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Compositional dependence of H_2O solubility along the joins $NaAlSi_3O_8$-$KAlSi_3O_8$, $NaAlSi_3O_8$-$LiAlSi_3O_8$, and $KAlSi_3O_8$-$LiAlSi_3O_8$

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ABSTRACT

The composition-dependence of the solubility of H_2O in silicate melts along the binary joins $NaAlSi_3O_8$-$KAlSi_3O_8$, $NaAlSi_3O_8$-$LiAlSi_3O_8$, and $KAlSi_3O_8$-$LiAlSi_3O_8$ has been determined at 2 kbar and 1040 °C. The study involved 1 atm dry oxide fusion, hydrothermal saturation, isobaric rapid quench and macroscopic analysis for H_2O using Karl Fischer titration (KFT) and microscopic investigation of homogeneity using infrared absorption spectroscopy, respectively.

The solubility of H_2O in these melts increases in the order $KAlSi_3O_8$ (5.12 wt%) < $NaAlSi_3O_8$ (6.03 wt%) < $LiAlSi_3O_8$ (7.32 wt%). The total relative weight percent variation in solubility is 43%, which corresponds to a relative mole percent variation of 23%. Along the joins, small but systematic deviations from additivity are observed at the 1σ uncertainty level. These deviations are positive on the $NaAlSi_3O_8$-$KAlSi_3O_8$ join but negative on the $LiAlSi_3O_8$-bearing joins.

The present results confirm the early suggestion of Voigt et al. (1981) that solubility variation along the $NaAlSi_3O_8$-$KAlSi_3O_8$ join is nonlinear and disagree in detail with the equimolal approximation of Burnham (1975, 1981) and Burnham and Davis (1974). Models of H_2O solubility must take into account not only the nonequimolal solubility of H_2O in feldspathic melts but also nonlinear binary variations as well. We interpret the relative solubilities of the end-member compositions in terms of the relative stability of the tectosilicate melt structure and the nonlinearities along the joins in terms of the next-nearest neighbor distributions of Al and Si in these melts.

INTRODUCTION

H_2O is one of the most abundant volatile species in magmas, and its presence strongly influences physical and chemical melt properties as well as crystal-melt phase relations. A few weight percent of dissolved H_2O drastically decreases the liquidus and solidus temperature of a melt and strongly affects the phase relations and the compositions of the minerals crystallizing from the evolving magma (Yoder 1965; Kushiro et al. 1968). The viscosity can be modified by more than five orders of magnitude (Shaw 1963; Dingwell 1987). Additionally, in the presence of H_2O, the electrical conductivity is enhanced (Lebedev and Khitarov 1964), and the diffusivities of some crystal-forming elements are increased (Watson 1979). Although partial molar volume estimates for H_2O vary (see review by Lange 1994), numerous studies have shown that the presence of H_2O decreases the density of silicate melts and glasses (e.g., Acocella et al. 1984; Silver et al. 1990; Romano et al. 1994).

Because of these consequences of the incorporation of H_2O into silicate melts, significant attempts at modeling the systematics of the dependence of the solubility of H_2O in silicate melts on melt composition, through the development of thermodynamic models, have been performed (Burnham 1975; Burnham and Davis 1974; Spera 1974; Stolper 1982b; Silver and Stolper 1989; Silver et al. 1990) and have met with some success. One of the best constraints on thermodynamic modeling of H_2O solution in silicate melts is highly precise and accurate solubility data. Surprisingly, much too few data exist (see reviews by McMillan and Holloway 1987; McMillan 1994), despite the long history of investigation of H_2O in silicate melts (Goranson 1931, 1936, 1938; Yoder et al. 1957; Yoder 1965; Burnham and Jahns 1962; Burnham and Davis 1971; Orlova 1962; Kadik and Lebedev 1968; Boettcher and Wyllie 1969; Oxtoby and Hamilton 1978a, 1978b; Voigt et al. 1981; Day and Fenn 1982; Dingwell et al. 1984; Hamilton and Oxtoby 1986; Holtz et al. 1992, 1993, 1995). Investigations of the microscopic interactions of H_2O in melts have also been pursued in an effort to develop structural models capable of generalizing the results of solubility studies in thermodynamic terms (Silver and Stolper 1985, 1989; Mysen and Virgo 1986; McMillan and Remmele 1986; Farnan et al. 1987; Kohn et al. 1989, 1992; Kümmerlen et al. 1993).

Inspired by evidence from recent studies pointing to significant compositional dependence of the solubility of

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H_2O in felsic melts (Holtz et al. 1992, 1993, 1995), and in an attempt to resolve controversy surrounding previous determinations, we turned our attention to melts of the feldspar stoichiometry (K,Na,Li)$AlSi_3O_8$.

In this study, we present a series of experiments specifically devoted to the determination of the compositional dependence of H_2O solubility in the systems $NaAlSi_3O_8$-$KAlSi_3O_8$, $NaAlSi_3O_8$-$LiAlSi_3O_8$, and $KAlSi_3O_8$-$LiAlSi_3O_8$ at 1040 °C and 2 kbar.

EXPERIMENTAL METHODS

Synthesis

The anhydrous starting glasses used in the present study were generated by the direct fusion of 100 g (decarbonated equivalent) batches of powder mixes of the alkali carbonates, SiO_2, and Al_2O_3. The powders of the starting materials were dried at 120 °C overnight prior to weighing, then mixed in plastic bottles by agitation for approximately 5–10 min. The powder mixes were fused in air in thinwalled 75 cm^3 platinum crucibles for approximately 2 h at 1650 °C. The products of the initial fusion were bubble-rich and inhomogeneous. To remove bubbles, react fully, and homogenize the starting glasses, the melted batches were transferred to a second furnace equipped with a high temperature viscometer and stirred at 50 or 100 rpm for hours to days at 1650 °C. The melts were periodically sampled by removal of the spindle to check for the presence of bubbles and crystals. The products of these second fusions were cooled slowly in the box furnace to <800 °C, and then removed and allowed to cool slowly to room temperature to prevent fracturing during quenching.

The composition of the starting glasses was determined by ICP-AES analyses. The results of the analysis are given in Table 1 as the proportions (in weight percent) of the oxides. The analyzed compositions deviate from the ostensible compositions by <0.05 in the Al/alkali ratio and <1 wt% in SiO_2 content.

