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Liquidus temperatures and phase compositions in the system Qz-Ab-Or at 5 kbar and very low water activities

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Abstract Liquidus phase relations have been experimentally determined in the systems Qz-Ab-Or-(H_2O), Qz-Ab-(H_2O) and Qz-Or-(H_2O) at H_2O-undersaturated conditions ($a_{H_2O} = 0.07$) and $P = 5$ kbar. Starting materials were homogeneous synthetic glasses containing 1 wt% H_2O. The liquidus temperatures were bracketed by crystallization and dissolution experiments. The results of kinetic studies showed that crushed glasses are the best starting materials to overcome undercooling and to minimize the temperature difference between the lowest temperature of complete dissolution (melting) and the highest temperature at which crystallization can be observed. At $P = 5$ kbar and $a_{H_2O} = 0.07$, the Qz-Ab eutectic composition is $Qz_{32}Ab_{68}$ at 1095 °C (± 10 °C) and the Qz-Or eutectic is $Qz_{38}Or_{62}$ at 1030 °C (± 10 °C). The minimum temperature of the ternary system Qz-Ab-Or is 990 °C (± 10 °C) and the minimum composition is $Qz_{32}Ab_{35}Or_{33}$. The Qz content of the minimum composition in the system Qz-Ab-Or-H_2O remains constant with changing a_{H_2O}. The normative Or content, however, increases by approximately 10 wt% with decreasing a_{H_2O} from 1 to 0.07. Such an increase has already been observed in the system Qz-Ab-Or-H_2O-CO_2 at high a_{H_2O} and it is concluded that the use of CO_2 to reduce water activities does not influence the composition of the minima in quartz-feldspar systems. The determined liquidus temperature in melts with 1 wt% H_2O is very similar to that obtained in previous nominally "dry" experiments. This discrepancy is interpreted to be due to problems in obtaining absolutely dry conditions. Thus, the hitherto published solidus and liquidus temperatures for "dry" conditions are probably underestimated.

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Introduction

Most liquidus phase relations in the granite system Qz-Ab-Or (Qz = SiO_2; Ab = $NaAlSi_3O_8$; Or = $KAlSi_3O_8$) are obtained for "dry" and water-saturated conditions (e.g., dry compositions: Schairer 1950; Schairer and Bowen 1935; Luth 1969; water-saturated conditions: Tuttle and Bowen 1958; Luth et al. 1964; Merrill et al. 1970; Steiner et al. 1975). Except for determinations of dry solidus temperatures (e.g., Huang and Wyllie 1975; Keppler 1989; Ebadi and Johannes 1991), data on dry minimum melt compositions of the ternary system Qz-Ab-Or at high P are not known. Dry minimum melt compositions, however, are key data and needed for any further thermodynamic calculations.

Few experiments have been performed at water-undersaturated conditions. The water contents in the melt, however were always higher than 2 wt% H_2O (Holtz et al. 1992). In addition, the experiments were performed with H_2O-CO_2 fluids and some CO_2 was dissolved in the melt. The experimental results obtained at water-undersaturated conditions do not agree with the calculations in which the thermodynamic model developed by Burnham (1979) is used and extended to granitic compositions by Burnham and Nekvasil (1986) and Nekvasil (1988). The discrepancies between experimental and calculated data are assumed to be due to the presence of CO_2 in the experimental melts (Nekvasil and Carroll 1996).

Early experiments performed at dry conditions have shown that equilibrium liquidus temperatures are difficult to obtain when glass is used as starting material because of nucleation and undercooling problems as a result of the high polymerization of dry melts. Schairer and Bowen (1935) did not reach equilibrium in quartz-alkali feldspar compositions even in long lasting runs (up to years). In preliminary experiments, Becker et al. (1995) could show that dry equilibrium conditions could not be obtained in long lasting experiments in which either crystalline phases, dry gels, or glasses are used as starting material.

In view of the facts that kinetic problems cannot be overcome at completely dry conditions and that the presence of CO_2 might affect the phase relationships, the phase relations in the system Qz-Ab-Or-H_2O have been investigated in compositions containing 1 wt% H_2O only. This study is an attempt to reach *equilibrium phase relations* at a_{H_2O} as closely as possible to dry conditions. Therefore, particular attention has been paid to perform kinetic investigations in order to determine the best experimental technique to bracket equilibrium liquidus temperatures. The results obtained in the ternary system Qz-Ab-Or are supplemented by eutectic data determined in the binary systems Qz-Ab and Qz-Or at same H_2O contents (1 wt% H_2O).

Starting materials

Starting materials for crystallization experiments were crushed glasses containing 1 wt% H_2O. The synthesis was conducted in three steps. First, a mixture of oxides (SiO_2, Al_2O_3) and carbonates (Na_2CO_3, K_2CO_3) was heated at 1600 °C for 24 hours in a box furnace. Some quartz crystals were present in the glasses and microprobe analyses showed that the glasses are not homogeneous. In a second step, these glasses were stirred at 1600 °C for 5 days with a device similar to that described by Dingwell (1989). The glasses were homogeneous and crystal-free. Concentration profiles along the synthesized glass blocks were not observed and it is concluded, therefore, that no significant alkali loss occurred during the glass preparation. The microprobe analyses of the 19 compositions used in this study are given in Table 1. The compositions do not depart significantly from the Qz-Ab-Or system and have less than 0.7% normative corundum or metasilicate.

The dry homogeneous glasses were ground and a mixture of equal amounts of glass fragments with approximately 500 and 200 µm grain size were used as starting materials. The dry glass mixture was sealed together with 1 wt% H_2O in Pt capsules. The sealed Pt capsules were heated in a gas pressure vessel at 1200 °C for 120 h at 5 kbar. Microprobe analyses of the hydrous glasses were identical to the dry glasses (maximal variation in normative Qz, Ab, Or components are less than 1% when compared to the dry glasses). The water content of all glasses was determined by Karl Fischer Titration (KFT). For some samples, up to three portions were separated at both ends and in the middle of the glass cylinders and analyzed. The water contents were found to be almost identical (maximal absolute variations are within the analytical uncertainty). The water contents of glasses are given in Tables 1 and 2. The distribution of water in five glass cylinders was also investigated by IR spectroscopy and the determined water contents are in agreement with KFT determinations (Tables 1, 2). Several sections were cut along the glass cylinder and the variation of total water content was less than 0.02 wt% H_2O. The water-bearing glasses were used as starting materials for crystallization experiments after grinding to fragments having grain sizes between 300 and 500 µm.

Apparatus

The experiments to determine phase relations and the preparation of the hydrous starting glasses were performed in an internally heated gas-pressure apparatus arranged vertically. The temperature gradients were minimized with two independent Mo wires (Holloway 1971). Temperature gradients along the 10 mm long samples are less than 2 °C. Four Ni-Cr-Ni thermocouples, calibrated at

Table 1 Composition of dry Qz-Ab-Or starting glasses (average of at least 6 analyses), CIPW norm and analyzed water contents

