass used for the investigation of T dependence was prepared by Schott Company (Mainz, Germany; melting number N8886)

and contained few bubbles.

The homogeneity and composition of the starting glasses were tested by electron microprobe analysis. The results of the analyses are given in Table 1 as the proportions of the oxides and as recalculated CIPW normative contents of quartz (Qz), albite (Ab) and orthoclase (Or). The compositions are also plotted in the Qz–Ab–Or ternary diagram in Figs. 1 and 2 (open circles for glasses prepared by ourselves, star for the glass prepared by Schott[®]).

2.2. Experimental procedure and apparatus

The same procedure was used for all experiments carried out in order to define the compositional dependence of H_2O solubility (experiments at 800°C). Small glass cylinders (diameter: 3 mm; length: 2–3 mm) were sampled by diamond coring tools, cleaned ultrasonically in acetone and then dried at 110°C to remove any residue of acetone. In each gold capsule (diameter: 4 mm; length: 15 mm), one cylinder was sealed together with ~10 wt.% of

TABLE 1

Composition of starting glasses (average values of 10 microprobe analyses, compositions normalized to 100%)

No. Qz/Ab/Or	HPG1 25/60/15	HBG2 25/50/25	HBG3 25/40/35	HPG4 25/30/45	HPG5 25/20/55	HPG6 35/60/05	HPG7 35/50/15	HPG8 35/40/25
Composition of major oxides (wt.%):								
K₂O	2.55	4.24	5.92	7.48	9.25	0.89	2.61	4.23
Na₂O	6.71	5.74	4.63	3.50	2.38	6.48	5.67	4.60
Al₂O₃	14.11	13.94	13.95	13.70	13.55	12.43	12.25	12.07
SiO₂	76.63	76.08	75.50	75.32	74.82	80.19	79.47	79.10
CIPW norms:								
Qz	27.85	26.75	26.14	26.86	26.70	39.10	36.51	36.38
Or	15.07	25.00	34.93	44.30	54.61	5.26	15.42	25.00
Ab	56.70	48.15	38.85	28.78	18.25	54.83	74.97	38.53
C	0.38	–	–	–	–	0.81	0.10	–
KS	–	–	–	–	–	–	–	–
NaS	–	0.10	0.08	0.21	0.44	–	–	0.09

No. Qz/Ab/Or	HPG9 35/30/35	HPG10 35/20/45	HPG11 35/10/55	HPG12 45/50/05	HPG13 45/40/15	HPG14 45/30/25	HPG15 45/20/35	HPG16 45/10/45	Schott® 28/38/34
Composition of major oxides (wt.%):									
K₂O	5.89	7.50	9.24	0.89	2.64	4.21	5.90	7.64	5.68
Na₂O	3.46	2.38	1.21	5.46	4.54	3.48	2.37	1.21	4.65
Al₂O₃	11.83	11.85	11.79	10.59	10.45	10.24	10.09	10.13	13.53
SiO₂	78.82	78.27	77.76	83.06	82.37	82.06	81.64	81.03	76.14
CIPW norm:									
Qz	36.86	36.27	35.96	47.90	45.86	45.84	45.85	45.13	28.16
Or	34.80	44.32	54.60	5.26	15.60	24.88	34.86	45.14	33.59
Ab	28.06	19.20	9.20	46.20	38.41	29.23	19.05	9.57	37.92
C	–	–	–	0.64	0.12	–	–	–	–
KS	–	–	–	–	–	–	–	–	–
NaS	0.28	0.22	0.24	–	–	0.05	0.23	0.16	0.33

