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Published on: 01 Jan 1993 - Contributions to Mineralogy and Petrology (Springer-Verlag)

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Effects of F, B₂O₃ and P₂O₅ on the solubility of water in haplogranite melts compared to natural silicate melts

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Received June 16, 1992 / Accepted October 12, 1992

Abstract. The effects of F, B₂O₃ and P₂O₅ on the H₂O solubility in a haplogranite liquid (36 wt. % SiO₂, 39 wt. % NaAlSi₃O₈, 25 wt. % KAlSi₃O₈) have been determined at 0.5, 1, 2, and 3 kb and 800, 850, and 900 °C. The H₂O solubility increases with increasing F and B content of the melt. The H₂O solubility increase is more important at high pressure (2 and 3 kb) than at low pressure (0.5 kb). At 2 kb and 800 °C, the H₂O solubility increases from 5.94 to 8.22 wt. % H₂O with increasing F content in the melt from 0 to 4.55 wt. %, corresponding to a linear H₂O solubility increase of 0.53 mol H₂O/mol F. With addition of 4.35 wt. % B₂O₃, the H₂O solubility increases up to 6.86 wt. % H₂O at 2 kb and 800 °C, corresponding to a linear increase of 1.05 mol H₂O/mol B₂O₃. The results allow to define the individual effects of fluorine and boron on H₂O solubility in haplogranitic melts with compositions close to that of H₂O-saturated thermal minima (at 0.5–3 kb). Although P has a dramatic effect on the phase relations in the haplogranite system, its effect on the H₂O solubility was found to be negligible in natural melt compositions. The concomitant increase in H₂O solubility and F can not be interpreted on the basis of the available spectroscopic data (existence of hydrated aluminofluoride complexes or not). In contrast, hydrated borates or more probably boroxol complexes have been demonstrated in B-bearing hydrous melts.

Introduction

The role of elements usually present in small amounts in granitic liquids, such as F, B, P, has been the subject of many experimental studies in recent years (e.g. Franz 1966; Manning 1981; Harrison and Watson 1984; Dingwell et al. 1985; Pichavant 1981, 1987; London 1987). Experimental studies in F-, B- and P-bearing systems have been conducted in order to define the effects of these

elements on liquidus and solidus phase relations (e.g. Chorlton and Martin 1978; Manning 1981; Pichavant 1981, 1987; London et al. 1990). The saturation of minerals containing B and P (tourmaline and apatite) has also been investigated in granitic liquids (Bénard et al. 1985; Harrison and Watson 1984). Although the existence of hydrated aluminofluorides, borate groups, and phosphorus-bearing units was suggested from some of these studies, the H₂O content of the melts was not determined or only determined within a large uncertainty range. In addition, when results are available, they are not always in agreement (compare for example Webster 1990, and Sorapure and Hamilton 1984, for F-bearing melts).

In view of the lack of H₂O solubility data, it appeared necessary to conduct experiments specifically devoted to the determination of H₂O solubility in F-, B- and P-bearing granitic melts. The granite composition used for this investigation belongs to the system SiO₂-NaAlSi₃O₈-KAlSi₃O₈ (Qz-Ab-Or) and was chosen to be near that of the minimum liquidus temperature point at P(H₂O) = 2 kb (Tuttle and Bowen 1958). In addition, and for comparison with data obtained in synthetic systems, the H₂O solubility was investigated in a natural F-, B-, and P-rich composition (Macusani glass, Peru).

Starting material and procedures

Starting glasses

The starting materials used for the experiments were glasses. One haplogranite glass (HPG 8) was prepared from powders of Na₂CO₃, K₂CO₃, Al₂O₃, SiO₂ and its CIPW normative composition is Qz₃₆Ab₃₉Or₂₅ (see composition given in Table 1). F-bearing glasses were obtained by adding AlF₃. For these samples, the amount of Al₂O₃ added to the mixtures was reduced in order to keep a molar ratio of Al₂O₃/(Na₂O + K₂O) = 1. The two F-bearing compositions (labelled HPG8-F3, HPG8-F5 in this study) were prepared to contain 5 and 10 wt. % F, substituting oxygen. B and P glasses were obtained by adding H₃BO₃ and NH₄PO₃, respectively, to the initial powder mixtures. The starting compositions for the B- and P-bearing glasses (labelled HPG8-B4, HPG8-B9, HPG8-P5, HPG8-P10 in this study) were chosen to represent 5 and 10 wt. % additions of B₂O₃ and P₂O₅ to the haplogranite composition HPG8.

Table 1. Composition of the synthetic starting glasses

	HPG8 ^a	HPG8-F3 ^b	HPG8-F5 ^b	HPG8-B4 ^c	HPG8-B9 ^c	HPG8-P5 ^a	HPG8-P10 ^a
SiO ₂	77.90	77.22	76.67	75.18	71.07	74.5	71.1
Al ₂ O ₃	11.89	11.84	11.13	11.79	11.60	11.50	11.29
K ₂ O	4.17	4.20	4.31	3.92	3.95	3.93	3.74
Na ₂ O	4.53	4.77	4.69	4.66	4.23	4.26	3.76
F	–	3.11(2.86)	4.25(4.55)	–	–	–	–
B ₂ O ₃	–	–	–	4.35	8.92	–	–
P ₂ O ₅	–	–	–	–	–	5.1	9.5
Total	98.49	101.14	101.05	99.90	99.77	99.31	99.36
O ≡ F		1.31	1.79				
Total		99.83	99.26				

^a Microprobe analysis; average of 10 to 20 analyses (Cameca SX50, Geoinstitut Bayreuth; for standard deviations, see Dingwell et al. 1992a, b)

^b Microprobe analysis; average of 13 and 12 analyses (Cameca SX50, BRGM-CNRS Orléans), F contents given in parentheses are obtained by wet-chemical techniques (CRPG, Nancy)

^c All elements analyzed by wet-chemical techniques (CRPG, Nancy)

–: not analyzed

The glasses were obtained by two cycles of melting at 1600 °C – 1700 °C and 1 atm (the duration of the second melting cycle was always 24 hours or more). The detailed procedure for the preparation of the glasses is given by Dingwell et al. (1992a, b). It is emphasized that the glass cylinders used in the experiments were always dry and free of bubbles. The compositions of HPG8, F- and P-bearing starting glasses were determined by electron microprobe analysis (Cameca SX 50; see Table 1). In order to check the quality of the determination of F by microprobe analysis (standard: topaz), the fluorine content of F-bearing glasses was also analysed by solution-based ICP-AES (at CRPG, Nancy, France). The relative variation between the two sets of data is 8% for HPG8-F3 and 6.6% for HPG8-F5 (F content of 2.86 and 3.11 wt. % for HPG8-F3, and 4.55 and 4.25 for HPG8-F5; see Table 1). Assuming that the analyses by solution-based ICP-AES are of higher quality, these data show that our microprobe analyses of F are correct to within ± 10% of the measured value (in this study, the F content of the glasses was considered to be that defined by ICP-AES analysis). B-bearing glasses were analyzed for all elements by solution-based ICP-AES (see composition in Table 1). The analyzed glass compositions given in Table 1 show that some samples lost significant quantities of the added F and B (in particular HPG8-F5). However, the Qz/Ab/Or normative proportions of the glasses do not deviate significantly from the base composition HPG8 (Qz₃₆Ab₃₉Or₂₅). The composition of the natural sample (MAC-JV1, Macusani glass, Peru) used in this study is given in Table 2. This glass is almost free of crystals, apart from some andalusite needles. Only glass pieces without andalusite crystals were selected as starting material for the experiments.