Glass cylinders (diameter: 0.3 cm; length: 0.3–0.4 cm) were drilled by water-cooled diamond coring tools, cleaned ultrasonically in acetone, and then dried at 110 °C to remove any residue of acetone. Glass samples (~0.1 g) were then loaded together with ~0.01 g of doubly distilled water in capsules formed from platinum tubing (outer diameter: 0.32 cm; length: 1.5 cm, wall thickness 0.015 cm) and sealed with an arc-welder.

The amount of added water was chosen to be about 3–4% higher than the expected solubility value. This value was high enough to prevent the effect of air enclosed in the capsule during preparation but low enough to minimize possible changes in the anhydrous stoichiometry of the melt resulting from incongruent dissolution of melt components in water.

TABLE 1. Analyzed anhydrous compositions (wt% oxide)

Comp.	SiO_2 (±0.6)	Al_2O_3 (±0.4)	Na_2O (±0.5)	K_2O (±0.5)	Li_2O (±0.5)	Total
Na_{100}	68.1	19.1	11.8			99.0
	68.7	*19.4*	*11.8*			
$Na_{90}K_{10}$	69.1	19.0	10.9	1.8		101.0
	68.3	*19.3*	*10.6*	*1.8*		
$Na_{70}K_{30}$	67.8	19.0	8.0	5.4		100.2
	67.5	*19.1*	*8.1*	*5.3*		
$Na_{50}K_{50}$	67.6	18.9	5.6	8.7		100.8
	66.7	*18.9*	*5.7*	*8.7*		
$Na_{30}K_{70}$	66.4	18.8	3.3	12.0		100.5
	65.9	*18.6*	*3.4*	*12.1*		
$Na_{10}K_{90}$	65.3	18.8	1.2	15.6		100.9
	65.1	*18.4*	*1.1*	*15.3*		
K_{100}	65.4	18.5		16.5		100.4
	64.8	*18.3*		*16.9*		
$K_{90}Li_{10}$	64.6	18.8		15.8	0.5	99.7
	65.6	*18.5*		*15.4*	*0.5*	
$K_{70}Li_{30}$	66.3	19.2		12.6	1.6	99.7
	67.0	*19.0*		*12.3*	*1.7*	
$K_{50}Li_{50}$	68.2	20.0		9.3	2.9	100.4
	68.7	*19.4*		*9.0*	*2.9*	
$K_{30}Li_{70}$	70.3	20.6		5.8	4.2	100.9
	70.5	*19.9*		*5.5*	*4.1*	
$K_{10}Li_{90}$	72.2	20.9		1.9	5.5	100.5
	72.3	*20.4*		*1.9*	*5.4*	
Li_{100}	73.7	20.7			6.2	100.6
	73.2	*20.7*			*6.1*	
$Li_{90}Na_{10}$	73.3	20.8	1.1		5.1	100.3
	72.8	*20.6*	*1.3*		*5.4*	
$Li_{70}Na_{30}$	72.2	20.5	3.6		3.5	99.8
	71.8	*20.3*	*3.7*		*4.2*	
$Li_{50}Na_{50}$	70.8	20.2	6.1		2.3	99.4
	70.9	*20.1*	*6.1*		*2.9*	
$Li_{30}Na_{70}$	69.6	20.4	8.4		1.1	99.5
	70.0	*19.8*	*8.4*		*1.7*	
$Li_{10}Na_{90}$	68.2	19.5	10.7		0.6	99.0
	69.2	*19.6*	*10.7*		*0.6*	

Note: Na_{100} = $NaAlSi_3O_8$ (albite), K_{100} = $KAlSi_3O_8$ (orthoclase). Compositions determined by ICP analysis (nominal compositions in italics).

The capsules were checked for possible leakage by testing for weight loss after drying in an oven at 100 °C for at least 1 h. After an hour at 100 °C, the added water was considered to be distributed randomly (space-filling) in the platinum capsule, and thus around the glass sample. The sealed capsules were placed in TZM vessels (argon pressure medium), pressurized to 2 kbar and heated to 1040 °C where they were held for a time sufficient to allow complete homogenization of H_2O dissolved in the melt by diffusion through the sample (experimental durations ranged from 70 to 216 h. See Table 2). Temperature was measured with a Ni-NiCr thermocouple (accuracy ±15 °C) and the pressure was measured with a strain-gauge manometer (accuracy ±0.05 kbar). After the high pressure–high temperature dwells, the samples were quenched rapidly and isobarically in the TZM vessels by dropping the sample into the cold part of the vessel (estimated quench rate 200 °C/s). Special care was taken during the quench to maintain isobaric conditions by opening the vessel to the pressure line ($2\pm^{0.05}_{0}$ kbar).

Synthesis of hydrous glasses was also performed in the Institut für Mineralogie, Universität Hannover, for some compositions along the $NaAlSi_3O_8$-$KAlSi_3O_8$ join. Dry glasses for Ab and Or end-members were prepared according to the procedure described in Behrens (1995). For intermediate compositions, the starting materials were hydrous glasses with approximately 2 wt% of H_2O. The