Glass no.	376	σ	384	σ	390	σ	377	σ	398	σ	389	σ	511	σ	510	σ	379	σ	425	σ
SiO_2	73.96	0.38	73.75	0.49	73.94	0.36	76.37	0.62	76.62	0.75	76.47	0.37	77.57	0.27	78.97	0.71	79.78	0.65	80.08	0.48
Al_2O_3	15.60	0.15	15.65	0.20	14.99	0.14	13.56	0.18	13.77	0.13	12.91	0.13	12.78	0.14	12.09	0.20	11.72	0.15	10.96	0.18
Na_2O	5.83	0.19	4.75	0.14	3.83	0.14	4.94	0.12	4.32	0.13	3.28	0.09	4.30	0.19	3.71	0.18	4.28	0.17	2.83	0.08
K_2O	5.69	0.18	7.10	0.24	8.37	0.17	4.74	0.09	6.09	0.17	7.15	0.22	5.38	0.09	5.54	0.14	4.25	0.15	6.14	0.19
Total	101.09		101.25		101.13		99.86		100.79		99.81		100.04		100.31		100.03		100.01	
Qz	18.51		18.71		20.49		29.61		27.98		30.75		32.29		36.10		38.62		41.14	
Ab	48.02		39.67		30.17		41.96		36.25		26.63		35.78		31.27		36.20		22.20	
Or	33.28		41.46		48.91		28.12		35.69		42.35		31.78		32.62		25.09		36.25	
C	0.00		0.15		0.00		0.30		0.08		0.00		0.00		0.00		0.09		0.00	
NaS	0.19		0.00		0.44		0.00		0.00		0.27		0.15		0.00		0.00		0.41	
KS	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00	
H_2O (KFT)[a]	1.04		1.08		1.07		1.05		1.05		0.98		1.08		1.00		0.94		1.10	
H_2O (IR)[b]	1.04		1.05		1.06												0.98		1.13	
a_{H_2O} at 5 kbar[c]	0.07		0.07		0.07		0.07		0.07		0.06		0.07		0.06		0.05		0.07	

[a] Karl-Fischer Titration

[b] Infrared spectroscopy

[c] Calculated after Burnham (1979)

5 kbar following the setup described by Chou (1982) against the melting points of NaCl (910 °C at 5 kbar) and Au (1092 °C at 5 kbar, Mirwald 1979) were used. The temperature accuracy is estimated to be approximately ± 5 °C. Pressure was measured using a tensile strength barometer with an accuracy of ± 100 bars. Heating up was performed isobarically and the duration needed to reach the experimental temperatures was between 20 and 40 minutes. Quenching was performed isobarically and the temperature in the vessel was 400 °C in 4 minutes after switching off the power.

Table 2 Composition of dry Qz-Ab and Qz-Or starting glasses (average of at least 6 analyzses), CIPW norm and analyzed water contents

Glass no.	641	σ	530	σ	575	σ	531	σ	393	σ	551	σ	576	σ	525	σ	526	σ
SiO_2	77.59	0.37	78.35	0.89	79.77	0.36	81.16	0.73	71.17	0.74	75.62	0.79	76.67	0.76	79.61	0.24	83.86	0.36
Al_2O_3	14.44	0.13	13.01	0.37	12.42	0.41	11.71	0.11	14.67	0.11	12.55	0.12	11.81	0.46	11.09	0.12	9.09	0.08
Na_2O	8.92	0.21	7.93	0.33	7.50	0.08	7.07	0.25	0.02	0.02	0.04	0.02	0.03	0.03	0.03	0.03	0.01	0.01
K_2O	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.02	13.94	0.38	11.99	0.21	10.90	0.30	10.45	0.06	8.49	0.24
Total	100.98		99.31		99.70		99.96		99.80		100.19		99.42		101.18		101.46	
Qz	26.12		32.54		36.18		39.98		19.09		30.91		35.09		39.75		50.92	
Ab	73.47		67.30		63.68		59.83		0.00		0.00		0.09		0.00		0.00	
Or	0.11		0.09		0.08		0.13		80.23		68.38		64.78		59.87		48.90	
C	0.00		0.00		0.06		0.06		0.00		0.00		0.00		0.00		0.00	
NaS	0.30		0.07		0.00		0.00		0.04		0.07		0.04		0.07		0.03	
KS	0.00		0.00		0.00		0.00		0.64		0.62		0.00		0.32		0.16	
H_2O (KFT)[a]	1.05		0.97		0.93		0.99		1.05		1.00		1.04		1.10		1.06	
a_{H_2O} at 5 kbar[b]	0.06		0.06		0.05		0.06		0.07		0.06		0.07		0.07		0.07	

[a] Karl-Fischer Titration

[b] Calculated after Burnham (1979)

Analytical techniques

Experimental products were analyzed optically for the presence of quartz and/or feldspar crystals. Chemical compositions of minerals and melts were determined with a Camebax electron microprobe. Analytical conditions were 15 kV, 18 nA. Counting time for Na and K were 5 s for minerals and 2 s for glasses. Counting time for Si and Al were 10 s for minerals and 5 s for glasses. The beam was defocused to a spot of at least 20 μm diameter for glasses. For crystalline phases, the beam was also slightly defocused whenever possible (up to 5 μm). Eight to ten crystals were analyzed in experimental products containing feldspars.

The KFT technique to determine water contents in glasses is described in Behrens (1995) and Behrens et al. (1996). The uncertainty in the determination of water contents with this technique is less than ± 0.15 wt% H_2O and depends on titration time (about 10 min in this study) and on the amount of analyzed samples (35–45 mg in this study). Infrared analyses were made with a Bruker IFS88 FTIR spectrometer purged with dry air and coupled to a A590 microscope (see Behrens et al. 1996 for detailed description of the IR apparatus). Doubly polished sections of approximately 100 μm were prepared and a spot size of 100 μm was analyzed. Water contents were calculated with help of the Lambert-Beer law from the peak intensities of the absorption bands at 5200 and 4500 cm^{-1}. Molar extinction coefficients are from H. Behrens (personal communication).

Experimental procedure and investigation of reaction kinetics

The water-bearing crushed glasses were sealed in Pt capsules. The highest temperatures at which crystallization was observed were determined in run series with temperature intervals of 20 °C. For binary compositions, 10 °C intervals were sometimes chosen. Preliminary experiments were performed with five compositions (Table 1: 376, 384, 390, 379, 425) to investigate the influence of: (1) the grain size of the starting material; (2) temperature path on nucleation and undercooling. After these experiments: (3) crystallization experiments were carried out for all investigated compositions; (4) dissolution experiments were performed for some ternary and binary compositions; (5) the run duration necessary to attain near equilibrium compositions of the run products was also determined.

(1) The effect of grain size

The effect of grain size of the starting material on the beginning of crystallization was investigated with either water-bearing glass blocks (blocks of 40–50 mg) or roughly crushed water-bearing glasses (300–500 μm).

These materials were directly brought to the experimental temperature (1000–1060 °C at 5 kbar) for 168 hours. As an example, for composition 376 (Table 1) crystals (feldspars) were observed at and below 1040 °C in experiments with crushed starting glasses. The temperature at which the first crystals were observed with the glass block as the starting material was 40 °C lower (1000 °C). Similar observations were made for the other four compositions. This demonstrates that crushed starting material may help to reduce undercooling. In experiments with crushed glasses, it can be noted that the crystals grow along the former grain boundaries. The nucleation process is enhanced at the grain boundaries.

(2) The effect of temperature path

The effect of temperature path on crystallization kinetics was investigated with crushed water-bearing glasses as starting material. In the first set of experiments, the samples were brought directly from room temperature to the experimental temperature (1020–1060 °C for example in case of composition 376). Crystals were observed at and below 1040 °C. In a second set of experiments, the temperature was first raised far above the liquidus temperature (1100 °C) for two hours and then cooled down within 5 minutes and held to the experimental temperature (1020–1060 °C) for 168 hours. These experiments yielded crystals at 1020 °C, which indicates undercooling. Thus, it is demonstrated that the direct run-up of crushed water-bearing glasses yields results closer to equilibrium conditions.

(3) Crystallization experiments

The experiments leading to partial crystallization from hydrated crushed glass brought directly to the experimental temperature are called "crystallization experiments". In these experiments, the experimental temperature is attained within 20 to 40 minutes (see above).