Experimental procedure

Experimental and analytical methods used to determine the solubility of H₂O in aluminosilicate melts are numerous (see reviews in Day and Fenn 1982; Dingwell et al. 1984; McMillan and Holloway 1987) and this may be the cause of significant variations in the data for given composition and P-T conditions (e.g. for albite melts, see the review of Dingwell 1987). Thus, in this study care was taken to use one single experimental and analytical technique to obtain a consistent dataset. Small dry glass cylinders (diameter, 3 mm; length, 2 to 3 mm; weight, 30 to 50 mg) were placed in gold capsules and sealed together with 4 to 13 wt. % of doubly distilled H₂O. The amount of added H₂O (given in Table 3) was chosen to be slightly higher than the expected H₂O solubility value (see section on “attainment of equilibrium”) to avoid variations of the melt composition due to incongruent dissolution in the fluid phase. The capsules were checked for leakage by testing for weight loss after drying at 100 °C for one to several hours.

Experimental pressure conditions were 0.5, 1, 2, and 3 kb. The investigated temperatures were 800, 850, and 900 °C. Because of the

Table 2. Composition of the Macusani starting glass

	MAC-JV1 ^a
SiO ₂	72.26
Al ₂ O ₃	15.83
K ₂ O	3.66
Na ₂ O	4.14
FeO ^b	0.61
MnO	0.06
MgO	0.02
CaO	0.22
TiO ₂	0.04
Li ₂ O	0.74
F	1.33
B ₂ O ₃	0.62
P ₂ O ₅	0.53
H ₂ O ⁺	0.46
Total	100.61
O ≡ F	0.56
Total	100.05

^a Whole-rock analysis (average of two duplicate analyses; source of data: Pichavant et al. 1987b)

^b Total Fe expressed as FeO

limits of the experimental apparatus (cold-seal pressure vessel), all experiments could not be performed at the same temperature (maximal *T* at 2 and 3 kb: 820–840 °C). Most of the 0.5 kb experiments are performed at 900 °C, the 1 kb experiments at 850 °C, and the 2 and 3 kb experiments at 800 °C. Temperature was measured with a Ni-NiCr thermocouple, and the actual temperatures are believed to be accurate to within ± 10 °C. Pressure was measured with a strain-gauge manometer (accuracy ± 20 bar). The experimental durations were 12 to 15 days (see Table 1). The quenching was performed by using a flow of compressed air. Special care was taken to obtain an isobaric quench by opening the vessel to the pressure line and pumping regularly in order to maintain the pressure at the experimental *P* condition (± 20 bar).

Analysis of H₂O contents

The H₂O content of the quenched glasses was determined by Karl Fischer titration (Mitsubishi CA 05, University of Hannover). This method consists in heating the sample progressively from 20 to 1300 °C using an induction furnace (detail on heating rates for the glasses is given by Holtz et al. 1992a), the liberated H₂O is then transported by a dry Ar stream in a titration cell. A detailed

Table 3. Experimental results and H₂O contents of quenched glasses

Glass no.	P (kb)	T (°C)	Added H ₂ O (wt. %)	Run Duration (days)	H ₂ O content (wt. % H ₂ O)	Observations
HPG8	0.5	900	4.0	13	2.45	
	1	850	5.4	14	3.81	
	2	800	10.0	14	5.94	
	5	800	13.1	12	9.90	
HPG8-F3	0.5	900	3.9	13	2.72	
	1	850	6.3	13	4.59	
	1	850	5.3	13	4.19	
	2	800	8.9	13	6.87	
	2	800	7.9	13	7.15	
HPG8-F5	1	850	6.2	13	4.91	
	1	850	6.2	13	5.10	
	2	800	9.6	13	8.28	Cloudy glass
	2	800	9.1	13	8.16	
HPG8-B4	1	850	7.7	14	4.77	
	2	800	9.9	14	6.90–6.83	
	3	800	10.8	14	8.65	
HPG8-B9	0.5	900	5.1	14	3.73	
	1	850	9.0	14	5.65	
	2	800	12.1	14	8.89–8.86	
	3	800	12.9	14	10.15	
HPG8-P5	1	850	5.7	13	3.91	
	2	850	10.2	15	6.19	
	2	800	9.1	13	6.31	< 1 vol. % quartz
HPG8-P10	1	850	6.0	13	nd	Glass + quartz
	2	800	9.2	13	nd	Glass + quartz
Mac-JV1	0.5	800	5.4	13	3.59	
	0.5	800	4.8	12	3.37	
	0.5	900	4.4	12	3.29	
	1	900	7.1	12	4.65	
	1	850	7.5	15	4.62	
	2	800	11.5	14	6.96	
	2	800	9.2	14	7.12	
	3	800	11.3	14	8.59	
	3	800	11.9	14	8.68	

Note: H₂O contents determined by Karl Fischer titration
 nd: not determined

description of the determination of H₂O contents by Karl Fischer titration (KFT) is given by Westrich (1987). The analytical method (KFT) used for this study was tested in using standards with known H₂O contents, such as calcium sulfate dihydrate, sodium tartrate dihydrate, phlogopites and chlorites, hydrous glasses (synthesized at superliquidus and H₂O-undersaturated conditions). The measured H₂O contents were always in good agreement with the expected values (Behrens submitted).

Titration by the method of Karl Fischer only requires small amounts of glass to obtain reliable data (typically 10 to 20 mg for glasses containing 6 wt. % H₂O). The pieces of glass with high H₂O contents (> 4 to 5 wt. % H₂O) were placed directly in the induction furnace (without crushing or grinding) in order to avoid errors due to absorption or desorption of H₂O (glasses with high H₂O contents may lose water very rapidly). Glasses with low H₂O contents were roughly crushed just before the titration. The use of crushed material was preferred to single pieces since spluttering of the glass may occur by explosive liberation of H₂O in such H₂O-poor glasses. Holtz et al. (1992a) made tests for one haplogranite glass at 2 kb and 750°C (H₂O content ≈ 6 wt. % H₂O) and showed that the measured H₂O content was similar using a single glass piece or roughly crushed material. The analytical precision for H₂O is better than ± 0.15 wt. % H₂O (see Holtz et al. 1992a). The analysis of the H₂O

content of some samples was duplicated and the variation is within this analytical precision (see Table 3, 2 kb experiments with samples HPG8-B4 and HPG8-B9).

In some experiments with haplogranitic glasses as starting material, the H₂O content of the glasses was also determined by the weight loss method, as a test for the H₂O solubility determinations by KFT. Before extracting the quenched glass from the capsules, the capsules were punctured and placed in a furnace at 105°C for one hour. The H₂O solubility from weight loss and KFT were in good agreement: in two experiments performed with sample HPG8, the H₂O contents measured by weight loss were 2.15 and 3.36 and the corresponding H₂O contents analyzed by KFT were 2.19 and 3.46 wt. % H₂O. Two other experiments with a haplogranitic glass of composition Qz₃₇Ab₂₈Or₃₅ yielded values of 2.09 and 3.38 wt. % H₂O by weight loss and corresponding KFT values of 2.09 and 3.19 wt. % H₂O, respectively (experimental conditions are given in Table 11 in Holtz et al. 1992b). These tests show the good quality of the H₂O determination by KFT. However, this kind of test could only be done for low H₂O contents of the melt. For H₂O contents higher than 6 wt. % H₂O, significant amounts of H₂O may leave the glass sample at 105°C (Behrens submitted), and the weight loss method, which would artificially decrease the H₂O solubility, can not be used.