Glasses labelled HPG were synthesized by ourselves. Glass labelled Schott® was synthesized by Schott Company, Mainz, Germany. Qz = quartz; Or = orthoclase; Ab = albite; C = corundum; NaS = Na₂SiO₃; KS = K₂SiO₃.
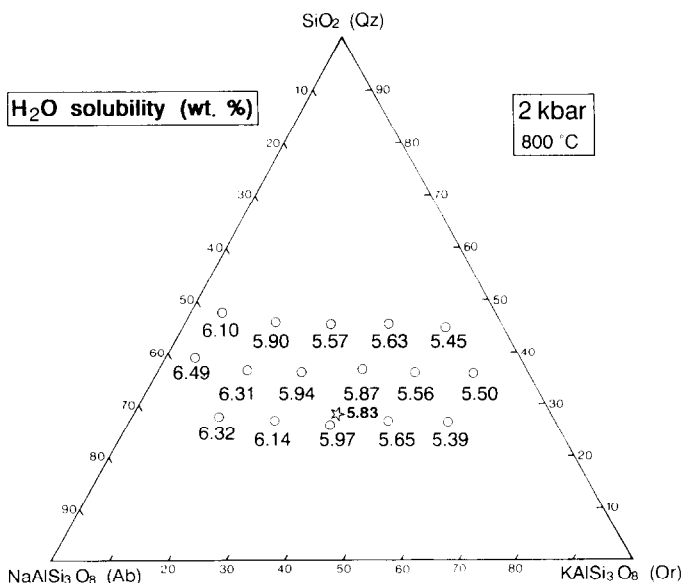
Fig. 1. H_2O solubility, expressed as wt.% H_2O, for 16 melt compositions (represented by *dots*) of the haplogranite system Qz–Ab–Or at 2 kbar, 800°C. The solubility value for each composition is indicated beneath the corresponding dot. The Qz, Ab and Or contents of the investigated compositions are given as wt.% normative proportions. All analytical data are given in Tables 1 and 2. The *star* represents the composition of Schott [®] glass ($Qz_{28}Ab_{38}Or_{34}$), for which the T dependence of H_2O solubility was investigated (see Fig. 3).
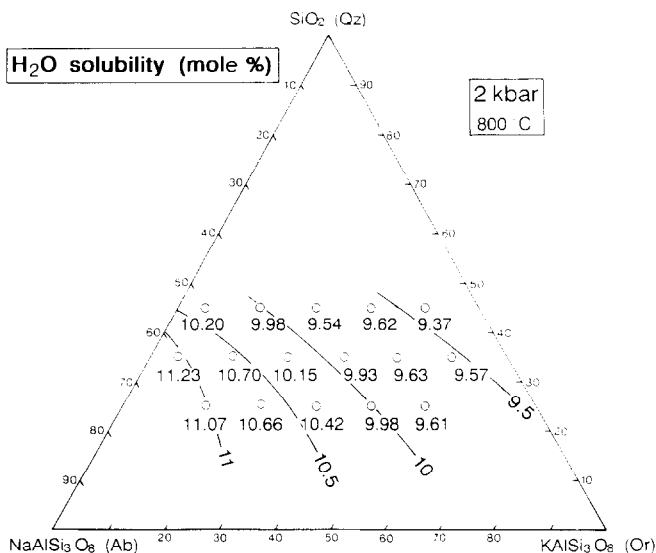

Fig. 2. H_2O solubility, expressed as mole% H_2O (calculated on one oxygen basis), for 16 melt compositions of the haplogranite system Qz–Ab–Or at 2 kbar, 800°C. *Lines* correspond to H_2O solubility isopleths (for further remarks, see Fig. 1).

double-distilled H_2O. The amount of added H_2O was chosen to be slightly higher than the expected solubility value (6.5 wt.% for a composition $Qz_{35}Ab_{39}Or_{26}$ at 685°C and 2 kbar; Luth, 1976). The capsules were checked for possible leakage by testing for weight loss after drying in an oven at 100°C for one to several hours. After such a period at 100°C, the added water was considered to be distributed randomly into the gold capsule, and thus around the glass sample.

Three different methods were used to prepare the charges for the investigation of T dependence. Some samples consisted of single glass blocks (see p.291). Other samples consisted of a glass block surrounded by a powder of glass, or only of glass powder (grain size of the powder: 200–500 μm).

The sealed capsules were placed, either in horizontal cold-seal pressure vessels (pressurized with H_2O) for experimental temperatures up to 850°C, or in an internally heated gas pressure vessel (Ar as pressure medium) for temperatures of >850°C. The capsules were run at the desired P and T for sufficient time to allow complete diffusion of H_2O through the sample (run duration ranging from 20 days to 10 hr at 750° and 1150°C, respectively; see Tables 2 and 3). Considering diffusion coefficients of H_2O of 10^{-8} to 10^{-7} cm^2 s^{-1} (Lapham et al., 1984), it can be shown that run durations of 10–20 days as applied for the experiments between 750° and 850°C are sufficient for complete diffusion of H_2O. However, it is worth noting that, if H_2O is only located on one side of the glass block, the run duration necessary to obtain complete diffusion of H_2O is four times higher than if H_2O is equally distributed at both extremities of the capsule. Temperature was measured with a Ni–NiCr thermocouple, and the actual temperatures are believed accurate to within ±10°C. Pressure was measured with a strain-gauge manometer (accuracy ±20 bar). Quenching in cold-seal pressure vessels was performed by using a flow of compressed air. Quenching in the internally-heated pressure vessel was obtained by turning of the heating power. Special care was given to obtain an isobaric quench (for cold-seal pressure vessels and internally-heated pressure vessels) by opening the vessel to the pressure line and by pumping regularly in order to maintain the pressure at a value of 2000 ± 20 bar.