(4) Dissolution experiments

As described above, in crystallization experiments, the highest or "first" crystallization temperatures for a given composition were obtained with crushed glasses as starting materials brought directly to experimental temperatures. This does not mean, however, that undercooling is ruled out in this procedure. Therefore, dissolution experiments are necessary to demonstrate that equilibrium conditions are approached. The technique used in this study is identical to that of Pichavant

Table 3 Experimental results for $a_{H_2O} = 0.07$: system Qz-Ab-H_2O, Qz-Or-H_2O. (*Crys.* Crystallization experiments, *Diss.* Dissolution experiments, *fsp* feldspar, *qtz* quartz, *gl* glass)

Experiment no.	Starting composition [wt%]	Temperature [°C]	Run duration [h]	Products
647	Glass 641 ($Qz_{26.1}$ $Ab_{73.5}$)	1100	120	fsp + gl
645	Glass 641	1120	168	gl
649 Crys.	Glass 641	1080	72	fsp + gl
649 Diss.[a]	Fsp + glass	1080 → 1120	72 → 96[b]	gl
648	Glass 530 ($Qz_{32.5}$ $Ab_{67.3}$)	1090	120	fsp + qtz + gl
569	Glass 530	1100	168	gl
650 Crys.	Glass 530	1080	72	fsp + qtz + gl
650 Diss.[a]	Fsp + qtz + glass	1080 → 1100	72 → 96[b]	gl
628	Glass 575 ($Qz_{36.2}$ $Ab_{63.7}$)	1120	168	qtz + gl
586	Glass 575	1140	192	gl
574	Glass 531 ($Qz_{40.0}$ $Ab_{59.9}$)	1140	120	qtz + gl
554	Glass 531	1160	168	gl
560	Glass 393 ($Qz_{19.1}$ $Or_{80.2}$)	1120	120	fsp + gl
571	Glass 393	1140	96	gl
579	Glass 551 ($Qz_{30.9}$ $Or_{68.4}$)	1060	120	fsp + gl
567	Glass 551	1080	96	gl
623 Crys.	Glass 551	1040	72	fsp + gl
623 Diss.[a]	Fsp + glass	1040 → 1080	72 → 96[b]	gl
584	Glass 676 ($Qz_{35.1}$ $Or_{64.8}$)	1020	120	fsp + qtz + gl
586	Glass 676	1040	120	fsp + gl
578	Glass 676	1060	120	gl
573	Glass 525 ($Qz_{39.8}$ $Or_{59.9}$)	1040	120	qtz + gl
580	Glass 525	1060	120	gl
557	Glass 526 ($Qz_{50.9}$ $Or_{48.9}$)	1160	96	qtz + gl
563	Glass 526	1180	120	gl

[a] The starting composition for the second step in this run corresponds to the product of the crystallization run (experiment labeled Crys. with the same experiment no.)

[b] 72 → 96 means that the run duration of the first step was 72 hours and that of the second step 96 hours

(1987) and Holtz et al. (1992). After the determination of the temperature at which first crystallization was observed, dissolution experiments were performed. For these experiments, samples were first brought for 72 hours 10 to 20 °C below the temperature of first crystallization. Two capsules were always run simultaneously for this first step; one was opened to check for the presence of crystals (experiments labeled "Crys" in Tables 3 and 4, see also Fig. 1a). The second capsule was not opened and was again heated up to a temperature 10 or 20 °C above the temperature of first crystallization and held here for 96 hours (experiments labeled "Diss" in Tables 3 and 4).

The run products of dissolution experiments (labeled "Diss") were either glass only or glass and feldspars. Quartz was never observed in the products of dissolution experiments. It is obviously completely dissolved within the applied run duration of 96 hours. In those runs in which feldspars are still observed (two of seven experiments in the feldspar primary field, Table 4), it occurs in form of rounded (partly dissolved) crystals (Fig 1b). We conclude that the dissolution of alkali feldspar is slower than that of quartz. The combination of crystallization and dissolution experiments constrains the liquidus temperature within a temperature interval of 10 °C (see experiment no. 650 in Table 3). However, the temperature steps chosen in this study and the limited number of runs bracket the liquidus temperatures in the present investigation only within 20 °C.

(5) Effect of run duration on phase compositions

Attainment of chemical equilibrium can also be tested by investigating the experimental products. Time dependent experiments were performed (0.2–240 hours) with crushed starting materials of five different ternary compositions. The temperature was 1000 °C and known to be below the liquidus temperatures. For compositions in the feldspar primary field, crystals were observed after 8 hours, the SiO_2 content of glasses increases with run duration within the first 72 hours and remains constant in longer runs (Fig. 2). For compositions in the quartz primary field, first crystals were observed after 24 hours, the SiO_2 content of glasses decreases between 24 and 168 hours and remains constant afterwards (Fig. 3). The

Table 4 Experimental results for $a_{H_2O} = 0.07$: system Qz-Ab-Or-H_2O (*Crys.* Crystallization experiments, *Diss.* Dissolution experiments, *fsp* feldspar, *qtz* quartz, *gl* glass *alk. fsp* alkali feldspar)

Experiment no.	Starting composition [wt%]	Or/Or + Ab	Temperature [°C]	Run duration	Products Observed phases	Wt% Or in alk. fsp.
477	Glass 376 ($Qz_{18.5}$ $Ab_{48.0}$ $Or_{33.3}$)	40.9	1040	240	fsp + gl	33.9
498	Glass 376		1060	192	gl	
515 Crys.	Glass 376		1020	72	fsp + gl	
515 Diss.[a]	Fsp + glass		1020 → 1060	72 → 96[b]	gl	
478	Glass 384 ($Qz_{18.7}$ $Ab_{39.7}$ $Or_{41.5}$)	51.1	1040	240	fsp + gl	58.0
499	Glass 384		1060	192	gl	
516 Crys.	Glass 384		1020	72	fsp + gl	
516 Diss.[a]	Fsp + glass		1020 → 1060	72 → 96[b]	fsp (diss.) + gl	
479	Glass 390 ($Qz_{20.5}$ $Ab_{30.2}$ $Or_{48.9}$)	61.8	1040	168	fsp + gl	73.2
500	Glass 390		1060	192	gl	
517 Crys.	Glass 390		1020	72	fsp + gl	
517 Diss.[a]	Fsp + glass		1020 → 1060	72 → 96[b]	fsp (diss.) + gl	
527	Glass 377 ($Qz_{29.6}$ $Ab_{42.0}$ $Or_{28.1}$)	40.1	980	120	fsp + qtz + gl	35.1
471	Glass 377		1000	168	gl	
537	Glass 511 ($Qz_{32.3}$ $Ab_{35.8}$ $Or_{31.8}$)	47.0	980	120	fsp + qtz + gl	38.4
543	Glass 511		1000	240	gl	
621 Crys.	Glass 511		960	72	fsp + qtz + gl	
621 Diss.[a]	Gsp + qtz + glass		960 → 1000	72 → 96[b]	gl	
506	Glass 398 ($Qz_{28.0}$ $Ab_{36.3}$ $Or_{35.7}$)	49.6	1000	168	fsp + gl	53.6
655	Glass 398		1020	168	gl	
507	Glass 389 ($Qz_{30.8}$ $Ab_{26.6}$ $Or_{42.4}$)	61.4	1000	168	fsp + gl	73.2
656	Glass 389		1020	168	gl	
538	Glass 510 ($Qz_{36.1}$ $Ab_{31.3}$ $Or_{32.6}$)	51.1	980	168	fsp + qtz + gl	52.8
544	Glass 510		1000	168	qtz + gl	
542	Glass 510		1020	168	qtz + gl	
586	Glass 510		1040	168	gl	
491	Glass 379 ($Qz_{38.6}$ $Ab_{36.2}$ $Or_{25.1}$)		1080	240	qtz + gl	
513	Glass 379		1100	168	gl	
632 Crys.	Glass 379		1060	72	qtz + gl	
632 Diss.[a]	Qtz + glass		1060 → 1100	72 → 96[b]	gl	
492	Glass 425 ($Qz_{41.1}$ $Ab_{22.2}$ $Or_{36.3}$)		1080	240	qtz + gl	
514	Glass 425		1100	168	gl	