Experimental results

Experimental products and reproducibility of the H₂O solubility data

Most of the quenched products consisted of bubble-free and crystal-free limpid glasses. The shape of the hydrated glass cylinders was preserved and similar to that of the dry starting glass pieces. In one experiment, a cloudy glass sample was obtained (composition HPG8-F5 at 3 kb). However, neither crystals nor fluid inclusions could be detected in this glass by microscopic examination. A few crystals of quartz were observed in the composition HPG8-P5 (less than 1 vol. %) at 2 kb and 800 °C and significant amounts of bipyramidal quartz were found in the experimental products of composition HPG8-P10. The H₂O content of all experimental products has been analyzed by KFT, except for composition HPG8-P10. The analytical data and the experimental conditions are given in Table 3.

Some of the experiments were duplicated, as a test for the reproducibility of our data. The results show relatively little variation in the H₂O contents of glasses obtained at the same *P* and *T* conditions (relative variation $\leq 4.1\%$, see Table 3) except for one composition (HPG8-F3, 1 kb, 850 °C, with relative variation of 9.5%). These variations may be due to small (uncontrolled) variations of pressure or more probably to spluttering of the sample during titration (explosive liberation of H₂O during heating up), rather than by incomplete diffusion of H₂O through the starting glass (see discussion later and Holtz et al. 1992a). Where experiments have been duplicated, the H₂O solubility data given in Table 4 represent average values. An additional test of the quality of our experiments is furnished by the comparison of experiments performed with the same composition at the same pressure, but at different temperatures. For a given composition, the H₂O content is systematically slightly lower at higher temperature, in agreement with the 2 kb data of Hamilton and Oxtoby (1986) and Holtz et al. (1992a).

Pressure and composition dependence of H₂O solubility

The pressure dependence of the H₂O solubility for each investigated composition is shown on Figs. 1–3. It has to be noted that the H₂O solubility curves in Figs. 1–3 are not obtained at isothermal conditions. The data reported in Figs. 1–3 have been obtained at 900 °C at 0.5 kb, 850 °C at 1 kb and 800 °C at 2 and 3 kb. However, the temperature dependence of the H₂O solubility in haplogranitic melts was shown to be very small at 2 kb (Hamilton and Oxtoby 1986; Holtz et al. 1992a). Thus, it can be considered that isothermal H₂O solubility curves should not deviate significantly from those of Figs. 1–3. Clearly, at all investigated pressures, increasing the F and B₂O₃ content of the melt produces a significant increase of the H₂O solubility. In contrast, the H₂O solubility increase is significantly less in P-bearing melts.

Effect of F. The effect of F on the H₂O solubility in HPG8 melt is illustrated on Figs. 1, 4. The curves on Fig. 4 show that the H₂O solubility increases with increasing F content in the melt (the F content of the melt is considered to be that determined by wet chemical analysis, see Table 1). Assuming a linear increase in the concentration range 0–3 wt. % F, increasing the F content of the melt by 1 wt. % F produces an H₂O solubility increase of 0.09 wt. % H₂O at 0.5 kb – 900 °C, of 0.20 wt. % H₂O at 1 kb – 850 °C, and of 0.37 wt. % H₂O at 2 kb – 800 °C (Fig. 4). The relative increase in H₂O solubility (due to addition of 1 wt. % F) is 3.7% at 0.5 kb, 5.2% at 1 kb and 6.2% at 2 kb. The increase of H₂O solubility as a function of the mol% F in the melt is given in Table 4. The data show that the H₂O solubility is not only dependent on the F content of the melt (Figs. 4, 5) but also on the bulk H₂O content of the melt (Fig. 5). At constant F content, the increase in H₂O solubility is more important at higher pressure (i.e. for higher H₂O contents of the melt) than at lower pressure (i.e. for lower H₂O contents of the melt).

Effect of B₂O₃. In B-bearing melts with B₂O₃ contents between 0 and 4.35 wt. %, the addition of 1 wt. % B₂O₃ produces an increase of 0.22 wt. % H₂O at 1 kb – 850 °C

Table 4. Effect of F, B₂O₃, and P₂O₅ on H₂O solubility in HPG8 melt

Composition	P (kb)	T (°C)	H ₂ O solubility (wt. %)	Increase of H ₂ O solubility compared to composition HPG8 ^a
HPG8-F3	0.5	900	2.72	0.10 mol H ₂ O/mol F (± 0.06)
HPG8-F3	1	850	4.39	0.21 mol H ₂ O/mol F (± 0.06)
HPG8-F3	2	800	7.01	0.39 mol H ₂ O/mol F (± 0.06)
HPG8-F5	1	850	5.00	0.28 mol H ₂ O/mol F (± 0.05)
HPG8-F5	2	800	8.22	0.53 mol H ₂ O/mol F (± 0.05)
HPG8-B4	1	850	4.77	1.00 mol H ₂ O/mol B ₂ O ₃ (± 0.18)
HPG8-B4	2	800	6.86	1.05 mol H ₂ O/mol B ₂ O ₃ (± 0.18)
HPG8-B4	3	800	8.65	1.46 mol H ₂ O/mol B ₂ O ₃ (± 0.18)
HPG8-B9	0.5	900	3.73	0.65 mol H ₂ O/mol B ₂ O ₃ (± 0.08)
HPG8-B9	1	850	5.65	0.94 mol H ₂ O/mol B ₂ O ₃ (± 0.08)
HPG8-B9	2	800	8.87	1.50 mol H ₂ O/mol B ₂ O ₃ (± 0.08)
HPG8-P5	1	850	3.91	0.47 mol H ₂ O/mol P ₂ O ₅ (± 0.31)
HPG8-P5	2	800	6.31	1.02 mol H ₂ O/mol P ₂ O ₅ (± 0.31)

^a Uncertainty range calculated assuming that the maximal error on the difference between the H₂O solubility of HPG8 and of F-, B-, and P-bearing samples is 0.20

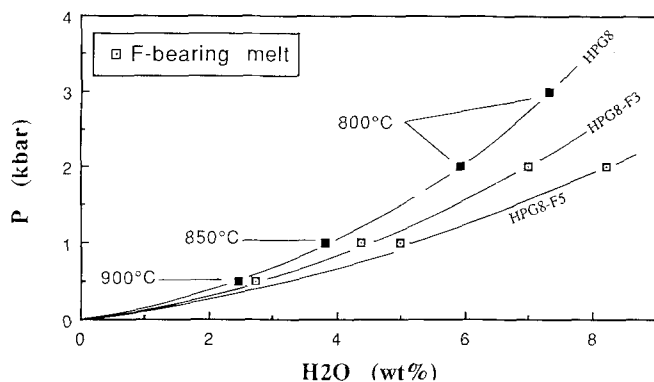


Fig. 1. H₂O solubility (wt.%) versus pressure for compositions HPG8 (0 wt.% F; filled squares), HPG8-F3 (2.86 wt.% F, open squares), HPG8-F5 (4.55 wt.% F, open squares). Data are given in Table 3