2.3. Analytical technique: Karl–Fischer titration

The H_2O content of the quenched glasses was determined by Karl–Fischer titration. Karl–Fischer titration is a well-known analytical procedure by which H_2O reacts quantitatively, in presence of specific reagents, with coulometrically generated iodine (coulometer used for this study: Mitsubishi® CA 05). This procedure has been successfully applied to determine relatively high water contents in silicate materials (up to 5 wt.%, e.g., Turek et al., 1976) as well as low H_2O contents (down to 0.1 wt.% H_2O, e.g., Westrich, 1987). Only small amounts of glass are necessary to get reliable data (typically 10–20 mg for substances containing ~6 wt.% H_2O). The glass was roughly crushed and the H_2O content was determined directly after crushing. This is necessary to avoid errors due to absorption of H_2O for glasses with low H_2O contents or due to desorption for glasses with high H_2O contents. For one glass (750°C, 2 kbar) Karl–Fischer titration using both a single piece and a freshly crushed powder yielded nearly identical H_2O contents (Table 3). This shows that crushing had no influence. The crushed glass was preferred to single pieces for the measurements since sputtering of the glass may occur by explosive liberation of H_2O in the latter case. The glasses were heated progressively from 20° to 1300°C using an induction furnace (typical rate for one measurement: 30°C min^{-1} from 20° to 100°C; 100°C min^{-1} from 100° to 400°C; 50°C min^{-1} from 400° to 800°C;

TABLE 2

Results of H_2O measurements by Karl–Fischer titration, and "preferred value" for H_2O solubility at 2 kbar, 800°C

No.	Measured H_2O contents				H_2O solubility	
					(wt.%)	(mole%)
HPG1	6.50[a]		6.15[b]	6.30[c]	6.32	10.76
HPG2	6.28[a]		6.00[b]	5.74[c]	6.14	10.42
HPG3	6.03[a]		5.91[b]	5.74[c]	5.97	10.32
HPG4	5.71[a]	5.68[a]	5.62[b]	5.62[c]	5.65	9.91
HPG5	5.48[a]		5.30[b]	5.39[c]	5.39	9.45
HPG6	6.69[a]		6.31[b]	6.48[c]	6.49	10.89
HPG7	6.31				6.31	10.70
HPG8	5.94				5.94	10.15
HPG9	5.87				5.87	9.93
HPG10	5.56				5.56	9.63
HPG11	5.50				5.50	9.57
HPG12	6.13[a]	6.08[a]			6.10	10.30
HPG13	5.90				5.90	9.98
HPG14	5.57				5.57	9.54
HPG15	5.63				5.63	9.62
HPG16	5.45				5.45	9.37
Schott®	see results in Table 3				5.83	9.92

Run duration of the experiments was 10–20 days. Starting material was always a single dry glass cylinder. When H_2O contents are followed by the same symbol ([a]), measurements were performed from the same glass piece, when followed by different symbols ([a], [b], [c]), measurements were performed from different glass pieces (test for reproducibility of the experiments).

$100°C$ min^{-1} from 800° to 1300°C). The liberated H_2O was transported by a dry Ar stream in the titration cell and is collected there. Titration started 4–6 min after beginning of the heating-up. The duration of the titration was 7–10 min.

The analytical precision for H_2O is mainly dependent on the duration of the titration (7–10 min) and can be estimated to be $\leqslant \pm 0.15$ wt.% (for solubility values ranging between 6.7 and 5.4 wt.%). Some analyses were duplicated (two measurements of coarse-grained powder obtained from the same glass piece) and the variation of H_2O solubility is largely within the analytical precision given above. As an example, from two measurements performed with composition $Qz_{45}Ab_{50}Or_{05}$ (HPG 12), H_2O solubilities of 6.08 and 6.13 wt.% H_2O were obtained (analytical data given in Table 2), corresponding to a variation of 0.8% relative. A variation of 0.6% relative (5.71 and 5.68 wt.% H_2O) was obtained in doing the same test

for composition $Qz_{25}Ab_{30}Or_{45}$ (HPG 4). Variations of the same order of magnitude are obtained for composition $Qz_{28}Ab_{38}Or_{34}$ for which the T dependence of H_2O solubility was investigated. In this case analyses were duplicated (or triplicated) systematically for 10 experimental products (see analytical data in Table 3).