[a,b] See explanation given in Table 3

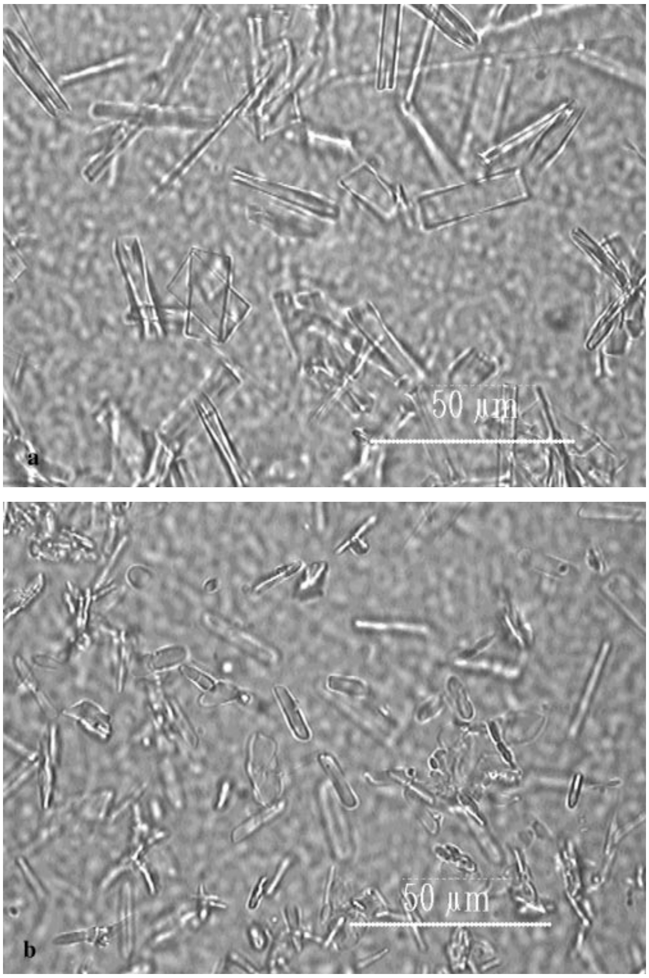


Fig. 1 Microphotographs of experimental products composed of glass and feldspars obtained in crystallization (a) and dissolution experiments (b). The crystallization experiment was performed with composition 390 (Table 1) at 1040 °C for 72 hours. The two-step dissolution experiment was performed with same composition first at 1040 °C (72 h) and then at 1060 °C (96 h). Note the rounded shape of feldspar crystals

longer run durations necessary to attain chemical equilibrium in compositions in the quartz primary field are attributed to the higher polymerization of SiO_2-rich glasses.

The change of Na_2O and K_2O contents of glasses and feldspars with experimental duration are shown in Figs. 4 and 5. Variations of the alkali contents can be observed for run durations shorter than 168 hours. For run durations of 168 hours or more, the variation of Na_2O and K_2O contents of glasses and crystals are within standard deviation. Equilibrium compositions seem to be approached after 168 hours.

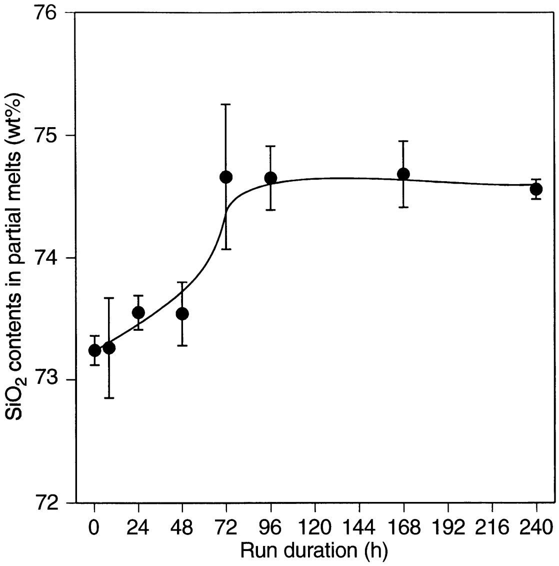


Fig. 2 Evolution of SiO_2 content of glasses with increasing run duration for composition 376 (Table 1) at 1000 °C, 5 kbar (liquidus temperature of this composition is 1050 °C). The *bars* correspond to the 2σ standard deviation

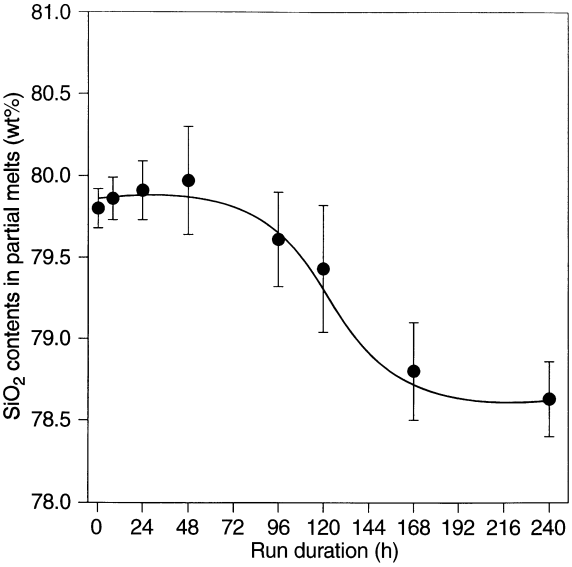


Fig. 3 Evolution of SiO_2 content of glasses with increasing run duration for composition 379 (Table 1) at 1000 °C, 5 kbar (liquidus temperature for this composition is 1090 °C). The *bars* correspond to the 2σ standard deviation

In conclusion, it is noted that equilibrium liquidus temperatures are best approached in experiments that are directly brought to the run temperature and in which hydrated crushed glasses were used as starting materials. Dissolution experiments show that it is possible to bracket liquidus temperatures within a temperature range of 20 °C in quartzofeldspathic melts containing 1 wt% H_2O. Experimental durations of 168 hours are sufficient to attain near equilibrium compositions.

Results

Experimental products consisted of glass or glass and crystals (crystals: quartz and alkali feldspars). The results of experiments performed with crushed starting

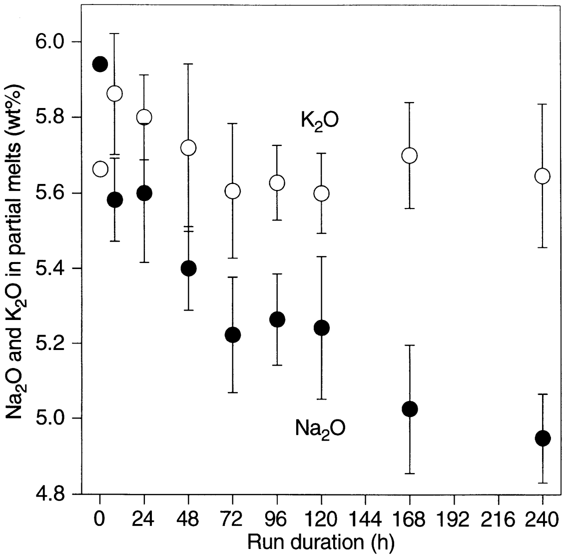


Fig. 4 Evolution of Na_2O and K_2O contents of glasses with increasing run duration for composition 376 (Table 1) at 1000 °C, 5 kbar (liquidus temperature of this composition is 1050 °C). The *bars* correspond to the 2σ standard deviation. *Dot and circle* at run duration 0 indicate Na_2O and K_2O content of starting material

materials and relevant for the determination of liquidus temperatures are given in Tables 3 and 4 (binary and ternary systems, respectively). In these experiments, the size of feldspar crystals was 3 to 50 μm and that of quartz was < 5 μm. It was observed that the shape of the crystals is characteristic of the degree of undercooling. For temperatures that are 10–20 °C below the liquidus temperature, feldspars are "tabular" (Fig. 6) and quartz shows the typical bipyramidal shape (Fig. 7, see also Swanson and Fenn 1986; Kirkpatrick 1975). At temperatures 40 °C or more below the liquidus temperature, alkali feldspars show skeletal structures and quartz is dendritic (Figs. 8 and 9).