TABLE 2. Experimental results

Comp.	Sample	*t* (h)	H_2O_{ex}* (wt%)	H_2O (wt%)	H_2O** (mol fr.)	Comp.	Sample	*t* (h)	H_2O_{ex}* (wt%)	H_2O (wt%)	H_2O** (mole fr.)	Comp.	Sample	*t* (h)	H_2O_{ex}* (wt%)	H_2O (wt%)	H_2O** (mole fr.)
K_{100}	341-1	84	8.19	5.04	0.170	$K_{50}Na_{50}$	Han-1†	70	6.30	5.61	0.182	$K_{30}Li_{70}$	335-1	88	9.39	6.40	0.195
K_{100}	184-1	74	6.39	5.20	0.175	$K_{40}Na_{60}$	Han-1†	70	10.30	5.84	0.188	$K_{30}Li_{60}$	335-1	88	9.39	6.43	0.196
K_{100}	Han-1†‡	70	8.50	5.09	0.172	$K_{40}Na_{60}$	Han-1†	70	7.60	5.86	0.188	$K_{10}Li_{90}$	336-1	92	9.17	6.96	0.206
$K_{90}Na_{10}$	95-1	72	9.50	5.26	0.176	$K_{30}Na_{70}$	Rq-1	82	9.90	6.03	0.192	$K_{10}Li_{90}$	336-1	92	9.17	6.94	0.205
$K_{90}Na_{10}$	95-4	72	9.50	5.28	0.176	$K_{30}Na_{70}$	Rq-1	82	9.90	5.96	0.190	Li_{100}	214-2	88	15.12	7.52	0.217
$K_{80}Na_{20}$	Han-1†	70	7.70	5.36	0.178	$K_{30}Na_{70}$	413-1	84	11.93	5.83	0.187	Li_{100}	214-2	88	15.12	7.37	0.214
$K_{70}Na_{30}$	326-1	100	9.06	5.58	0.183	$K_{10}Na_{90}$	394-1	144	8.90	6.05	0.191	Li_{100}	214-1	88	15.12	7.19	0.209
$K_{70}Na_{30}$	326-1	100	9.06	5.70	0.186	$K_{10}Na_{90}$	394-3	144	8.90	6.00	0.189	Li_{100}	214-4	88	15.12	7.19	0.209
$K_{70}Na_{30}$	103-1	96	9.36	5.45	0.180	$K_{10}Na_{90}$	412-1	84	10.00	5.99	0.189	$Na_{90}Li_{10}$	339-1	82	8.81	6.11	0.191
$K_{70}Na_{30}$	103-4	96	9.36	5.46	0.180	$K_{10}Na_{90}$	412-1	84	10.00	6.00	0.189	$Na_{90}Li_{10}$	339-3	82	8.81	6.13	0.191
$K_{70}Na_{30}$	359-1	70	8.89	5.41	0.178	Na_{100}	325-1	72	8.50	5.99	0.188	$Na_{70}Li_{30}$	200-1	70	12.05	6.38	0.196
$K_{70}Na_{30}$	103-4	96	9.36	5.51	0.181	Na_{100}	Rq-1	216	9.30	5.99	0.188	$Na_{70}Li_{30}$	200-1	70	12.05	6.20	0.191
$K_{70}Na_{30}$	415-1	84	10.25	5.48	0.180	Na_{100}	176-1	108	9.28	6.10	0.191	$Na_{70}Li_{30}$	200-3	70	12.05	6.27	0.193
$K_{70}Na_{30}$	415-1	84	10.25	5.53	0.182	Na_{100}	176-1	108	9.28	6.05	0.190	$Na_{50}Li_{50}$	334-1	82	9.39	6.38	0.194
$K_{70}Na_{30}$	415-1	84	10.25	5.50	0.181	Na_{100}	Han-1†‡	70	10.00	6.05	0.190	$Na_{50}Li_{50}$	334-1	82	9.39	6.58	0.199
$K_{70}Na_{30}$	98-1	104	10.55	5.48	0.180	$K_{90}Li_{10}$	338-1	84	8.51	5.36	0.177	$Na_{50}Li_{50}$	203-1	70	15.30	6.39	0.194
$K_{50}Na_{50}$	149-2	72	9.20	5.80	0.188	$K_{90}Li_{10}$	338-3	84	8.51	5.27	0.175	$Na_{50}Li_{50}$	203-1	70	15.30	6.40	0.194
$K_{50}Na_{50}$	149-1	72	9.20	5.83	0.188	$K_{70}Li_{30}$	333-1	92	8.24	5.45	0.177	$Na_{50}Li_{50}$	203-4	70	15.30	6.60	0.200
$K_{50}Na_{50}$	149-4	72	9.20	5.83	0.188	$K_{70}Li_{30}$	333-1	92	8.24	5.65	0.183	$Na_{50}Li_{50}$	203-4	70	15.30	6.42	0.195
$K_{50}Na_{50}$	358-1	72	9.68	5.56	0.181	$K_{70}Li_{30}$	333-3	92	8.24	5.60	0.181	$Na_{30}Li_{70}$	206-2	74	14.42	6.89	0.205
$K_{50}Na_{50}$	358-1	72	9.68	5.58	0.181	$K_{70}Li_{30}$	213-1	146	13.12	5.62	0.182	$Na_{30}Li_{70}$	206-1	74	14.42	6.82	0.203
$K_{50}Na_{50}$	414-1	84	10.00	5.58	0.181	$K_{50}Li_{50}$	185-2	108	11.13	5.82	0.184	$Na_{30}Li_{70}$	206-4	74	14.42	6.72	0.201
$K_{50}Na_{50}$	414-1	84	10.00	5.55	0.181	$K_{50}Li_{50}$	185-2	108	11.13	5.91	0.186	$Na_{30}Li_{70}$	206-4	74	14.42	6.79	0.202
$K_{50}Na_{50}$	414-1	84	10.00	5.72	0.186	$K_{50}Li_{50}$	185-2	108	11.13	6.05	0.190	$Na_{10}Li_{90}$	340-1	80	9.66	7.15	0.210
$K_{50}Na_{50}$	Han-1†	70	11.40	5.77	0.187	$K_{50}Li_{50}$	185-1	108	11.10	6.04	0.190	$Na_{10}Li_{90}$	340-3	80	9.66	7.12	0.210

Note: Compositions are of anhydrous glasses. Sample numbers are representative of single experiments. Each experiment has been measured by KFT for H_2O determination at different times to observe possible variation of solubility values due to absorption processes, dissolution processes, or both (see text); 1 = first determination, few hours to few days from the quench of the experiments, 2 = 3 months after the quench, 3 = 6 months after the quench, and 4 = 9 months after the quench.

* Excess of H_2O in the capsule during the synthesis of the wet glasses.

** Mole fraction of H_2O calculated on 2 O atom basis.

† Experiments performed in the Institut für Mineralogie, Universität Hannover, Germany.

‡ The value is referred to an average of several experiments.

hydrous glasses were prepared from gels by fusion in an internally heated gas pressure vessel for more than 20 h at 1100 °C and 2 kbar (H_2O undersaturated conditions).

The hydrous synthesis was performed in a horizontal gas pressure vessel (argon as pressure medium) at $P = 2$ kbar (accuracy ±0.02 kbar) and $T = 1100$ °C (accuracy ±10 °C).