3. Results

3.1. Run products

The quenched run products consisted of bubble- and crystal-free limpid glasses. In experiments with single glass cylinders as starting material, the shape of the glass pieces after hydration were similar to those of the starting glass cylinders except for surface "healing" of the drill marks. The glasses obtained from charges consisting of a glass block plus glass

TABLE 3

Results of H_2O measurements by Karl–Fischer titration, and "preferred value" for H_2O solubility at 2 kbar, for composition $Qz_{28}Ab_{38}Or_{34}$

No.	T (°C)	SM	Duration (hr)	Measured H_2O contents			H_2O solubility (wt.%)	(mole%)
048	750	bp	336	5.97	6.03*		6.00	10.25
036	800	bp	336	5.80	5.75		5.77	9.84
060	800	b	360	5.85	5.86		5.86	9.99
061	800	bp	360	5.87	5.81		5.84	9.96
019	850	b	46	5.70	5.76		5.73	9.79
042	900	bp	192	5.79	5.81		5.80	9.91
053	950	bp	120	5.67	5.32	5.46	5.48	9.36
037	1,000	p	110	5.50	5.41		5.45	9.31
021	1,050	b	15	5.53	5.61		5.57	9.52
044	1,100	bp	90	5.13	5.49		5.31	9.07
002	1,150	p	96	5.31	5.29	5.44	5.35	9.14
028	1,150	p	20	5.53	5.41		5.47	9.35

Each measurement was made using a complete slice of glass (1 mm thickness) cutted from the glass block obtained after the experiment (see text). SM = starting material (b = glass block; p = glass powder; bp = glass block surrounded by glass powder).
*Titration performed using a single glass piece. For the other analyses, titration performed on roughly crushed glass fragments.

powder or only glass powder were also free of bubbles.

3.2. Homogeneity of H_2O distribution in glasses

The homogeneity of the glasses was tested in two ways. Some large glass samples (7–10 mm length; 3 mm diameter) were cut in slices of ~1 mm thickness, perpendicular to the capsule elongation. Each slice was analyzed individually by Karl–Fischer titration. The water contents given in Table 3 result from analyses performed in this way and show good homogeneities of the quenched melts. Some other samples, initially consisting of single glass pieces as well as glass block plus powder, were analyzed with an infrared microscope (Bruker® A590 with spectrometer IFS 88). Several measurements were performed from the rim to the core of the glass pieces. Local resolution of the measurements was ~100 μm. There was no significant change in the background subtracted peak height, at 4500 cm^{-1} (due to hydroxyl groups) and at 5230 cm^{-1} (due to molecular H_2O), suggesting that H_2O is homogeneously distributed throughout the sample and that the run durations were long enough to produce complete hydration of the sample.

3.3. Reproducibility of the experiments

The reproducibility of our solubility experiments was tested for seven compositions. For these compositions the experiments (and hence the analysis of H_2O content of the glass) were repeated (triplicates or duplicates). In the case of six compositions ($Qz_{25}Ab_{60}Or_{15}$, $Qz_{25}Ab_{40}Or_{35}$, $Qz_{25}Ab_{30}Or_{45}$, $Qz_{25}Ab_{20}Or_{55}$, $Qz_{35}Ab_{60}Or_{05}$, $Qz_{28}Ab_{38}Or_{34}$), the maximum difference between two analyzed H_2O contents is 0.38 wt.% H_2O (Tables 2 and 3), which corresponds to a variation of 5.8% relative or less of the H_2O solubility value. Thus the uncertainty due to the reproducibility of our experiments appears to be more important than that due to the analytical method (see p.294). The more important variation observed for one

composition ($Qz_{25}Ab_{50}Or_{25}$, difference of 0.54 wt.% H_2O, see Table 2) is attributed either to a bad distribution of water in the capsule during the experiment in case of the sample with the lowest H_2O content (part of the water was probably not in contact with the glass sample and was isolated on one side of the capsule) or to incomplete diffusion. Therefore, in this case only the two highest values were averaged to calculate the "preferred" solubility value in Table 2. It is worth noting that the H_2O content of the sample is not only dependent on the run duration but also on the location of the 10 wt.% added H_2O in the capsule before the experiment, a factor which is difficult to control.

3.4. Compositional dependence of the H_2O solubility at 800°C

Solubility values at 800°C are given in Table 2 for the sixteen investigated compositions. The H_2O solubility values expressed as wt.% H_2O are also plotted in Fig. 1. The H_2O solubilities expressed as mole% (one oxygen basis) are illustrated in Fig. 2. H_2O solubility is dependent on anhydrous melt composition; the highest values are obtained for Ab-rich compositions (6.49 and 6.32 wt.% H_2O for compositions with 60 wt.% normative Ab), and the lowest for Or-rich compositions (5.50 and 5.39 wt.% H_2O for compositions with 60 wt.% normative Or).