Binary systems

Phase relationships for the binary systems are shown in Figs. 10 and 11. The given liquidus curves are bracketed by crystallization and dissolution experiments (Table 3). For the system Qz-Or, the eutectic composition is clearly constrained between glass compositions with 35 and 40% normative Qz (Fig. 10). The graphic interpolation of the data fixes the eutectic point for $a_{H_2O} = 0.07$ at $Qz_{38}Or_{62}$ and 1030 ± 10 °C. For the system Qz-Ab, the lowest liquidus temperature is 1095 ± 10 °C. It is bracketed by two experiments performed at 1090 and 1100 °C (Fig. 11). The composition of the eutectic is almost $Qz_{32}Ab_{68}$. The composition of the glasses obtained in experimental products are given in Table 5. The feldspars have been analyzed for identification.

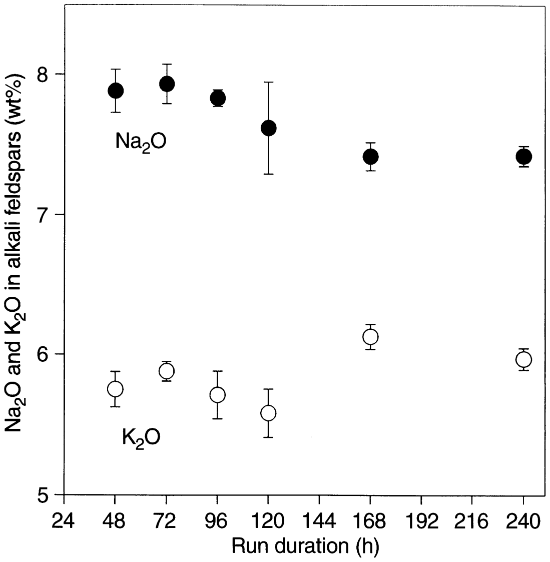


Fig. 5 Evolution of Na_2O and K_2O contents of feldspars with increasing run duration for composition 376 (Table 1) at 1000 °C, 5 kbar (liquidus temperature of this composition is 1050 °C). The *bars* correspond to the 2σ standard deviation

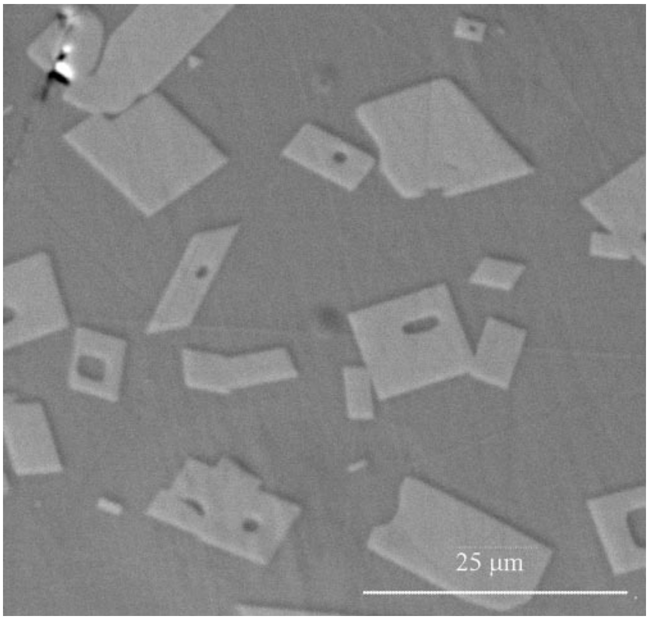


Fig. 6 Back scattered image of an experimental product composed of glass and feldspars obtained in a crystallization experiment with composition 390 (Table 1) at 1040 °C after 120 hours. The experimental temperature is 10 °C below the liquidus temperature

Ternary system

The phase relationships of the ternary system are shown in Fig. 12. This figure is based on the data obtained in the two binary systems Qz-Ab and Qz-Or and on the results achieved with ternary compositions. The isotherms are fixed by results of crystallization experiments

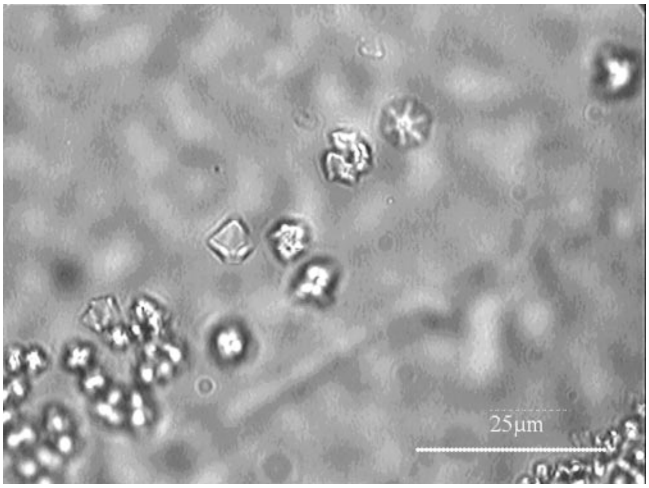


Fig. 7 Microphotograph of an experimental product composed of glass and bipyramidal quartz obtained in a crystallization experiment with composition 379 (Table 1) at 1080 °C after 240 hours. The experimental temperature is 10 °C below the liquidus temperature

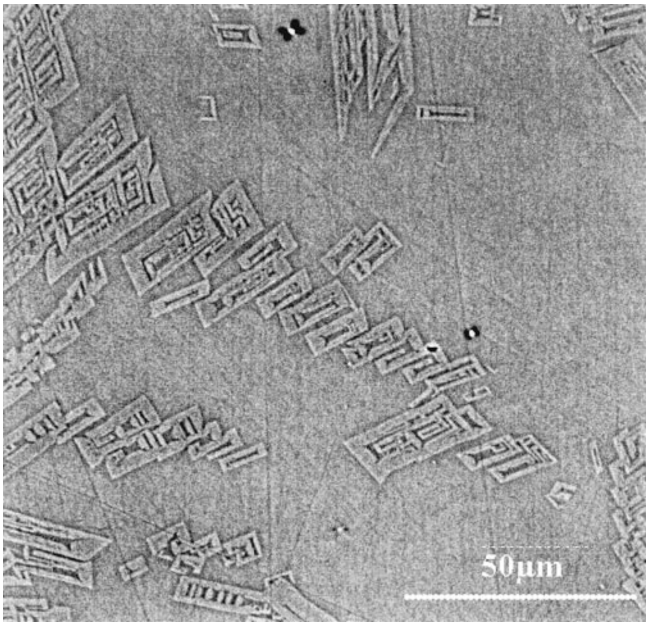


Fig. 8 Back scattered image of an experimental product composed of glass and feldspars obtained in a crystallization experiment with composition 390 (Table 1) at 1000 °C after 120 hours. The experimental temperature is 50 °C below the liquidus temperature. Note the skeletal shape of alkali feldspars

with either quartz or feldspar coexisting with the melt (Tables 3 and 4) and by the composition of the glasses (Table 6). The composition of glasses coexisting with quartz or feldspar are always shifted toward the composition of the cotectic line, as to be expected. In some experiments, quartz and alkali feldspar coexist with the melt (three experiments are given in Table 4 and shown in Fig. 12). The composition of these melts and the corresponding temperatures fix the cotectic line. The minimum is constrained by two melt compositions (Table 6. No. 537 and 538), one having an Ab/Or ratio higher than the coexisting feldspar and the other having an Ab/Or ratio lower than the coexisting feldspar. The composition (for composition of feldspars see Table 6) and temperature of the ternary minimum is