Composition of the starting glasses was determined by microprobe analyses. The results of the analysis are given in Table 3 as the proportions (in weight percent) of the oxides.

TABLE 3. Analyzed anhydrous compositions (wt% oxide)

Comp.	SiO_2	Al_2O_3	Na_2O	K_2O	Total
Na_{100}	69.19	18.83	11.96	0.02	100.00
$Na_{60}K_{40}$	66.54	18.78	7.57	7.12	100.01
$Na_{50}K_{50}$	67.00	18.59	5.86	8.55	100.00
$Na_{20}K_{80}$	65.65	18.52	2.24	13.59	100.00
K_{100}	66.02	18.18	0.02	15.76	99.98

Note: Na_{100} = $NaAlSi_3O_8$ (albite), K_{100} = $KAlSi_3O_8$ (orthoclase). Compositions determined by microprobe analysis (CAMECA CAMEBAX MB Hanover) with a defocused beam (20–30 μm). Five to ten measurements were collected for each composition.

Karl Fischer titration (KFT)

The H_2O contents of the quenched glasses were determined by KFT. This analytical procedure has been established to be a powerful method for determination of H_2O contents in mineral and glasses in several recent studies (Turek et al. 1976; Westrich 1987; Holtz et al. 1992, 1993, 1995; Behrens 1995; Behrens et al. 1996). The method is based on a titration involving the reaction of H_2O, in presence of specific reagents, to generate the I^- ion whose concentration is determined coulometrically. The coulometer used for this study is a Mitsubishi CA 05. This technique has been successfully applied to determine relatively high H_2O 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). An advantage of the KFT is that only small amounts of glass are necessary to obtain reliable measurements (typically 10–20 mg for substances containing ~6 wt% H_2O). A schematic illustration of the apparatus is provided in Figure 1. The reader is referred to Behrens (1995) for further details.

In this study single chips have been used for analysis with the added precaution against sputtering that single specimens were wrapped in platinum foil. For several glasses that did not undergo sputtering, either with or without the foil, KFT yielded essentially identical results.

Measurements were performed both within a few hours after the experimental quench and after periods of several months in air. Again, no detectable difference was observed in the determined H_2O contents, confirming that single chips of the investigated samples do not lose or gain H_2O as a function of time (Table 2).

The glasses were heated progressively from 20 to 1300 °C using a radio frequency induction furnace (Fa. Linn, HTG 1000/1,3). The temperature was measured with a $Pt-Pt_{90}Rh_{10}$ thermocouple, 3 mm below the sample. The chosen heating procedure depended on the anticipated H_2O concentration in the samples. The heating program was chosen to give a relatively low heating rate (50 °C/min) below 100 °C to remove and analyze the H_2O adsorbed on the surface of the sample; subsequently, a higher heating rate was employed (100 °C/min) up to the onset of the maximum extraction rate and was followed by a lower heating rate (50 °C/min) until the final temperature was reached. The heating rate must be kept reasonably low during the dehydration of the glass to avoid sputtering of the sample, as well as to allow a complete liberation of H_2O within the time of the measurement. An example of a heating program for a glass of albitic composition is: 50 °C/min from 20 to 100 °C, 100 °C/min from 100 to 400 °C, 50 °C/min from 400 to 800 °C, and finally 100 °C/min from 800 to 1300 °C. The liberated H_2O is transported by a dried Ar gas stream in the titration cell and collected there. Titration starts 4–6 min after the start of the heating experiment. The duration of the titration is 7–10 min.

The analytical precision of the H_2O analysis depends mostly on the duration of the titration. For a typical measurement time of 12 min and a sample mass of 0.01 g the maximum uncertainty is about 0.15 wt%. Duplicate analyses on the same samples indicate that accuracy may be higher than this (Holtz et al. 1992, 1993, 1995; Behrens 1995).

An important point in any bulk extraction technique, including the KFT determination, is the complete, reproducible extraction of H_2O during the dehydration process. Behrens (1995) has demonstrated that a residual H_2O content of 0.1 ± 0.05 wt%, regardless of the duration of the titration or of the composition of the starting material, remains in all glasses after the extractions under the conditions used in the present study. The H_2O solubility data determined by KFT have accordingly been corrected for this H_2O.

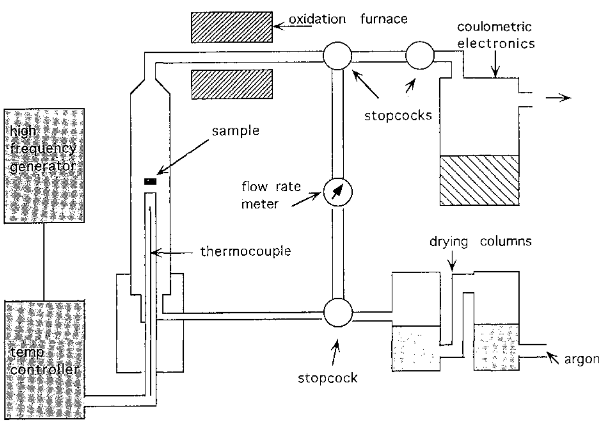

Figure 1. Scheme of the apparatus used for the Karl Fischer titration. Argon is used as the gas medium to transport the water liberated in the induction furnace to the titration cell. The gas is dried by two columns containing granulated phosphorus pentoxide (Fa. Baker, Granusic A).

RESULTS

The quenched experimental products consisted of bubble- and crystal-free limpid glasses. The homogeneity of the glasses was investigated in two ways. Samples were cut into two slices, perpendicular to the capsule elongation. One slice was cut again into two or three pieces (depending on the total length of the original material), each was analyzed individually by KFT. The other half of the samples was then analyzed with an infrared spectrometer (Bruker IFS 120 HR). Several measurements were performed along perpendicular and parallel sections and showed no differences in the background-subtracted peak area at ~4500 cm^{-1} (OH groups) and at ~5230 cm^{-1} (molecular H_2O), indicating that H_2O was homogeneously distributed throughout the samples and that the experimental durations were sufficient to produce complete hydration and equilibration of the samples.

The reproducibility of the hydration experiments was tested by multiple syntheses and analyses. The maximum difference between two analyzed H_2O contents has been found to be 0.3 wt% H_2O (Table 2), corresponding to a maximum variation of 6.0% relative to the solubility value. The multiple determinations of H_2O content of separate experimental products for the most intensively investigated composition here ($K_{70}Na_{30}$) yields a mean of 5.51 wt% and a standard deviation of ±0.08 wt% (n = 10).