At constant Qz content H_2O solubility decreases with decreasing Ab content in the melt (Fig. 1), in agreement with solubility data for alkali feldspar melts obtained by Oxtoby and Hamilton (1978b) and Voigt et al. (1981). The difference in H_2O solubility between Ab- and Or-rich melts is more pronounced for compositions with lower quartz contents (difference of 0.65 and 0.99 wt.% H_2O between compositions $Qz_{45}Ab_{50}Or_{05}/Qz_{45}Ab_{10}Or_{45}$ and $Qz_{35}Ab_{60}Or_{05}/Qz_{35}Ab_{10}Or_{55}$, respectively).

At constant Or content there is a marked increase in H_2O solubility with increasing Ab content (decreasing Qz content) in case of Ab-rich melts (H_2O solubility in melts with 15 wt.% normative Or: 5.90 wt.% H_2O for composition $Qz_{45}Ab_{40}Or_{15}$, 6.32 wt.% H_2O for composition $Qz_{25}Ab_{60}Or_{15}$). In contrast, the variation of H_2O solubility in Or-rich melts is much lower (H_2O solubility value between 5.65 and 5.39 for melts containing more or as much as 45 wt.% normative Or content). However, even for Or-rich melts, a small increase in H_2O solubility with increasing Na content (decreasing Qz) at constant Or content is observed (H_2O increases from 5.45 for composition $Qz_{45}Ab_{10}Or_{45}$ to 5.65 for composition $Qz_{25}Ab_{30}Or_{45}$).

At constant Ab content there is no systematic dependence of the H_2O solubility on Qz (or Or) content. The changes in H_2O solubility values are much less important than for sections at constant Qz content or for sections at constant Or contents and high Ab/(Ab+Or) ratios.

3.5. Temperature dependence of the H_2O solubility for composition $Qz_{28}Ab_{38}Or_{34}$

The H_2O contents of the analyzed glasses and the H_2O solubility values for composition $Qz_{28}Ab_{38}Or_{34}$ are given in Table 3 and plotted in Fig. 3. There is a small decrease in H_2O solubility from 6.00 to 5.41 wt.% H_2O with increasing T from 750° to 1150°C. Although obtained by the use of three different starting materials (single glass piece, glass + powder, powder), the results are internally consistent. At 800°C, with the starting material consisting of a glass block plus glass powder, the H_2O solubility is 5.83 wt.% H_2O. The composition with approximately the same Qz:Ab:Or ratio ($Qz_{25}Ab_{40}Or_{35}$ or HPG 3), determined from a glass cylinder only, yielded a solubility value of 5.97 (see Fig. 1), suggesting a good agreement between solubility values determined from similar starting material but with different ways of sample preparation.
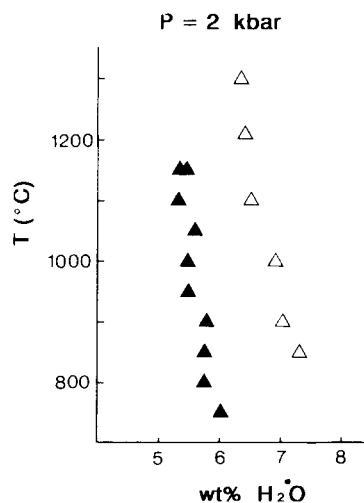
Fig. 3. Temperature dependence of H_2O solubility at 2 kbar for a melt with a composition $Qz_{28}Ab_{38}Or_{34}$ (*solid triangles*). For comparison data of Hamilton and Oxtoby (1986) for albite melts at 2 kbar have been reported (*open triangles*). Analytical data are given in Table 3.

4. Discussion

4.1. Comparison with previous data

Although the acquisition of H_2O solubility data for aluminosilicate melts of granitic composition has been the focus of several studies, the present data for haplogranite melts are comparable with only a very few of them. This results from a difference in experimental strategy. Almost all the previous studies: (1) have used a single melt composition, commonly either that of albite (e.g., Goranson, 1931; Burnham and Jahns, 1962; Orlova, 1963; Oxtoby and Hamilton, 1978b; Blamart et al., 1988), or of a complex natural rock type such as Harding Pegmatite, New Mexico, U.S.A. (Burnham and Jahns, 1962); and (2) have focused their efforts upon describing the variation of H_2O solubility as a function of either pressure or temperature (or both). In contrast our principal objective has been to measure the variation of H_2O solubility in a large number of simple melt compositions under isobaric and isothermal conditions, with a view to documenting precisely the compositional depen-

dence of H_2O solubility. A direct comparison of our results with those of the previous studies is therefore impossible.