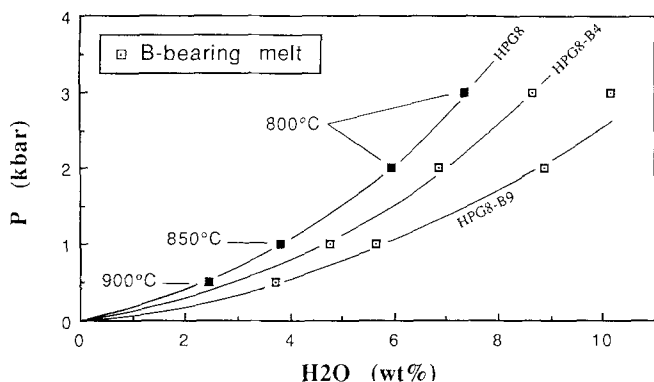


Fig. 2. H₂O solubility (wt.%) versus pressure for compositions HPG8 (0 wt.% B₂O₃, filled squares), HPG8-B4 (4.35 wt.% B₂O₃, open squares), HPG8-B9 (8.92 wt.% B₂O₃, open squares). Data are given in Table 3

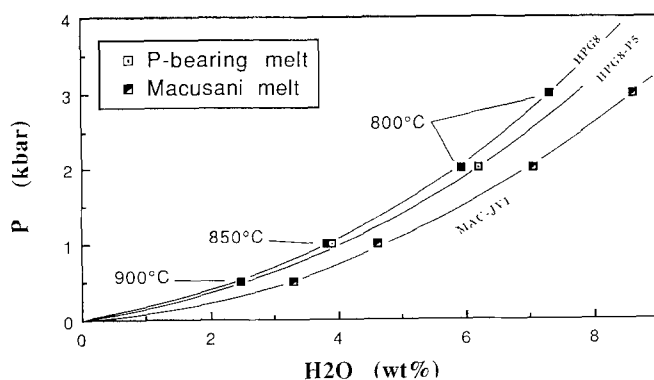


Fig. 3. H₂O solubility (wt.%) versus pressure for compositions HPG8 (0 wt.% P₂O₅, filled squares), HPG8-P5 (5.1 wt.% P₂O₅, open squares), MAC-JV1 (Macusani glass, Peru, half-filled squares). Data are given in Table 3

and of 0.21 wt. % H₂O at 2 kb – 800 °C (Fig. 6). The relative increase in H₂O solubility (due to addition of 1 wt. % B₂O₃) is 5.8% at 1 kb and 3.6% at 2 kb. The H₂O solubility increase observed at the investigated conditions ranges between 0.65 and 1.5 mol H₂O/mol B₂O₃ (Table 4). As in the case of F-bearing melts, the increase in H₂O solubility (absolute value) is more important at higher

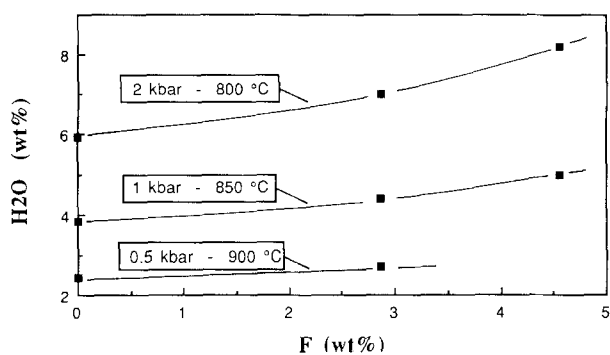


Fig. 4. Variation of the H₂O solubility (wt.%) with changing F content in the melt at 0.5 kb – 900 °C, 1 kb – 850 °C, 2 kb – 800 °C. H₂O solubility data are given in Table 3. The F contents of the melt reported in the diagram are those of the dry starting glasses (0, 2.86, and 4.55 wt.% F)

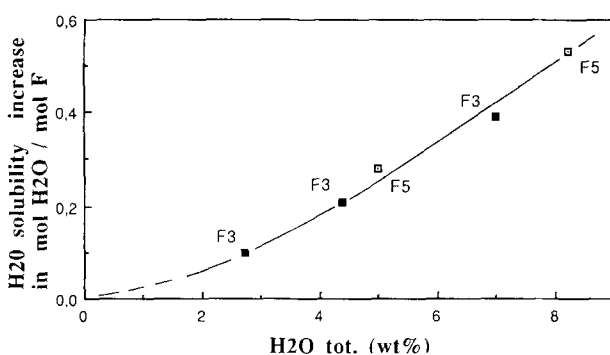


Fig. 5. H₂O solubility increase expressed as mol H₂O/mol F (compared to the base composition HPG8) for compositions HPG8-F3 (F3) and HPG8-F5 (F5) as a function of the H₂O content of the melt. Data are given in Table 4

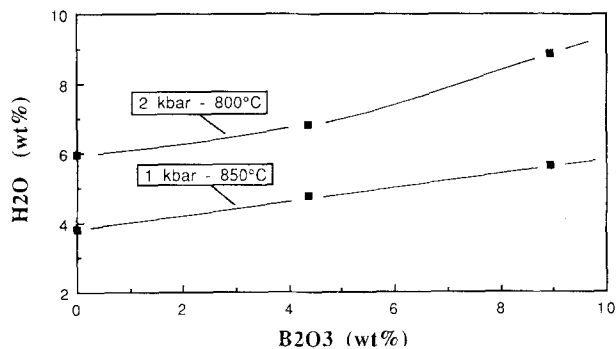


Fig. 6. Variation of the H₂O solubility (wt.%) with changing B₂O₃ content in the melt at 1 kb – 850 °C, 2 kb – 800 °C. H₂O solubility data are given in Table 3. The B₂O₃ contents of the melt reported in the diagram are those of the dry starting glasses (0, 4.35, and 8.92 wt.% B₂O₃)

pressure (i.e. for high water contents; see Fig. 7). However, the relative increase in H₂O solubility is positively correlated with pressure in F-bearing melts and negatively correlated with pressure in B-bearing melts.

Effect of P₂O₅. There is a slight increase in H₂O solubility with increasing P₂O₅ content (Fig. 3). Addition of 5.1 wt. % P₂O₅ produces an increase of 0.10 wt. % H₂O at

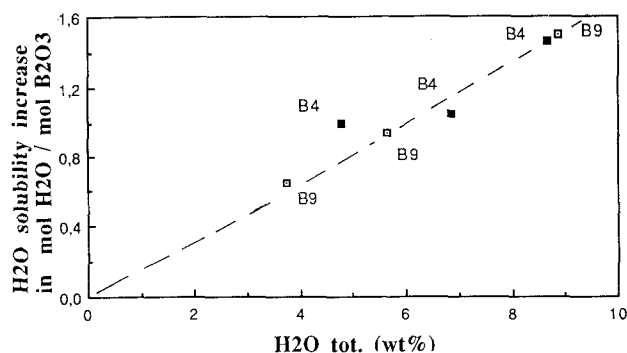


Fig. 7. H₂O solubility increase expressed as mol H₂O/mol B₂O₃ (compared to the base composition HPG8) for compositions HPG8-B4 (B4) and HPG8-B9 (B9) as a function of the H₂O content of the melt. Data are given in Table 4

1 kb – 850 °C and of 0.25 wt. % H₂O at 2 kb – 800 °C (Fig. 3). The H₂O solubility increase due to the addition of 1 mol % P₂O₅ corresponds to 0.47 mol % H₂O at 1 kb and 1.02 mol % at 2 kb (Table 4).

Macusani melt. The H₂O solubility in Macusani melt JV1 is significantly higher than that of the melt HPG8 (both melts have approximately the same Qz/Ab/Or ratio). Compared to HPG8, there is an H₂O solubility increase of 42.0 % relative at 0.5 kb, 21.3 % at 1 kb and 18.5% at 2 kb (Fig. 3). When compared to HPG8, the magnitude of the H₂O solubility increase is approximately similar to that obtained with the melt HPG8-B4 or HPG8-F3.