The solubility data for H_2O in melts along the joins of alkali feldspar stoichiometry $NaAlSi_3O_8$-$KAlSi_3O_8$, $NaAlSi_3O_8$-$LiAlSi_3O_8$, and $LiAlSi_3O_8$-$KAlSi_3O_8$ determined at 2 kbar and 1040 °C are given in Table 2. The H_2O solubility values (expressed as weight percent H_2O) are plotted in Figure 2. The H_2O solubility values expressed as mole percent (two O atom basis) are shown in Figure 3. H_2O solubility is dependent on anhydrous melt composition; the total H_2O content decreases in the order $LiAlSi_3O_8$ (7.32 wt% H_2O) > $NaAlSi_3O_8$ (6.03 wt% H_2O) > $KAlSi_3O_8$ (5.12 wt% H_2O).

Hydration experiments were also performed in the Institut für Mineralogie, Universität Hannover, for some compositions on the $NaAlSi_3O_8$-$KAlSi_3O_8$ join (Table 2; Figs. 2a and 3a). Both sets of data show excellent agreement. This equivalence of data, obtained for different materials synthesized in different laboratories and with different starting materials, confirms the validity of the KFT as method for highly accurate and reproducible H_2O solubility determinations.

The present data indicate a 23% relative increase in the molar solubility from $KAlSi_3O_8$ to $LiAlSi_3O_8$. The variation in solubility along the binary joins $NaAlSi_3O_8$-

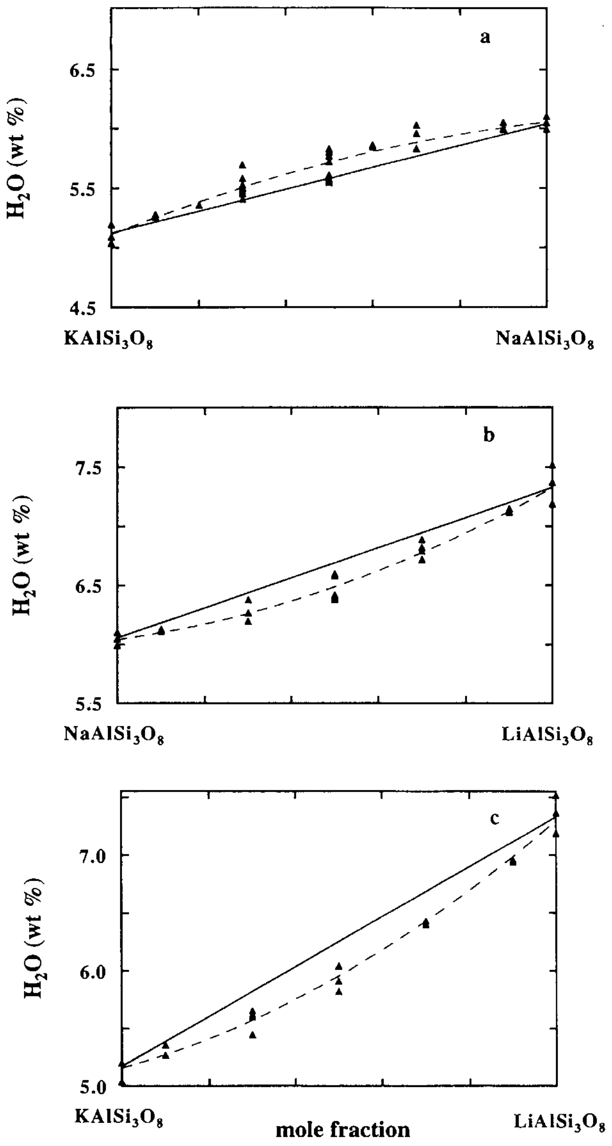

FIGURE 2. Composition dependence of H_2O solubility in (**a**) $NaAlSi_3O_8$-$KAlSi_3O_8$, (**b**) $NaAlSi_3O_8$-$LiAlSi_3O_8$, and (**c**) $LiAlSi_3O_8$-$KAlSi_3O_8$. The solubilities are expressed in weight percent.

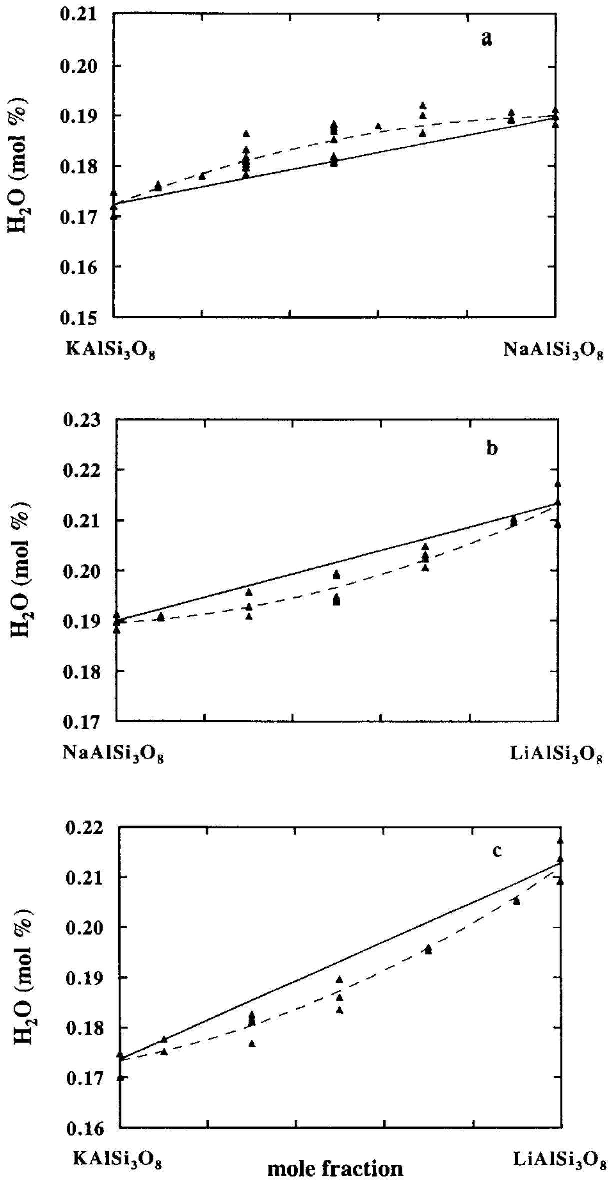

FIGURE 3. Molar H_2O solubilities (two O atom basis). (**a**) $NaAlSi_3O_8$-$KAlSi_3O_8$, (**b**) $NaAlSi_3O_8$-$LiAlSi_3O_8$, and (**c**) $LiAlSi_3O_8$-$KAlSi_3O_8$.