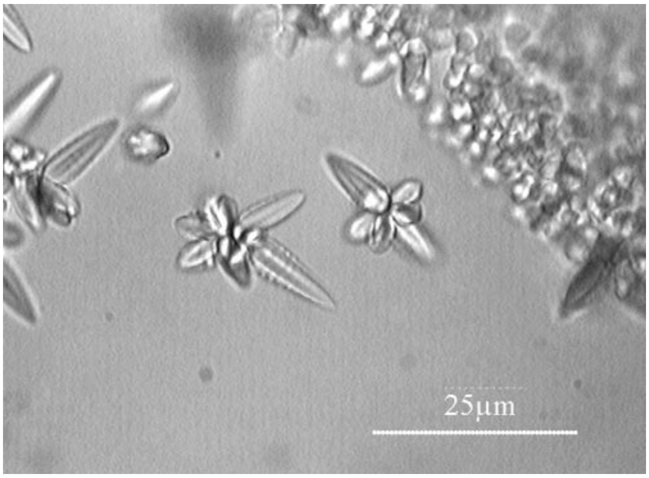


Fig. 9 Microphotograph of an experimental product composed of glass and skeletal quartz obtained in a crystallization experiment with composition 379 (Table 1) at 1040 °C after 240 hours. The experimental temperature is 50 °C below the liquidus temperature

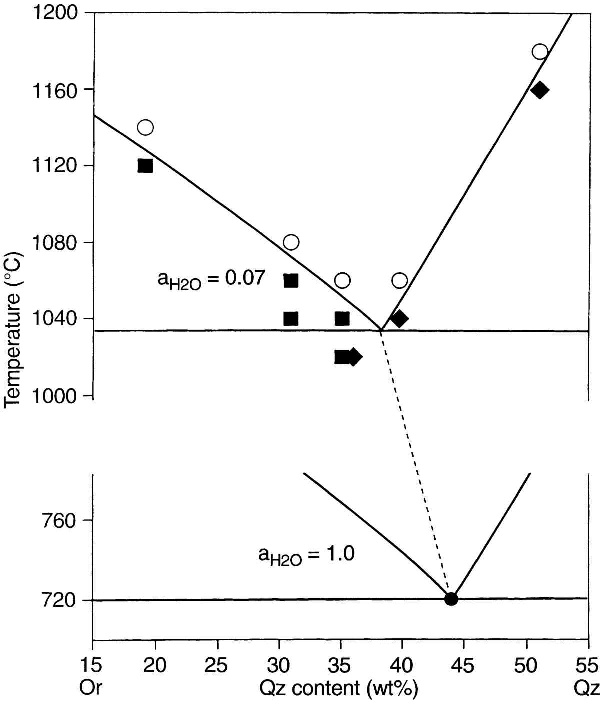


Fig. 10 *T-X* diagram showing phase relations of the systems Qz-Or-H_2O at 5 kbar for $a_{H_2O} = 1.0$ (data from Pichavant et al. 1992) and $a_{H_2O} = 0.07$ (this paper). *Black squares and diamonds* represent experimental products composed of glass + feldspar and glass + quartz, respectively. *Circles* represent experimental products composed of glass only. The liquidus curve at $a_{H_2O} = 0.07$ is represented by the *line* passing in between *circles* and *black symbols*. The *horizontal lines* correspond to the solidus curves

Table 5 Microprobe analyses of glasses (melts) obtained in crystallization experiments in the systems Qz-Ab-H_2O and Qz-Or-H_2O (average of at least 6 analyses)

Experiment no. Temperature [°C]	647 1100	648 1090	628 1120	574 1140	560 1120	579 1060	584 1020	586 1040	573 1040	557 1160
SiO_2	76.09	78.45	78.83	80.41	71.87	74.58	77.22	77.06	79.02	81.38
Al_2O_3	14.33	13.04	12.40	11.53	13.93	12.33	11.37	11.64	10.50	8.92
Na_2O	8.60	8.10	7.47	7.00	0.05	0.07	0.05	0.05	0.04	0.04
K_2O	0.02	0.03	0.02	0.08	13.22	11.44	10.62	10.68	9.65	8.62
Total	99.04	99.62	98.73	99.02	99.06	98.43	99.26	99.42	99.21	98.97
Qz	26.23	32.27	35.73	39.97	22.57	31.36	37.16	36.15	42.24	50.07
Ab	73.50	67.19	64.04	59.44	0.00	0.00	0.00	0.39	0.26	0.00
Or	0.10	0.16	0.14	0.50	76.77	68.42	62.56	63.45	57.48	49.20
C	0.16	0.00	0.09	0.00	0.00	0.00	0.00	0.01	0.00	0.00
NaS	0.00	0.38	0.00	0.09	0.09	0.14	0.10	0.00	0.02	0.09
KS	0.00	0.00	0.00	0.00	0.57	0.08	0.18	0.00	0.00	0.63

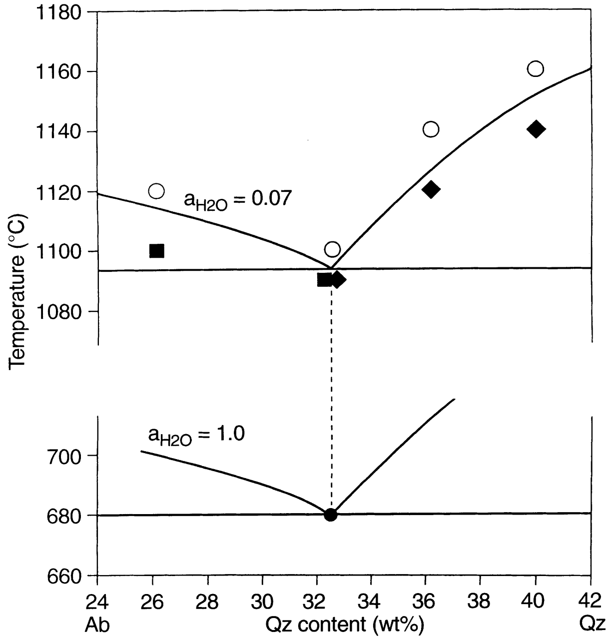


Fig. 11 *T-X* diagram showing phase relations of the system Qz-Ab-H_2O at 5 kbar for a_{H_2O} = 1.0 (data from Pichavant et al. 1992) and a_{H_2O} = 0.07 (this paper). *Black squares* and *diamonds* represent experimental products composed of glass + feldspar and glass + quartz, respectively. *Circles* represent experimental products composed of glass only. The liquidus curve at a_{H_2O} = 0.07 is represented by the *line* passing in between *circles* and *black symbols*. The *horizontal lines* correspond to the solidus curves

$Qz_{32}Ab_{35}Or_{33}$ and 990 °C at a_{H_2O} = 0.07 and 5 kbar (1 wt% H_2O in the melt).