Discussion

Attainment of equilibrium

Three main points have to be demonstrated in order to show that equilibrium is attained in the experiments: (1) the experimental duration must be long enough to allow complete diffusion of H₂O throughout the initially dry glass sample; (2) the H₂O must be distributed homogeneously in the melt; (3) the melt must be saturated with respect to H₂O.

The experimental duration was kept nearly constant (12 to 15 days) in this study. The time dependence of the experimental results was investigated by Holtz et al. (submitted) using larger samples than those in this study, with a composition of Qz₂₈Ab₃₈Or₃₄ (proportions in wt. %) which is close to that of HPG8. In the experiments of Holtz et al. (submitted), the H₂O contents of the quenched glasses at 1 kb and 800 °C were 4.01 and 4.10 wt. % H₂O for experimental durations of 240 and 504 h, respectively. At 5 kb and 800 °C, the H₂O contents were 9.76, 9.92, and 9.97 for durations of 240, 480, and 672 h, respectively. This shows that durations of 12 to 15 days are long enough to allow complete diffusion of H₂O throughout the initially dry glass samples used in this study. This is also confirmed by the study of Lapham et al. (1984), in which H₂O diffusion coefficients of 10⁻⁷ to 10⁻⁸ cm²/s in a rhyolitic obsidian were determined experimentally.

The homogeneity of H₂O distribution within the glasses was checked by KFT (Holtz et al. 1992a). For 1 mm

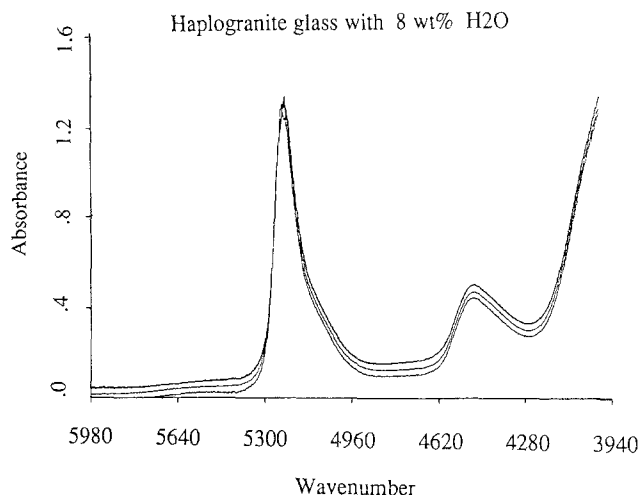


Fig. 8. Infrared spectra of a hydrous haplogranitic glass (anhydrous composition: Qz₂₈Ab₃₈Or₃₄) containing 8 wt. % H₂O (wavenumber in cm⁻¹). Spectra were obtained along a section in the glass sample (distance between each measurement: 0.6 mm). Local resolution for each measurement is approximately 100 μm

thick slices of large glass samples of the composition Qz₂₈Ab₃₈Or₃₄, cut perpendicular to the capsule elongation, no significant variation of the measured H₂O contents was observed (typical variations for 4 slices from a glass synthesized at 800 °C and 1 kb: 4.05, 4.20, 4.05, 4.11 wt. % H₂O; Holtz et al. submitted). Glasses of the composition Qz₂₈Ab₃₈Or₃₄ were analyzed by microscopic infrared spectroscopy (Bruker A 590 at Hannover, Nicolet FTIR 710 at Orléans). Local resolution of the measurements was approximately 100 μm. Measurements were performed along sections through the hydrous glasses and no significant change in the background subtracted peak height (at 4500 and 5230 cm⁻¹) was observed, suggesting that H₂O is distributed homogeneously throughout the sample (see Fig. 8).

Melt is saturated with respect to H₂O if free H₂O is present in the capsule after the experiment. In experiments at low pressure, melts have low H₂O contents and excess H₂O is confirmed by the weight loss method (see section “analysis of H₂O contents”). For most of the samples with higher H₂O contents, the presence of free water in the capsule after the experiment was confirmed, either visually or by measuring a weight loss at 40 °C (loss of weight due to evaporation of H₂O from a punctured capsule, placed for a few minutes in a furnace at 40 °C). In addition, the amount of H₂O added to the dry glass is always higher than the H₂O content of the glasses determined by KFT: the difference between measured and added H₂O is 1.1 to 1.8 wt. % H₂O at 0.5 kb, 1.1 to 3.3 at 1 kb, 0.75 to 4.9 at 2 kb, and 2.7 to 3.2 at 3 kb (see Table 3). Finally, in three cases (HPG8-F3, 1 kb, 850 °C; HPG8-F3, 2 kb, 800 °C, Mac-JV1, 2 kb, 800 °C), experiments were carried out at the same *P*-*T* conditions but different amounts of H₂O were added to the dry starting glasses (differences corresponding to 1 to 2.3 wt. % H₂O). The H₂O content of the quenched glasses determined by KFT did not reveal any systematic variation as a function of the initial amount of added H₂O, thus implying that the H₂O solubility was reached in both cases.

In conclusion, all analyses and observations show that the experimental and analytical procedures used in this study ensured that equilibrium between superliquidus hydrous melts and coexisting H₂O fluid phases was attained.

Composition of the melt phase

It has been demonstrated that the solubility of silicate melt in a coexisting aqueous fluid increases with increasing concentrations of F in the system (e.g. Webster 1990). Pichavant (1983) and London et al. (1988) have shown that B is preferentially partitioned in the vapour phase coexisting with a granitic melt. Thus, it may be possible that the composition of the melt in our experiments may be different from that of the anhydrous dry glass.

In order to avoid important variations of the melt composition due to incongruent dissolution of the silicate melt in the fluid phase, care was taken to add amounts of H₂O only slightly above the expected H₂O solubility. Due to the high ratio melt/fluid during the experiment, the composition of melt will be very little affected by dissolution of silicate in the fluid. In F-bearing melts, the amount of dissolved silicates in the fluid can be particularly high (up to 16 wt. % dissolved silicate; Webster 1990), but D_F (wt. % F in fluid/wt. % F in melt) is < 1 for melts containing less than 8 wt. % F at 2 kb and 800 °C (Webster 1990). Thus, in our experiments, no significant change of the F content of the melt is expected when compared to that of the starting glass.

The quenched hydrous glasses were analyzed (microprobe analysis) in order to compare their composition with that of the starting material. Only F- and P-bearing melts were analyzed. The results are given in Tables 5 and 6. The variations between the recalculated F-free

compositions and that of HPG8 are very small (compare Table 5 and 1). The most important variations are observed for SiO₂. However, the F contents do not vary significantly when comparing dry (starting) and hydrous glasses. Glasses at the rim of the quenched samples could represent quenched silicate material which was dissolved in the fluid. Therefore, these were analyzed separately in two F-bearing experimental samples. The glass compositions are very similar to that obtained in the central part of the glass samples (Table 5). P-bearing quenched glasses of composition HPG8-P5 also show recalculated compositions close to HPG8. Due to the presence of quartz in the experimental products of HPG8-P10, the glass compositions have lower SiO₂ and higher Al₂O₃, Na₂O, K₂O and P₂O₅ contents (Table 6).