$KAlSi_3O_8$, $NaAlSi_3O_8$-$LiAlSi_3O_8$, and $KAlSi_3O_8$-$LiAlSi_3O_8$ appears to be a nonlinear function of the molar composition. The deviation from linearity along the Na-K join is positive, whereas that along the $NaAlSi_3O_8$-$LiAlSi_3O_8$ and $KAlSi_3O_8$-$LiAlSi_3O_8$ joins is negative.

DISCUSSION

Comparison with previous work

Although the acquisition of H_2O solubility data for aluminosilicate melts of silicic composition has been the focus of several studies, the present data are directly comparable with relatively few of them. Comparable H_2O solubility measurements include those previously conducted on end-members and intermediate compositions of the $NaAlSi_3O_8$-$KAlSi_3O_8$ system.

The albite composition melt has been intensively investigated in the past 30 years (Goranson 1936; Tuttle and Bowen 1958; Burnham and Jahns 1962; Kadik and Lebedev 1968; Oxtoby and Hamilton 1978a, 1978b; Sorapure 1981; Voigt et al. 1981; Day and Fenn 1982; Blamart et al. 1986; Hamilton and Oxtoby 1986; Richet et al. 1986; Paillat et al. 1992; Silver et al. 1990; see reviews by Dingwell 1986; McMillan and Holloway 1987; McMillan 1994). The H_2O solubility data obtained in the present study for both albite and orthoclase compositions show marked differences from data reported in previous investigations. In the case of the albitic composition, most previous studies reported higher solubility values (Hamilton and Oxtoby 1986: 1000 °C, H_2O = 6.91 wt%; 1100 °C, H_2O = 6.52 wt%; Orlova 1962: 1125 °C, H_2O = 6.45 wt%). This difference might be partly explained by the difference in the physical state of the starting materials. The starting materials used in most previous studies were fine- or coarse-grained glass powders. The use of powder as a starting material can lead to an overestimation of the H_2O content because of the presence of inclusions or bubbles in the experimental products, corresponding to undissolved H_2O at the pressure and temperature conditions of synthesis. A retrograde dissolution of H_2O into the melt during the quench (for the low pressure case of negative temperature dependence of H_2O, Paillat et al. 1992; Holtz et al. 1995) could also be responsible for the observed differences.

The retrograde solubility of H_2O in albitic melt at low pressure, when applied to the solubility data of Kadik and Lebedev (1968; 1200 °C, H_2O = 6.6 wt%), Goranson (1938; 1200 °C, H_2O = 6.32 wt%), and Paillat et al. (1992; 1400 °C, H_2O = 6.01 wt%), also generates (for the T conditions of our experiments) higher solubilities than those reported by the present study. For the case of the Goranson (1938) and Kadik and Lebedev (1968) data, the use of powder or crushed glass as starting material could have yielded apparently higher solubility values.

Day and Fenn (1982) obtained lower solubilities than those reported in this study (2.5 kbar, 1000 °C, 5.3–5.9 wt%). The discrepancy could be due in this case to the method employed for the determination of H_2O solubility (weight loss), which tends to underestimate the total H_2O content dissolved in the melt. The criteria for the detection of H_2O saturation used by the authors are the presence of two-phase bubbles in the glass (quench bubbles) and the presence of large bubbles, the latter interpreted as precursors of the indentation process (dimples on the surface). The presence of those bubbles was interpreted to indicate the attainment of two-phase equilibrium (fluid-melt). However, bubbles in the interior of glasses are not an unequivocal indication of saturation of H_2O at high pressure. In fact, in the low pressure experiments, inclusion bubbles formed by using powder as starting material could be responsible for the two-phase equilibrium observed, even in undersaturated conditions (Behrens 1995). In the case of the Day and Fenn (1982) study, the duration of the experiments probably was not long enough to remove such bubbles from the original material, thus explaining the low values reported by the authors.

The present data for orthoclase composition melt indicate, in contrast, a slightly higher solubility of H_2O compared with the data of Oxtoby and Hamilton (1978a; 4.4 wt% H_2O, P = 2 kbar, T = 1000 °C). This discrepancy could be due to the analytical procedure (a weight-loss technique) adopted by those authors to determine the H_2O content of the glasses. In the weight-loss technique, H_2O concentration is obtained by comparison of the weight of H_2O added to the charge before the experiment with the weight of the postexperimental hydrous glass after the charge has been pierced and heated to 110 °C. This technique tends to underestimate the H_2O solubility, especially for high H_2O contents, because of the loss of H_2O during drying at 110 °C. The preferential dissolution of H_2O in albite-rich melts vs. orthoclase-rich melts has been consistently observed (Oxtoby and Hamilton 1978b; McMillan and Holloway 1987; Holtz et al. 1992).

The variation of the solubility of H_2O along the join $NaAlSi_3O_8$-$KAlSi_3O_8$ itself has been more controversial. Early in the development of the equimolar solubility model of Burnham (1975) and Burnham and Davis (1974), the solubilities of H_2O in albite and orthoclase melts were assumed to be equimolal. According to Voigt et al. (1981), however, the molar H_2O solubility remains almost constant between Ab and $Ab_{25}Or_{75}$ compositions and then drops to almost half the value obtained for albite melt in the case of orthoclase melts. Such a large drop in solubility near orthoclase composition is not seen in the present study.