However, some broad comparisons are possible. H_2O solubility measurements in the system Qz-Ab-Or have been conducted primarily for the end-members and also for compositions close to the thermal minimum. Although there are some significant differences in the measured H_2O concentrations that have been reported in these studies for specific compositions (especially for albite melts, the most studied composition), the preferential dissolution of H_2O in Ab-rich melts by comparison to Or-rich melts has been observed consistently (see Oxtoby and Hamilton, 1978b; Voigt et al., 1981; and the review in McMillan and Holloway, 1987). In a similar way, an examination of the solubility of H_2O in cotectic compositions in the system Qz–Ab–Or at 2 kbar (i.e. compositions along the quartz–feldspar boundary) indicates that the solubility increases from 5.6 wt.% H_2O for the Qz–Or eutectic composition, to 6.5 wt.% H_2O for the minimum composition, to $\cdot > 7$ wt.% H_2O for the Qz–Ab eutectic composition (H_2O solubility data of Tuttle and Bowen, 1958 compiled in Luth, 1976). Although our H_2O solubility data yield slightly lower values (~ 0.5 wt.% H_2O less for the minimum composition) the general evolutionary trend summarized in Luth (1976) is remarkably consistent with that of increasing H_2O solubility in more Ab-rich melts shown by our data.

Although the compositional dependence of H_2O solubility in haplogranite melts was the focus of the present study, a series of experiments were conducted to investigate the effects of T on one selected sample ($Qz_{28}Ab_{38}Or_{34}$). The results are given in Table 3. There is a slight decrease of H_2O solubility with increasing T (Fig. 3). Although the solubility of H_2O is higher in albite melts at any given T (e.g., 7.3 wt.% H_2O at 850°C in albite in comparison to 5.73 wt.% H_2O in our haplogranite melt), the slope of the trend observed

with increasing T (Fig. 3) is very similar for melts of both albite and haplogranite of composition $Qz_{28}Ab_{38}Or_{34}$. Such a relationship suggests that H_2O solubility data obtained at a given T can be extrapolated to other temperatures, at least for 2 kbar and compositions with Ab contents between 100 and 35 normative weight percent.

The H_2O solubility data (at ~ 2 kbar) for natural granitic rocks with comparable bulk compositions to those of our experimental melts are extremely limited in number; they include those for the Harding Pegmatite ($Qz_{45}Ab_{37}Or_{18}$) with measured solubilities of 6.0–6.8 wt.% H_2O at $T = 670°C$ (Burnham and Jahns, 1962). Although such values are quite similar to those of the solubility field at $T = 800°C$ as defined in this study (Fig. 2), any direct comparison with the H_2O solubility data for the Harding Pegmatite is impeded by the significant concentrations of other volatiles, specifically Li and F, which the pegmatite melt is known to contain (Burnham and Jahns, 1962, table 1), and also by the peraluminous character (normative corundum = 2.4 wt.%) of the pegmatite.

4.2. Importance for H_2O solubility mechanisms in aluminosilicate melts

Our experimental results constitute the first systematic set of data demonstrating the isobaric, isothermal effect of composition on H_2O solubility in the Qz–Ab–Or system. Thus, they provide important constraints on the solubility mechanisms of H_2O in quartzofeldspathic melts. The changes in H_2O solubility are characterized by: (1) a marked contrast between Qz–Ab- and Qz–Or-rich melts, with H_2O solubility varying significantly in Qz–Ab-rich melts but remaining near constant in Qz–Or-rich melts; and (2) a significant increase in H_2O solubility with increasing Ab content, either at the expense of Or (constant Qz) or at the expense of Qz (constant Or). By contrast there is no systematic and substantial varia-

tion of H_2O solubility for melt compositions with constant Ab content. These data suggest that the effect of exchanging Na and K in haplogranitic melts may strongly influence the H_2O solubility and, hence, H_2O dissolution mechanism.

In most of the models seeking to explain the incorporation of H_2O in aluminosilicate melts (e.g., Burnham, 1981; Kohn et al., 1989) it has been suggested that an exchange between M (M for K, Na), balancing the charge of the Al atom, and H cations (either from OH or H_2O) takes place (see Pichavant et al., 1992 in this issue for a review). Our solubility data suggest that the exchange of M for H is more important in the case of Na than of K (higher solubility for Na-rich melts) and that K has a relatively "passive" role when compared to Na (strong variation of solubility data for Na-rich melts, almost constant values for K-rich melts). The very low ability of exchange of K-bearing units has been confirmed by Holtz et al. (1992) and Pichavant et al. (1992 in this issue) investigating liquidus phase relationships in the system Qz–Ab–Or under H_2O-saturated and -undersaturated conditions (at constant P). With decreasing H_2O content of the melt (decreasing a_{H_2O}) liquidus temperatures for quartz and alkali feldspar increase significantly, with the magnitude of the temperature increase being more marked for Qz–Ab-rich than for Qz–Or-rich compositions, thus confirming the preferential association of Na with H_2O (see also Pichavant, 1987).