Comparison with previous data

F-bearing melts. The increase of H₂O solubility with increasing F content in the melt observed in this study is in agreement with the data of Sorapure and Hamilton (1984), investigating the effect of F on the H₂O solubility in albite melt. Although Sorapure and Hamilton (1984) did not observe any significant variation of the H₂O solubility at 1 kb and 950 °C in melts with 0, 3.5 and 7 wt. % F, they clearly noted an increase of the H₂O solubility at 2 kb and 950 °C (H₂O solubility of approximately 7, 10, 12.5 wt. % H₂O for melts with 0, 3.5 and 7 wt. % F, respectively). The H₂O solubility increase defined by Sorapure and Hamilton (1984) in albite melt at 2 kb (0.84 to 0.94 mol H₂O/mol F) is higher than that observed with HPG8 melt (0.39 to 0.53 mol H₂O/mol F), which may be related to some difference in melt composition (higher alkali content). The increasing H₂O solubility with increasing F content was also noticed by Koster van

Table 5. Composition of F-bearing hydrous glasses

Glass no.	HPG8-F3	HPG8-F3	HPG8-F3	HPG8-F5	HPG8-F5	HPG8-F5
P (kb)	1	1	2	1	1	2
T (°C)	850	850	800	850	850	800
H ₂ O (wt. %) ^a	4.59	4.59	7.15	4.66	4.66	8.16
n ^b	10	6	9	11	6	5
	core	rim	core	core	rim	core
SiO ₂	74.82	74.19	72.47	74.39	73.97	71.58
Al ₂ O ₃	11.24	11.16	10.91	10.54	10.50	10.07
K ₂ O	3.92	3.78	3.99	3.97	4.00	3.78
Na ₂ O	4.26	4.21	3.87	4.28	4.20	3.85
F	3.22	3.02	2.87	4.26	4.23	4.44
Total	97.46	96.36	94.11	97.45	96.90	93.72
Haplogranite composition recalculated to 100%						
SiO ₂	79.39	79.48	79.43	79.83	79.82	80.17
Al ₂ O ₃	11.93	11.96	11.96	11.32	11.33	11.28
K ₂ O	4.16	4.05	4.37	4.26	4.32	4.23
Na ₂ O	4.52	4.51	4.24	4.59	4.53	4.32
Total	100.00	100.00	100.00	100.00	100.00	100.00

Note: analyzed with Cameca SX50 electron microprobe at Orléans (BRGM – CNRS), analytical conditions: 6 nA, 15 Kv, 20 µm defocused beam, 5 s counting time for Na and K, 10 s counting time for Si, Al, F

^a Measured by Karl Fischer titration (Table 3)

^b Number of analyses

Table 6. Composition of P-bearing hydrous glasses

Glass no.	HPG8-P5	HPG8-P5 ^c	HPG8-P10 ^d	HPG8-P10 ^d
P (kb)	1	2	1	2
T (°C)	850	800	850	800
H ₂ O (wt%) ^a	3.91	6.31	nd	nd
n ^b	6	9	6	5
SiO ₂	72.09	69.79	64.67	57.74
Al ₂ O ₃	11.30	11.18	11.98	13.80
K ₂ O	3.84	3.83	4.01	4.63
Na ₂ O	4.33	4.04	4.07	4.77
P ₂ O ₅	4.83	4.82	9.80	12.11
Total	96.39	93.66	94.53	93.05
Haplogranite composition recalculated to 100%				
SiO ₂	78.73	78.55	76.48	71.33
Al ₂ O ₃	12.33	12.58	14.17	17.05
K ₂ O	4.20	4.31	4.74	5.72
Na ₂ O	4.72	4.55	4.81	5.89
Total	100.00	100.00	100.00	100.00

Note: analyzed with Cameca electron microprobe at Hannover (University), analytical conditions: 18 nA, 15 Kv, 20 μm defocused beam, 2 s counting time for Na and K, 5s counting time for Si, Al, P
^a Measured by Karl Fischer titration (Table 3)

^b Number of analyses

^c Melt coexisting with a very low amount of quartz (< 1 vol. %)

^d Melt coexisting with a significant amount of quartz

Groos and Wyllie (1968) and is in agreement with the hypothesis of Manning (1981), suggesting that hydrated aluminofluoride groups may exist.

In contrast, our data and those of Sorapure and Hamilton (1984) are not in agreement with the recent data of Webster (1990). Webster (1990) investigated the partitioning of F between H₂O and CO₂ fluids and melt and noted that the solubility of H₂O in the melt is independent of the F concentration of the system with up to 6.7 wt. % F in the melt (at 2–5 kb and 775–1000 °C). However, except for eight compositions, the water content of the melts was calculated using Burnham's (1981) equimolar water solubility model (as described by Burnham and Nekvasil 1986). On the basis of liquidus phase relationships and H₂O solubility data, Holtz et al. (1992b) and Pichavant et al. (1992a) showed that this model has to be reconsidered for haplogranite compositions, due to the significant compositional dependence of H₂O solubility in these melts. Webster (1990) determined the H₂O contents of eight experimental glasses by SIMS (ion microprobe). As described by Webster (1990), this method is particularly complicated in F-bearing glasses and the analytical conditions had to be changed as a function of the F content. This, and the use of F-free granitic standards, may have influenced the measured ¹H/³⁰Si ratio. The data obtained by Webster at 2 kb and 800 °C (Webster 1990, Fig. 2, p. 430) are given with an uncertainty of ± 0.5 to 0.7 wt. % H₂O. Compared to H₂O determination by SIMS, the precision of the method used in this study is better (relative variation < 5 wt. %; see also Holtz et al. 1992a) and most of our data (especially for low F contents) are within the uncertainty range given by Webster (1990). Another possible explanation for the differences between Webster (1990) and this study is the use of different starting materials (topaz rhyolite by Webster 1990; synthetic glass in this study).

Manning et al. (1980) suggested that the addition of F to haplogranitic melts produces the formation of aluminofluoride complexes (AlF₆³⁻) and this was confirmed by NMR investigations of anhydrous F-bearing glasses of nepheline, jadeite, and albite composition, in which six-coordinated aluminofluoride complexes have been detected (Kohn et al. 1991; Schaller et al. 1992). Our data clearly show a positive correlation between H₂O solubility and F content in the melt. However, on the basis of the available spectroscopic data, it is not possible to determine if this correlation is the result of the formation of hydrated aluminofluoride complexes or not.

B-bearing melts. The increase of the H₂O solubility with increasing B₂O₃ content in the melt is in agreement with previous data obtained by Pichavant (1981, 1983) at 1 kb, demonstrating an increase of the H₂O solubility of approximately 1 mol H₂O/mol B₂O₃. Similar values have been obtained in this study for melts containing 4.35 and 8.92 wt. % B₂O₃ at 1 kb and 850 °C (+ 1.00 and 0.94 mol H₂O/mol B₂O₃, see Table 4). At higher pressure (2 kb), the observed increase of H₂O solubility with increasing B₂O₃ content is in agreement with 2 kb data obtained by Morgan (personal communication 1992).

In contrast to F-bearing melts, the positive correlation between H₂O solubility and B₂O₃ content of the melt is clearly attributed to the formation of hydrated B-bearing complexes (mainly borate or boroxol groups, e.g. Morgan et al. 1990, for a review see Pichavant 1983).

P-bearing melts. There are almost no data on the effect of P on the H₂O solubility in felsic melts. London et al. (1990) determined an increase of the solubility of H₂O in a haplogranite melt by 7.5 mol H₂O/mol P₂O₅ up to 3.0 wt. % P₂O₅ in the melt (at 2 kb) and observed no further increase in H₂O solubility with higher P contents. In contrast, we determined a significantly lower H₂O solubility increase (< 1.1 mol H₂O/mol P₂O₅, see Table 4) for a composition with 5.1 wt. % P₂O₅. Obviously, more data on H₂O solubility and phase relations in P-bearing melts are needed to clarify this discrepancy.