Discussion and summary

The evolution of eutectic compositions and temperatures of the two binary systems Qz-Ab and Qz-Or with changing water activities from 0.07 to 1 are shown in Figs. 10 and 11. The data obtained at 5 kbar and a_{H_2O} = 1 by Pichavant et al. (1992) have been used for comparison. In the system Qz-Or, the Qz content of the eutectic composition decreases with decreasing water activity (variation of approximately 5% normative Qz). In contrast, almost no change of the eutectic composition is observed in the system Qz-Ab (the composition is close to $Qz_{32}Ab_{68}$). Similar results for both Qz-Or and Qz-Ab systems have been obtained by Pichavant et al. (1992) at 2 kbar for water activities decreasing from 1 to 0.5. The effect of water activity on eutectic temperatures is significantly more pronounced in the system Qz-Ab than in the system Qz-Or. The temperatures increase by 415 and 310 °C, respectively, for water activities changing from 1 to 0.07 (Fig. 13). This effect was also noted by Holtz et al. (1992) at 2 kbar for decreasing water activities from 1 to 0.3. The more pronounced effect of a_{H_2O} on eutectic temperatures in the system Qz-Ab may be related to the higher water solubility in Qz-Ab than Qz-Or eutectic melts. At 5 kbar the difference in water solubility between the two eutectic compositions is approximately 2 wt% H_2O (Holtz et al. 1995).

The effect of water activity on the temperature of the ternary minimum is shown in Figs. 13 and 14. The temperature increases from 645 °C at a_{H_2O} = 1 to 990 °C at a_{H_2O} = 0.07. In Fig. 14, the minimum temperatures predicted from the model of Burnham (1979) are also shown. For a_{H_2O} ranging from 1 and 0.3, the model of Burnham (1979) shows slightly higher temperatures than those determined experimentally. At very low water activities, however, the experimental liquidus temperatures are significantly higher than those calculated (difference of approximately 80 °C at a_{H_2O} = 0.07). This difference may be attributed to the experimental data at "dry" conditions that have been used in the model of Burnham (1979). To constrain phase relations, Burnham (1979) necessarily used experimental data that were mainly obtained at water-saturated and at nominally dry conditions (data at reduced a_{H_2O} were not available). It is notoriously difficult to obtain absolutely dry conditions at high *P* and *T*, which results in a high uncertainty on the determination of the dry minimum temperatures given in the literature (Tuttle

Table 6 Microprobe analyses of glasses (melts) and coexisting alkali feldspars obtained from crystallization experiments in the system Qz-Ab-Or-H_2O (averages of at least 6 analyses). Structural formulae calculated on the basis of 8 oxygen atoms

Experiment no.	477	478	479	527	537	506	507	538	544	542	491	492
Temperature [°C]	1040	1040	1040	980	980	1000	1000	980	1000	1020	1080	1080
Composition of partial melts												
SiO_2	72.88	72.77	73.11	78.05	77.18	75.84	76.17	77.93	79.00	78.42	79.17	79.65
Al_2O_3	14.90	14.90	14.46	13.40	12.89	13.47	12.70	12.75	12.44	12.17	11.84	11.24
Na_2O	5.74	4.80	3.94	4.44	4.72	4.15	3.23	4.10	4.09	3.89	4.30	2.80
K_2O	5.53	6.69	7.89	5.25	5.42	5.97	7.07	5.72	5.70	5.67	4.33	6.31
Total	99.06	99.16	99.40	101.15	100.20	99.43	99.18	100.49	101.23	100.14	99.64	100.00
Qz	20.06	20.11	21.77	31.76	31.12	29.03	31.37	32.58	34.31	35.12	37.70	39.80
Ab	46.28	39.78	30.64	37.14	36.07	35.28	26.15	33.59	31.89	31.00	36.51	2.70
Or	33.01	39.84	46.91	30.70	31.94	35.50	42.15	33.61	33.27	33.45	25.71	37.28
C	0.00	0.00	0.00	0.40	0.00	0.18	0.00	0.00	0.00	0.00	0.08	0.00
NaS	0.64	0.28	0.68	0.00	0.88	0.00	0.34	0.22	0.53	0.43	0.00	0.23
KS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Composition of alkali feldspars												
SiO_2	67.99	66.73	67.06	68.88	68.71	68.95	69.16	68.19				
Al_2O_3	18.66	18.71	18.34	18.13	18.28	17.82	17.78	18.32				
Na_2O	8.17	5.18	3.12	7.08	6.87	5.21	3.07	5.65				
K_2O	5.57	9.77	12.20	5.49	6.14	8.57	11.82	8.69				
Total	100.39	100.39	100.72	99.58	100.00	100.55	101.84	100.86				
Si	3.01	3.00	3.02	3.06	3.05	3.07	3.07	3.03				
Al	0.97	0.99	0.97	0.95	0.96	0.93	0.93	0.96				
Na	0.73	0.47	0.28	0.63	0.61	0.47	0.27	0.51				
K	0.32	0.56	0.70	0.31	0.35	0.49	0.67	0.49				

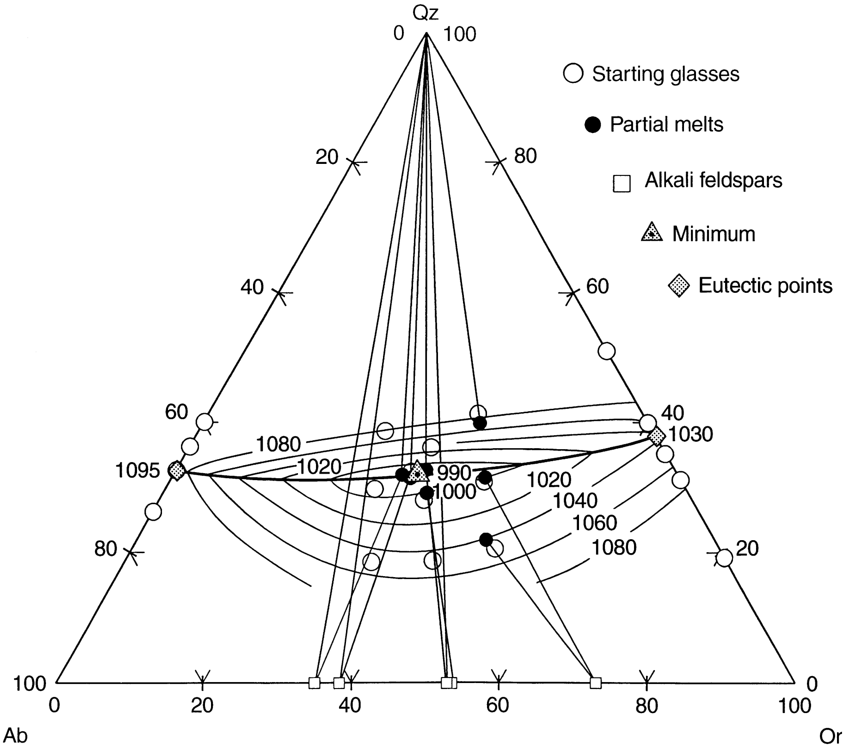


Fig. 12 Triangular diagram showing liquidus phase relationship of the system Qz-Ab-Or-H_2O at 5 kbar and $a_{H_2O} = 0.07$. The *dots* represent the compositions of melts connected by conjugation lines with coexisting quartz or feldspar or quartz and feldspar, respectively. The *heavy line* is the projected cotectic curve. The anhydrous composition of the minimum is $Qz_{32}Ab_{35}Or_{33}$. The *continuous lines* labeled 1000, 1020 etc. are isotherms on the liquidus surface

and Bowen 1958; Huang and Wyllie 1975; Keppler 1989; Ebadi and Johannes 1991). The minimum temperature determined in this study for a water content of the melt of 1 wt% H_2O (990 °C ± 10 °C) is very close or identical to that obtained from solidus experiments at dry conditions (1010 °C in Huang and Wyllie 1975; 1000 °C in Ebadi and Johannes 1991). Huang and Wyllie (1975) mentioned that their starting material, consisting of 95% synthetic feldspar crystals and 5% quartz crystals, was not fully crystallized, but still contained a proportion of unreacted gel (which is never dry). In addition, the analysis of feldspars synthesized following the same