Amongst the recent H_2O speciation models, there is now overall agreement that water is present as both molecular H_2O and OH groups (e.g., Silver and Stolper, 1989; Silver et al., 1990). However, the amounts of both species present in the melt is still under discussion. Stolper and coworkers, on the basis of spectroscopic studies of quenched glasses, suggest that there is a solubility maximum for water incorporated as OH groups at 1.7–2.3 wt.% H_2O. This maximum is attained for a total water content of ~ 4 wt.% H_2O. At H_2O contents

higher than 4 wt.%, all additional water is incorporated as molecular H_2O. Since our melts all contain more than 4 wt.% H_2O, their OH content should correspond to the maximum value, according to Stolper and coworkers' measurements. The maximum amount of H_2O incorporated as OH groups is thus 2.3 wt.% H_2O in Ab melts (Silver and Stolper, 1989) and 2 wt.% H_2O in Or melts (Silver et al., 1990).

Consequently the difference in solubility between Ab and Or melts is only of the order of 0.3 wt.% H_2O dissolved as OH groups. Considering our compositions, the difference between Qz–Ab and Qz–Or melts should be even lower. Thus, according to Stolper and coworkers' model, the higher H_2O solubilities observed in our Na-rich melts (~ 1 wt.% more H_2O dissolved in Na-rich than in K-rich melts; see, e.g., difference of H_2O solubility between compositions $Qz_{35}Ab_{60}Or_{05}$ and $Qz_{35}Ab_{10}Or_{45}$, Table 1) should be related to the higher amounts of molecular H_2O in these melts. This means that the incorporation mechanisms of molecular water should be strongly dependent on the melt composition (Na/K ratio). In addition, there are also arguments showing that the melt composition has a significant effect on the amount of water dissolved as OH groups. For example, H_2O solubility data for Qz, Ab, Or and Qz–Ab melts (Kennedy et al., 1962; Oxtoby and Hamilton, 1978a, b; see review in McMillan and Holloway, 1987) indicate that the difference in H_2O solubility between melts of different compositions strongly increases with increasing pressure from 0 to 2 kbar (i.e. at low H_2O contents and thus for high proportions of OH groups) whereas this difference remains almost constant for pressures between 2 and 10 kbar (i.e. when most of H_2O is supposed to be incorporated as molecular H_2O).

More recent work indicates that the disproportionation of H_2O recorded in silicate glasses can be strongly quench-rate dependent (Dingwell and Webb, 1990a; Silver et al., 1990). This dependence upon the quench rate indicates a strong temperature dependence of the speciation, and comparable estimates of a reaction enthalpy of 25 kJ mol^{-1} have been obtained using quite different methods (Dingwell and Webb, 1989, 1990b; Silver and Stolper, 1989; Zhang et al., 1991). One important consequence of the temperature dependence of H_2O speciation is that speciation data must be corrected to fictive temperature (i.e. the structural temperature frozen into the glass during the quench). Such estimates result in much higher concentrations of OH in rhyolite melt $+5$ wt.% H_2O at 800°C, for example, than are quenched in at the glass transition of this material during hydrothermal quenches (Dingwell and Webb, 1989, 1990b). The result is that OH groups may still dominate the speciation of H_2O in the present glassses at temperature and thus the composition dependence of the H_2O solubility may originate in the relative stability of various OH species rather than molecular H_2O.

The temperature dependence of the solubility of water can be compared with the temperature dependence of water speciation to gain further insight into the mechanisms of water solution in these melts. The temperature dependence of water solubility in the Schott® glass is illustrated in Fig. 3. These data are described by: wt.% $H_2O = (6.92 \pm 0.13) - (0.00137 \pm 0.00021)T$ where wt.% H_2O refers to the total dissolved water; and T is the temperature in °C. (Standard deviations are indicated for the equation.) The temperature-dependent proportions of OH and H_2O dissolved in this melt may be estimated from the relaxation analysis of Dingwell and Webb (1989, 1990b) for a natural rhyolite (Silver and Stolper, 1989). The results of that analysis yield disproportionation values (molar fraction of OH/2 to H_2O) equal to 0.48 at 750°C and 0.62 at 1150°C (from data given in Table 3). These values yield, in turn, temperature-dependent values for the wt.% of water dissolved as hydroxyl and as molecular H_2O as functions of temperature. Hydroxyl content shows little or

no temperature dependence (recalling analytical errors of ±0.15%). Molecular water in contrast shows a strongly negative temperature-dependent solubility.