Phosphorus is known to form aluminophosphate units in peraluminous melts (Pichavant et al. 1992b) and the existence of AlPO₄ complexes (Mysen et al. 1981) and both Al and alkali ortho-phosphate complexes (Gan and Hess 1992) is suggested from spectroscopic studies. This is further confirmed by experimental results (London et al. 1990; this study) clearly showing a dramatic increase of the activity of SiO₂ with increasing P content, and the lowering of the activity of feldspar components, suggesting that part of the Al is not associated with alkalis in P-bearing melts. However, the very small increase in H₂O solubility with increasing P-content demonstrated in this study is not interpreted, and, to our knowledge, no spectroscopic investigations of hydrous P-bearing glasses were undertaken to demonstrate the existence of hydrated complexes (such as diatomic hypophosphate complex, Morgan personal communication 1992, or structures close to amblygonite).

Macusani melt. Recently London et al. (1988, 1989) performed experiments using the Macusani glass as starting material (composition identical to the sample JV1 used in this study) and measured the H₂O contents of the quenched glasses. The H₂O solubility determined at 2 kb and

$T < 800^\circ\text{C}$ was found to be particularly high (11.5 ± 0.5 wt. % H_2O). In this study, we were not able to reproduce this H_2O solubility value (H_2O solubility in this study is 7.04 ± 0.15 wt. % H_2O at 2 kb and 800°C , see Table 3). The dramatic difference in H_2O solubility between the data of London et al. (1988) and this study requires a careful examination since many interpretations concerning the physical and chemical properties of Macusani melt (very low viscosity and solidus temperature) are based on the high H_2O solubility in this melt (London 1987; London et al. 1988, 1989). The hypothesis that our solubility data are too low is considered first. Our experimental and analytical method was tested on haplogranite melts (Behrens et al. 1991; Holtz et al. 1992a) and the data are in very good agreement (or even slightly higher at pressure > 2 kb) with those of Oxtoby and Hamilton (1978) and Hamilton and Oxtoby (1986). Using a bubble-free starting material, no water vesicles are formed during the experiment and the measured H_2O solubility cannot be increased artificially by the presence of water-bearing fluid inclusions. Migration of water out of the glass during the quench could explain slightly lower H_2O solubility data, but would not explain a difference of 40% relative in the H_2O solubility. Furthermore, no effect of the quenching rate (experiments with cold seal and internally-heated pressure vessels) on H_2O solubility determined by KFT and with dry glass as starting material was observed by Holtz et al. (submitted). If water leaves the melt during the quench (i.e. there is an oversaturation of water in the melt), H_2O -bearing fluid inclusions should be formed in the glasses (which was not observed). In addition, the presence of small inclusions would not affect significantly the amount of measured H_2O , since roughly crushed glasses or single glass pieces are used for the titration. Finally, some water may migrate out of highly hydrated glass samples after quenching but this is excluded for glasses with H_2O contents < 8 wt. % H_2O (Behrens submitted).

London et al. (1988) used different methods to determine the H_2O solubility in the Macusani melt, but some of the methods (weight loss, changes in melt composition, electron microprobe analysis) probably tend to overestimate the H_2O solubility. The water contained in the fluid inclusions trapped in the experimental products of London et al. (1988) may not be released by heating the sample at 100°C , which may increase artificially the H_2O content of the melt. Changes in melt composition due to the presence of a water-bearing fluid phase are probably not significant for H_2O contents just over saturation. It has to be noted that the H_2O solubility data obtained by ion microprobe analysis (9.5 ± 2.0 wt. % H_2O ; London et al. 1988) are lower than those obtained by the other methods. We therefore conclude that the value of 11.5 wt. % H_2O considered as the approximate concentration of H_2O at saturation in the Macusani melt (London et al. 1988) is very probably overestimated.

Petrologic implications

Certain granitic systems can concentrate fluorine up to 2.4 wt. % F (e.g. Pichavant et al. 1987a; London et al.

1988), boron up to 1 wt. % B_2O_3 (e.g. Pichavant and Manning 1984) and phosphorus up to 0.5 wt. % P_2O_5 (e.g. Bea et al. 1992; Pichavant et al. 1987b and Table 1). Thus, the amounts of F, B, and especially P, present in the investigated glass compositions are higher than those occurring in relatively common natural rocks (except some very particular compositions representing probably highly differentiated melts). However, our data allow us to estimate the maximum increase in H_2O solubility in natural melts due to addition of F, B and P. At 2 kb for example, an increase of approximately 0.35 and 0.2 wt. % H_2O was observed by addition of 1% F and B_2O_3 , respectively (values obtained by comparing HPG8 with HPG8-F3 and HPG8-B4). The increase in H_2O solubility, in addition to the effect of F and B, will contribute to decrease the viscosity of the melt. In contrast, the effect of P on the H_2O solubility is negligible. It has been shown however that very high amounts of P can be incorporated in Ca-free melts and that the presence of P increases considerably the activity of SiO_2 (see also London et al. 1990).

It is not clear whether the individual effects of F and B might be additive in mixed (F- and B-bearing systems) systems and only experimental data from more complex systems would help to solve this problem. However, by comparing the H_2O solubility in Macusani melt with that of B- and F-bearing melts, the linearly added effects of F and B would only produce an increase in H_2O solubility of 0.55 wt. % H_2O at 2 kb. This value is lower than the H_2O solubility increase observed experimentally ($+ 1.07$ wt. % H_2O when compared to HPG8). Thus, in addition to F and B, other factors must increase the H_2O solubility in this melt (Li, peraluminous composition). The comparison of the H_2O solubility data from the haplogranitic HPG8 melt and the Macusani melt obtained for similar pressures (0.5 to 3 kb) show a maximal difference of 1.3 wt. % H_2O . By comparison with the Macusani melt which can be considered as particularly rich in elements favouring a high H_2O solubility, it can be concluded that, at $P(\text{H}_2\text{O}) < 3$ kb, an H_2O solubility variation of more than 1.5 wt. % H_2O from the H_2O solubility in a haplogranite melt with the same normative Qz/Ab/Or proportions is not to be expected in common granitic melts.

Acknowledgements. This work was supported by Procope (German-French research program No. 92053 between Hannover and Orléans). Technical assistance was provided by F. Schulze, J. Koepcke, O. Rouer. Comments of M. Pichavant and R. Linnen were helpful. The manuscript benefitted from reviews of D. Hamilton, D. London, and G.B. Morgan VI.

References

- Bea F, Fershtater G, Corretge LG (1992) The geochemistry of phosphorus in granite rocks and the effect of aluminium. *Lithos* (in press)
- Behrens H, Holtz F, Dingwell DB, Taylor RP (1991) Compositional dependence of water solubility in haplogranitic melts. *EOS* 72: 533-534
- Bénard F, Moutou P, Pichavant M (1985) Phase relations of tourmaline leucogranites and the significance of tourmaline in silicic magmas. *J Geol* 93: 271-291
- Burnham CW (1981) The nature of multicomponent aluminosilicate melts. In: Richards DT, Wickman FE (eds) *Chemistry and*