There are several possible explanations for the difference between the present data and those of Voigt et al. (1981). Those authors considered the presence of dimples on the surface of the quenched melts as an indication of excess H_2O in their experiments. However, the dimple technique cannot be applied easily to determine H_2O solubility. H_2O dimples can form on the surface of the melts even if there is insufficient H_2O to saturate the whole melt, leading to an erroneous interpretation of the saturation conditions of the experiment. Moreover, at pressures below 2 kbar, the L = L + V technique requires the careful addition of small amounts of H_2O to experimental charges and the execution of H_2O-undersaturated experiments on melts for which equilibrium is difficult to achieve.

No H_2O solubility studies have been conducted on Li-bearing melts, with compositions similar to those investigated in this study. Burnham and Jahns (1962) reported solubility data for the Harding pegmatite, which contains significant concentrations of Li and F; however, the peraluminous character of the pegmatite (normative corundum = 2.4 wt%), as well as the high silica content (quartz normative = 45%), precludes a direct comparison between those results and the data presented here.

Structural interpretation

The experimental results presented here provide important constraints on the solubility mechanisms of H_2O in feldspathic melts. The changes in H_2O solubility reported indicate: (1) an increase of H_2O solubility as a function of the cation charge-balancing, in the order K < Na < Li and (2) a nonlinear variation of solubility along the $NaAlSi_3O_8$-$LiAlSi_3O_8$, $KAlSi_3O_8$-$LiAlSi_3O_8$, and $NaAlSi_3O_8$-$KAlSi_3O_8$ joins. The deviation is positive for the $NaAlSi_3O_8$-$KAlSi_3O_8$ join and negative for the

$NaAlSi_3O_8$-$LiAlSi_3O_8$ and $KAlSi_3O_8$-$LiAlSi_3O_8$ joins. These data suggest that the effect of exchanging the alkali cation in aluminosilicate melt strongly influences the H_2O solubility and hence the H_2O dissolution mechanism.

It has been established from several spectroscopic studies (Stolper 1982a, 1982b; Silver and Stolper 1985, 1989; Silver et al. 1990) that water dissolves in aluminosilicate melts both as molecular H_2O and as OH groups, according to the equilibria (Stolper 1982a, 1982b)

$$H_2O_{fl} = H_2O_m \qquad K_2 \qquad (1)$$

$$H_2O_m + O^{2-}{}_m = 2OH^-{}_m \qquad K_1 \qquad (2)$$

where m = melt and fl = fluid.

The equilibrium constants K_1 and K_2 have been demonstrated to be a function of T, P, and composition (Stolper 1982a, 1982b, 1989; Silver and Stolper 1985, 1989; Dingwell and Webb 1990; Silver et al. 1990; Zhang et al. 1991; Romano et al. 1995). Differences in H_2O solubility reported in our investigation can thus in general reflect changes in the OH or H_2O concentration in the melt.

Changes in H_2O solubility might be expected to arise from variable reactivities of O atoms with H_2O molecules. Thus in any model of significant chemical interaction between dissolved H_2O and the solvent silicate melt matrix, one factor governing the dissolution of H_2O and therefore the total amount of H_2O dissolved in the melt is the chemical bonding of O atoms in the aluminosilicate structure. Changes in O bonding environments related to the exchange of alkalis can be expected to be reflected in the relative stability of the aluminosilicate framework with differing alkali cations serving as network stabilizing cations.

The stabilization of the T-O-T framework linkage has long been inferred to be a function of the strength of the bond between the bridging O atom and the charge-balancing alkali cation (see discussion in Pichavant et al. 1992). On the basis of calorimetrically obtained enthalpies of solution and molecular orbital calculations, Geisinger et al. (1985) and Navrotsky et al. (1985) observed a positive correlation between the extent of perturbation of the T-O bond length and the z/r^2 of the charge-balancing cation at a given Al/(Al + Si). The perturbation, expressed as a narrowing of the T-O-T angle and a lengthening of the bridging T-O bonds, increases in the order K < Na < Li. Strengthening of the metal-oxygen (M-O) bond with increasing atomic number of M along a row of the periodic table is assessed to be the primary cause of weakening and lengthening of the T-O bonds (Navrotsky et al. 1985).

EXAFS studies along the $NaAlSi_3O_8$-$KAlSi_3O_8$ join (Brown et al. 1988) have demonstrated that the K-O bond is longer (3.06 Å) and has a lower field strength than the Na-O bond in the liquid (bond length = 2.6 Å). Recent neutron diffraction studies (Zotov et al. 1995) report that the average T-O_1 distances (where for O_1 is intended the next-nearest-O atom to the Si or Al) increase while the average O-O_1 distances decrease along the $KAlSi_3O_8$-$NaAlSi_3O_8$ join, which also suggests a strengthening of the M-O bond and a weakening of T-O bond length with increasing Na content in that system.

Observations of the macroscopic physical and chemical properties of these systems (including phase equilibria, heat of solution, viscosity, and immiscible melt chemistry) support these arguments (Hess and Wood 1982; Urbain et al. 1982; DeYoreo et al. 1990; Pichavant et al. 1992).

According to all these data, the T-O-T framework linkage is more destabilized in presence of Li than in presence of Na and K, and this is consistent with a higher reactivity toward hydration in aluminosilicate melts. The relation between degree of stabilization of $MAlO_2$ component and the polarizing power of charge-balancing cation in the liquid would therefore appear to be a reasonable explanation for the observed variation in solubility for the end-members compositions $NaAlSi_3O_8$, $KAlSi_3O_8$, and $LiAlSi_3O_8$.

The observed deviations from linearity of the solubility of H_2O along the binary join $NaAlSi_3O_8$-$KAlSi_3O_8$, $LiAlSi_3O_8$-$KAlSi_3O_8$, and $NaAlSi_3O_8$-$LiAlSi_3O_8$ also require explanation.

The nonlinear variation of the physical properties of glasses when a given cation is partially substituted by a second one, generally referred to as the mixed alkali effect, has been known in silicate glasses for many years (Isard 1969; Hayward 1976; Day 1976; Dietzel 1983) and is still an active area of research (see review in Scholze 1988). Most observations of the mixed alkali effect concern transport properties (e.g., viscosity, electrical conductivity, cationic diffusivities). Nonlinear behavior has also been observed for properties in the $KAlSi_3O_8$-$NaAlSi_3O_8$ system including density, refractive index, atomic polarizability, electrical conductivity, and enthalpy of solution (Klonkowski 1983; Hayward 1976; Hervig and Navrotsky 1984; Hovis 1984; Rogez et al. 1983; Fraser et al. 1983, 1985; Fraser and Bottinga 1985; Rammensee and Fraser 1982, 1987). Also, similar deviations from linearity of the electrical conductivity along joins in the system Na_2O-Li_2O-Al_2O_3-SiO_2 have been reported by Lapp and Shelby (1987).