4.3. Geological implications

The H_2O solubility data presented in this paper may have important petrological implications concerning both physical and chemical properties of granitic melts. The viscosity of silicate melts is known to be dramatically dependent on the H_2O content of melts (e.g., Burnham, 1963; Friedman et al., 1963; Dingwell, 1987). The higher H_2O solubility in Na-rich melts demonstrated here implies that these melts are less viscous than K-rich ones (in H_2O-saturated conditions). In addition, Urbain et al. (1984) have shown that $KAlSi_3O_8$ liquids are more viscous than $NaAlSi_3O_8$ liquids at the same temperature. In natural magmatic processes, H_2O-saturated melts mainly occur at the end of the crystallization history as aplitic dykes, corresponding to residual melts. This mode of emplacement (dykes) only occurs if the viscosity of the melts is relatively low. Our results suggest that residual Na-rich melts are better candidates to form dykes than K-rich residual melts. Investigations of leucogranitic rocks associated with dyke swarms show that these leucogranites are very often rich in Na and Al (e.g., Nabelek et al., 1992).

As already mentioned by Pichavant (1990), the compositional dependence of H_2O solubility in the Qz–Ab–Or system implies that phase relations in this system have to be reconsidered if they are used to interpret the composition and formation of granitic rocks. Liquidus phase relations in the system Qz–Ab–Or, currently used in petrology and determined by Tuttle and Bowen (1958) and Luth et al. (1964), are presented as isobaric polythermal sections, in which the H_2O content of the melts is not considered. Obviously, the position of the liquidus surface will be strongly changed if a Qz–Ab–Or section is constructed at constant pressure and H_2O content of the melt. For example, in the case of a section at 2 kbar with 5 wt.% H_2O in the melt, a Qz–Or eutectic melt would be slightly H_2O-undersaturated (melts are saturated with respect to H_2O for values close to 5 wt.% H_2O at 800°C), whereas a Qz–Ab eutectic melt would be strongly H_2O-undersaturated (H_2O solubility at 800°C close to 7 wt.% H_2O). This in turn implies that, for a H_2O content of the melt of 5 wt.%, liquidus temperatures for Qz–Ab-rich melts will be considerably higher than that given in the 2-kbar H_2O-saturated section of Tuttle and Bowen (1958), whereas they will be almost similar for Qz–Or-rich melts. More generally, the compositional dependence of the solubility of H_2O in the haplogranite system allows one to quantitatively describe the process of crystallization-induced saturation or "second boiling". It is clear from Fig. 1 that crystallization trends on the quartz–feldspar cotectic could either increase or decrease the solubility of H_2O in the resultant melt phase depending on the alkali distribution between feldspar and melt.

In this study, the temperature dependence of H_2O solubility was investigated for a composition close to the minimum melt composition at a PH_2O of 2 kbar, allowing good comparison of our data with granitic rocks. The H_2O solubility variation between 750° and 1150°C is relatively low and corresponds to 0.6 wt.% H_2O. With the formation of most crustal granitic rocks occurring at temperatures below 850°C, it would appear that the increase of H_2O solubility in melts due to cooling is negligible, with the most important factor controlling the H_2O solubility in cooling, ascending melts being pressure. In addition, however, the results of this study show that the role of melt composition on H_2O solubility is significantly more important than the role of temperature especially for albite-rich melts.

5. Conclusions

Though the aim of this work is not to consider in detail the bonding of H_2O in silicate

melts or the structure of silicate melts, our results clearly show: (1) the preferential association of Na with H_2O, demonstrated by increasing H_2O solubilities with increasing Ab content of the melt (especially in case of Na-rich melts); and (2) the relatively passive role of K for the incorporation mechanisms of H_2O, demonstrated by the low variations of H_2O solubility in K-rich melts. Future theories on the structure of hydrous melts should account for the results presented here.

The significant variation in H_2O solubility in the Qz–Ab–Or system as a function of the composition of the melts has dramatic implications concerning the interpretation of granitic rocks, especially when using phase relationships to discuss the formation or the crystallization histories of these rocks. The H_2O content of the melts is an important parameter which should be taken into account in petrogenetic investigations of granitic rocks. The results of this study, in confirming a strong composition dependence of the solubility of H_2O in silicate melts, set the stage for an investigation of the effect of light elements on the solubility of H_2O in leucogranitic systems (e.g., B, Li, F).

Acknowledgements

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