- geochemistry of solutions at high temperatures and pressures, physics and chemistry of the earth. Pergamon, New York, pp 197–229
- Burnham CW, Nekvasil H (1986) Equilibrium properties of granite pegmatite magmas. *Am Mineral* 71: 239–263
- Chorlton LB, Martin RF (1978) The effect of boron on the granite solidus. *Can Mineral* 16: 239–244
- Day HW, Fenn PM (1982) Estimating the P-T-X(H₂O) conditions during crystallization of low calcium granites. *J Geol* 90: 485–507
- Dingwell DB (1987) Melt viscosities in the system NaAlSi₃O₈-H₂O-F₂O-1. In: Mysen BO (ed) *Magmatic processes: physicochemical principles*. The Geochemical Society, Spec Publ 1: 423–431
- Dingwell DB, Knoche R, Webb SL (1992a) The effect of fluorine on the density of haplogranite melt. *Am Mineral* (in press)
- Dingwell DB, Knoche R, Webb SL, Pichavant M (1992b) The effect of B₂O₃ on the viscosity of haplogranitic liquids. *Am Mineral* 77: 457–461
- Dingwell DB, Harris DM, Scarfe CM (1984) The solubility of H₂O in melts in the system SiO₂-Al₂O₃-Na₂O-K₂O at 1 to 2 kbar. *J Geol* 92: 387–395
- Dingwell DB, Scarfe CM, Cronin DJ (1985) The effect of fluorine on viscosities of melts in the system Na₂O-Al₂O₃-SiO₂: Implications for phonolites, trachytes and rhyolites. *Am Mineral* 70: 80–87
- Franz H (1966) Solubility of water vapour in alkali borate melts. *J Am Ceram Soc* 49: 473–477
- Gan H, Hess PC (1992) Phosphate speciation in potassium aluminosilicate glasses. *Am Mineral* 77: 495–506
- Hamilton DL, Oxtoby S (1986) Solubility of water in albite-melt determined by the weight-loss method. *J Geol* 94: 626–630
- Harrison TM, Watson EB (1984) The behaviour of apatite during crustal anatexis: equilibrium and kinetic considerations. *Geochim Cosmochim Acta* 48: 1468–1477
- Holtz F, Behrens H, Dingwell DB, Taylor RP (1992a) Water solubility in aluminosilicate melts of haplogranite compositions at 2 kbar. *Chem Geol* 96: 289–302
- Holtz F, Pichavant M, Barbey P, Johannes W (1992b) Effects of H₂O on liquidus phase relations in the haplogranite system at 2 and 5 kbar. *Am Mineral* 77: 1223–1241
- Kohn SC, Dupree R, Mortuza MG, Henderson CMB (1991) NMR evidence for five- and six-coordinated aluminum fluoride complexes in F-bearing aluminosilicate glasses. *Am Mineral* 76: 309–312
- Koster van Groos AF, Wyllie PJ (1968) Melting relationships in the system NaAlSi₃O₈-NaF-H₂O to 4 kilobars pressure. *J Geol* 76: 50–70
- Lapham KE, Holloway JR, Delaney JR (1984) Diffusion of H₂O and D₂O in obsidian at elevated temperatures and pressures. *J Non-Cryst Solids* 67: 179–1912
- London D (1987) Internal differentiation of rare-element pegmatites: effects of boron, phosphorus, and fluorine. *Geochim Cosmochim Acta* 51: 403–420
- London D, Hervig RL, Morgan GB VI (1988) Melt-vapor solubilities and elemental partitioning in peraluminous granite-pegmatite systems: experimental results with Macusani glass at 200 MPa. *Contrib Mineral Petrol* 99: 360–373
- London D, Morgan GB VI, Hervig RL (1989) Vapor-undersaturated experiments with Macusani glass + H₂O at 200 MPa, and the internal differentiation of granitic pegmatites. *Contrib Mineral Petrol* 102: 1–17
- London D, Loomis JL, Huang W, Morgan GB VI (1990) Behavior and effects of phosphorus in the system Ab-Or-Qz-H₂O at 200 MPa (H₂O). *Geol Soc Am Abstr with Prog*: 302
- Manning DAC (1981) The effect of fluorine on liquidus phase relationships in the system Qz-Ab-Or with excess water at 1 kbar. *Contrib Mineral Petrol* 76: 257–262
- Manning DAC, Hamilton DL, Henderson CMB, Dempsey MJ (1980) The probable occurrence of interstitial Al in hydrous, F-bearing and F-free aluminosilicate melts. *Contrib Mineral Petrol* 75: 257–262
- McMillan P, Holloway JR (1987) Water solubility in aluminosilicate melts. *Contrib Mineral Petrol* 97: 320–332
- Morgan GB VI, London D, Kirkpatrick RJ (1990) Reconnaissance spectroscopic study of hydrous sodium aluminum borosilicate glasses. *Geol Soc Am Abstr with Prog* 22: A167
- Mysen BO, Ryerson FJ, Virgo D (1981) The structural role of phosphorus in silicate melts. *Am Mineral* 66: 106–117
- Oxtoby S, Hamilton DL (1978) The discrete association of water with Na₂O and SiO₂ in NaAl silicate melts. *Contrib Mineral Petrol* 66: 185–188
- Pichavant M (1981) An experimental study of the effect of boron on a water-saturated haplogranite at 1 kbar pressure: geological applications. *Contrib Mineral Petrol* 76: 430–439
- Pichavant M (1983) Melt-fluid interaction deduced from studies of silicates-B₂O₃-H₂O systems at 1 kbar. *Bull Mineral* 106: 201–211
- Pichavant M (1987) Effects of B and H₂O on liquidus phase relations in the haplogranite system at 1 kbar. *Am Mineral* 72: 1056–1070
- Pichavant M, Manning DAC (1984) Petrogenesis of tourmaline granites and topaz granites; the contribution of experimental data. *Phys Earth Planet Inter* 35: 31–50
- Pichavant M, Boher M, Stenger JF, Aissa M, Charoy B (1987a) Relations de phase des granites de Beauvoir à 1 et 3 kbar en conditions de saturation en H₂O. In: Cuney M, Aufran A (eds) *Géologie de la France. Mémoire GPF vol 1, no 2–3*, pp 77–86
- Pichavant M, Valencia Herrera J, Boulmier S, Briquieu L, Joron JL, Juteau M, Marin L, Michard A, Sheppard SMF, Treuil M, Vernet M (1987b) The macusani glasses, SE Peru: evidence of chemical fractionation in peraluminous magmas. In: BO Mysen (ed) *Magmatic processes: physicochemical principles*. The Geochemical Society, Spec Publ 1: 359–373
- Pichavant M, Holtz F, McMillan P (1992a) Phase relations and compositional dependence of H₂O solubility in quartz-feldspar melts. *Chem Geol* 96: 303–320
- Pichavant M, Montel JM, Richard LR (1992b) Apatite solubility in peraluminous liquids: experimental data and an extension of the model of Harrison and Watson (1984). *Geochim Cosmochim Acta* 56: 3855–3861
- Schaller T, Dingwell DB, Keppler H, Knöller W, Merwin L, Sebald A (1992) Fluorine in silicate glasses: a multinuclear nuclear magnetic resonance study. *Geochim Cosmochim Acta* 56: 701–707
- Sorapure R, Hamilton DL (1984) The solubility of water in melts of albite composition with varying additions of fluorine. In: Henderson CMB (ed) *Progress in experimental petrology*. NERC Prog Exp Pet 6: 28–29
- Tuttle OF, Bowen NL (1958) Origin of granite in the light of experimental studies in the system NaAlSi₃O₈-KAlSi₃O₈-SiO₂-H₂O. *Geol Soc Am Mem* 74: 1–156
- Webster JD (1990) Partitioning of F between H₂O and CO₂ fluids and topaz rhyolite melt. *Contrib Mineral Petrol* 104: 424–438
- Westrich HR (1987) Determination of water in volcanic glasses by Karl-Fischer titration. *Chem Geol* 63: 335–340

Editorial responsibility: W. Schreyer