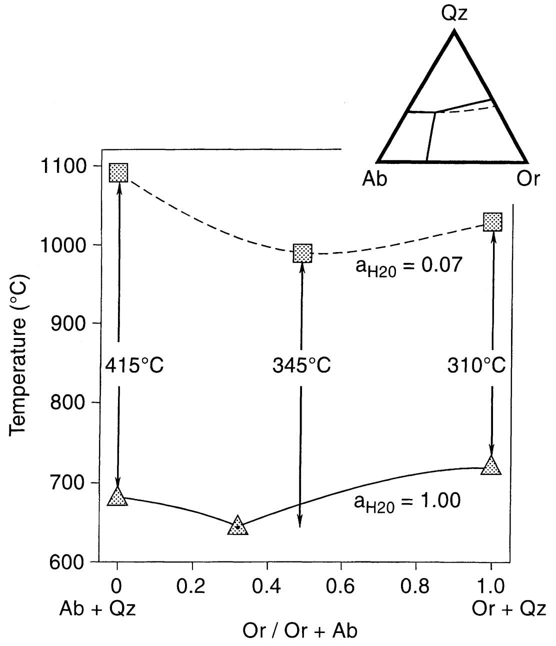


Fig. 13 Evolution of the cotectic temperatures of the system Qz-Ab-Or-H_2O at $a_{H_2O} = 1$ (from Pichavant et al. 1992 and Holtz et al. 1992, continuous curves) and $a_{H_2O} = 0.07$ (this study, *dashed curves*). *Triangles* and *squares* indicate eutectics and the ternary minimum for $a_{H_2O} = 1$ and $a_{H_2O} = 0.07$, respectively

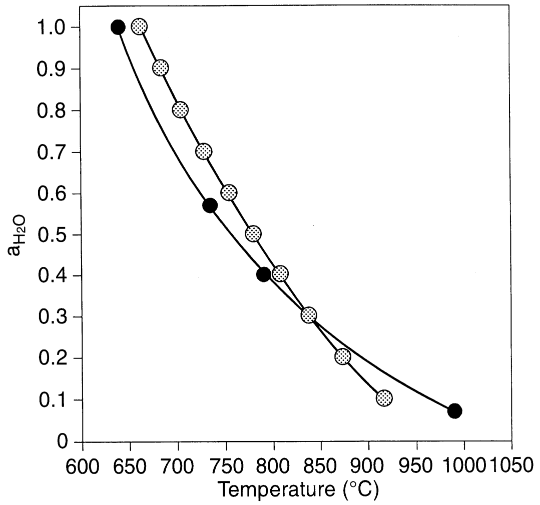
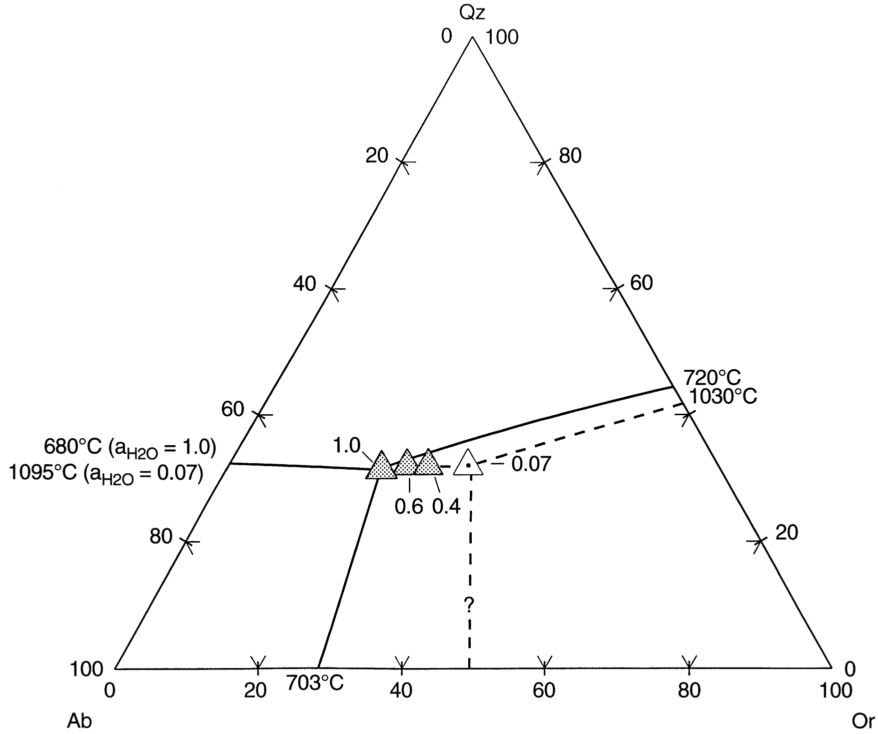


Fig. 14 $a_{H_2O} - T$ diagram showing the minimum temperatures in the system Qz-Ab-Or-H_2O at 5 kbar as a function of water activity. (*Black dots* experimental data obtained by Holtz et al. (1992) and in this study, *grey dots* data calculated by Nekvasil, 1988, using the model of Burnham, 1979)

procedure as Huang and Wyllie (1975) show that these products contained between 0.1 and 0.3 wt% H_2O after heating for 1 hour at 800 °C (the water content was determined by weight loss as well as Karl Fischer Titration). This water must be incorporated either in unreacted gel (probably glass) or in feldspars. It is concluded, therefore, that the dry fluid-absent liquidus temperature given for the minimum composition for 5 kbar in the literature is probably underestimated. As a consequence, the decrease of the liquidus temperatures with increasing a_{H_2O} at low water activities (between 0 and 0.3) is significantly more pronounced than previously assumed.

Fig. 15 Triangular diagram showing eutectic and minimum melt compositions of the system Qz-Ab-Or-H_2O for 5 kbar and various water activities. *Continuous* and *dashed lines* are cotectic lines for $a_{H_2O} = 1$ and $a_{H_2O} = 0.07$, respectively. Qz-Ab-Or values and temperatures of the minimum (eutectic) melts are for $a_{H_2O} = 1$: $Qz_{31}Ab_{47}Or_{22}$, $T = 645$ °C; $a_{H_2O} = 0.6$: $Qz_{32}Ab_{43}Or_{25}$, $T = 735$ °C; $a_{H_2O} = 0.4$: $Qz_{32}Ab_{40}Or_{28}$, $T = 790$ °C; $a_{H_2O} = Qz_{32}Ab_{35}Or_{33}$, $T = 990$ °C. The eutectic temperature for the subsystem Ab-Or-H_2O is from Morse (1970). For the source of all other data see text and Figs. 10–13



The evolution of the compositions of the 5 kbar minima with changing water activity is shown in Figs. 13 and 15. It is noted that the Qz content of the minimum determined at $a_{H_2O} = 0.07$ is practically identical to that determined by Holtz et al. (1992) for water activities of 1, 0.6, and 0.4 (31 to 32 wt% normative Qz). The Ab/Or ratio of the minimum composition determined in this study is in agreement with the trend observed by Holtz et al. (1992), showing a decrease of this ratio with decreasing a_{H_2O}. The minimum melt composition varies from Qz_{31}-Ab_{47}-Or_{22} at $a_{H_2O} = 1$ to Qz_{32}-Ab_{35}-Or_{33} at $a_{H_2O} = 0.07$. The decrease in a_{H_2O} results in a change of the Ab/Or ratio from 2.1. to 1.1.

When compared to results obtained by Holtz et al. (1992) and Pichavant (1992) in CO_2-bearing systems the results obtained in this study for CO_2-free systems demonstrate that small amounts of CO_2 dissolved in quartzofeldspathic melts at 5 kbar do not affect noticeably the phase relationships. (The maximal solubilities of CO_2 are 1000–1500 ppm in granitic compositions, see reviews by Blank and Brooker 1994; Holloway and Blank 1994). The liquidus temperature at $a_{H_2O} = 0.07$ and 5 kbar is 990 °C, which is considerably higher than expected from previous investigations at nominally dry conditions.

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