Despite these investigations, a model that coherently explains the mixed alkali effect has yet to be presented. Nevertheless, some useful information can be derived from spectroscopic studies of these glasses. Recent neutron diffraction studies performed on $NaAlSi_3O_8$-$KAlSi_3O_8$ glasses (Zotov et al. 1995) have shown a nonlinear decrease of the width of the first sharp diffraction peak (FSDP) which the authors attribute to a decrease of the medium-range order (MRO) with increasing mole fraction of K_2O. The change in MRO with increasing Na/(Na + K) has been related to increasing Si-Al order in the glassy network upon substitution of Na for K.

Raman spectroscopic studies of $KAlSi_3O_8$ and $NaAlSi_3O_8$ glasses (McMillan et al. 1982) indicate that Na has stronger preference for the formation of Q^4 (2Al) rather than Q^4(1Al) groups. The increase of the ^{29}Si MAS NMR peak width in feldspar glasses with increasing Na/

(Na + K) ratio can also be interpreted (Oestrike et al. 1987) in terms of an increase of the relative abundances of different Q^4 (*n*Al) species.

The relative abundance of the Si-O-Si, Si-O-Al, and Al-O-Al groups can affect the stability of the overall structure. It has been demonstrated on the basis of thermodynamic measurements of heats of solutions as well as molecular orbital calculations (Navrotsky et al. 1985; DeJong and Brown 1980), that Si-O-Al groups should be more stable than Si-O-Si and Al-O-Al because of polarization of the bridged O atom, and hence reduced O competition between the tetrahedral cations.

Moreover, it has also been observed that in the Al-O-Al groups, the average T-O bond length increases and the T-O-T angle decreases compared to Si-O-Si and Si-O-Al groups (Al-O has been predicted to be 1.72 Å, whereas Si-O is known to be 1.63 Å). Given the inverse relationship between bond length and strength, the Al-O-Al bonds are weaker than Si-O-Si and Si-O-Al bonds and thus potentially more reactive with H_2O.

From the comparison of Figures 2a and 4 (from Zotov et al. 1995) a direct proportionality between the solubility of H_2O and the Si-Al correlation length order can be inferred. We therefore suggest that in the system $KAlSi_3O_8$-$NaAlSi_3O_8$ the solubility of H_2O is directly related to the stability of the structure by the stability of $MAlO_2$ component (responsible for the observed variation for the end-members) and by the Si-Al distribution along the system (responsible for the deviation from linearity observed along the join).

The solubility of H_2O in Li-bearing systems shows a negative deviation from linearity, which is somehow difficult to interpret in the absence of direct structural data on these melts.

In this context we must point out that the speciation of H_2O in melts along the $NaAlSi_3O_8$-$KAlSi_3O_8$ join, when corrected for fictive temperature effects (Romano et al. 1995), appears to be independent of the identity of the alkali but is a simple function of total H_2O content. Therefore it appears that the higher solubility in albitic glasses is both due to an increase of OH and H_2O in comparison with orthoclasic composition. Moreover it has also been demonstrated (Dingwell and Webb 1990; Romano et al. 1995; Nowak and Behrens 1995) that, even though the molecular H_2O is still a stable species in high *T* melt, the amount of OH groups is significantly higher than previously expected up to 70–80 wt% of the total dissolved H_2O in the melt.

We can therefore assume that the progress of Reaction 2 is governed by the chemical stability of the structure and that the molecular H_2O plays a less important role in influencing the total amount of volatile dissolved in these melts. It has been suggested (Pichavant et al. 1992) that molecular H_2O enters the structure by occupying the free volume available. Pichavant et al. (1992) proposed that this free volume could be inversely related to the size of the cations (or directly related to their field strength), and that, consequently, the relative amount of H_2O_{mol} clustering around those cations would increase in the order K < Na < Li, in agreement with the observed trend in H_2O solubility here reported. Although the hypothesis of molecular H_2O filling holes in the structure is consistent with the trends observed, such a mechanism implies that the partial molar volume of H_2O in the melt should be close to zero, resulting in a corresponding increase in the density of the melt. Acocella et al. (1984) have demonstrated, however, that the partial molar volume of molecular H_2O and water as OH is 12 cm^3/mol for total water contents up to 5 wt%, beyond which value the volume of molecular water increases (and the density decreases), whereas that of water as OH decreases (with increasing density). Such a partial molar volume for H_2O, similar to the partial molar volume per O for other oxide components (Lange 1994), indicates that the solubility of H_2O_{mol} in the melt should not be viewed as the case of passively filling the available free volume or "holes" in the structure.

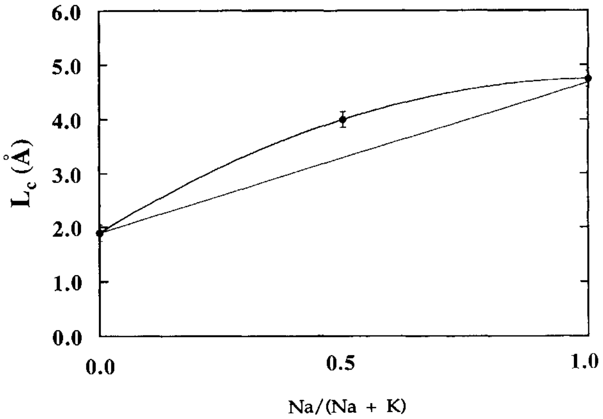

Figure 4. The width of the first sharp diffraction peak (FSDP), expressed as correlation length (L_c), as a function of composition (redrawn from Zotov et al. 1995).

Pichavant et al. (1992) also proposed (on the basis of enthalpies of hydration of gaseous alkali ions in water at 25 °C) that hydration of the clusters is promoted in the order K < Na < Li yielding the higher solubility in Li-bearing system in comparison with Na- and K-bearing systems. The solvation energies of alkali ions in H_2O could provide a reasonable explanation for the contribution of molecular water to the total water solubility along the present joins.

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