

Water solubility in monzogranite melts: experimental and calculated water contents at 6 kbar

Solubilidad de agua en fundidos monzograníticos: contenidos en agua experimentales y calculados a 6 Kb

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ABSTRACT

Several piston-cylinder crystallisation experiments have been performed with a synthetic monzogranitic glass with different initial water contents at 6 kbar. Comparison with calculated water contents shows: 1) some differences of the order of 10% of X_{H_2O} ; 2) "non-linear" behaviour in X_{H_2O}/T curves; and 3) similar pattern in the X_{H_2O}/T curves in both measured and calculated data.

Resumen

Se han realizado varios experimentos de cristalización en aparatos "piston-cylinder" a 6 kbar, usando como material de partida vidrios monzograníticos con diferentes contenidos de agua inicial. La comparación con los contenidos de agua calculada han puesto de manifiesto que: 1) existen diferencias del orden del 10% de X_{H_2O} ; 2) las curvas X_{H_2O}/T muestran comportamiento no lineal; y 3) la forma de las curvas X_{H_2O}/T calculadas y medidas son similares.

Key words: granitic melts, water solubility, crystallisation experiments, cordierite monzogranites.

RESUMEN

Se han realizado varios experimentos de cristalización en aparatos "piston-cylinder" a 6 kbar, usando como material de partida vidrios monzograníticos con diferentes contenidos de agua inicial. La comparación con los contenidos de agua calculada han puesto de manifiesto que: 1) existen diferencias del orden del 10% de X_{H_2O} ; 2) las curvas X_{H_2O}/T muestran comportamiento no lineal; y 3) la forma de las curvas X_{H_2O}/T calculadas y medidas son similares.

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Water is the most important volatile phase in natural silicate melts, as it is the most abundant and it has very strong effects on the physical properties of magmas. It is fundamental to understand the behaviour of water in melts and how it is incorporated in the melt structure. Many experimental studies have tried to model this behaviour (Burham and Nekvasil 1986, Burham 1994, Holtz 1995, Yamashita 1999 among others), but many uncertainties still remain, as most of these studies are focused in the haplogranitic system at low pressure.

Determination of water solubility is a difficult task due to analytical problems. Many of the published data have to be taken with care, as different analytical techniques have been used to determine water content in melts with their own uncertainties, generally too simplified systems.

It is well known that pressure is the most important parameter controlling

water solubility, but few investigations deal with the critical behaviour of water at high pressure (Paillat *et al.* 1992). This critical behaviour together with the influence of anhydrous composition (Behrens & Jantos 2001) is taken into account in this contribution to try to interpret the experimental results on a real granitic system.

Experimental studies at 6 kbar in a granitic system.

Crystallisation experiments at 6 kbar have been performed in a piston cylinder apparatus at the University of Huelva (Spain). For experimental details see Castro *et al.* (1999). Three different synthetic glass with the same anhydrous composition (Table 1), of a cordierite monzogranite from the Cabeza de Araya Batholith (Cáceres, Spain), and three different water contents (2, 4 and 6wt%) have been

Chemical composition	Starting glass composition (anhydrous)
SiO ₂	72.48
TiO ₂	0.44
Al ₂ O ₃	14.49
FeO(t)	2.49
MgO	0.62
CaO	1.15
Na ₂ O	3.63
K ₂ O	4.69
Total	100.00

Table I.- Anhydrous composition of the experimental starting materials.

Tabla I.- Composición química anhidra de los materiales experimentales de partida

used as starting materials. Experimental conditions were 6 kbar pressure and crystallisation temperatures from 975 °C to

Experiment #n	P (kbar)	T (°C)	Duration (hours)	wt %H ₂ O (initial/final)	Melt (vol.%)
OG69a	6	975→700	70,5	2/5.7	35
OG75b	6	975→700	72	4/5	80
OG75a	6	975→700	72	6/10.5	57
OG66a	6	975→750	64	2/9	22
OG66b	6	975→750	64	4/13	30
OG67	6	975→750	64	6/13	45
OG63a	6	975→800	74	2/3	65
OG63b	6	975→800	74	4/4.4	90
OG62b	6	975→800	74	6/6.2	97
OG71a	6	975→850	73	2/3	66
OG71b	6	975→850	73	4/4.2	96
OG72	6	975→850	73	6/6.6	91
OG73a	6	975→900	48	2/4.65	43
OG73b	6	975→900	48	4/5.2	77
OG74	6	975→900	48	6/9.4	64
OG78a	6	975	24	2/2.1	97
OG78b	6	975	24	4/4	99
OG79	6	975	23	6/6	98

Table II.- Melt volumes estimated from back-scattered electron images of the experimental results and water contents: initial (of the starting glass) and final (in the experimental melt).

Tabla II.- Volúmenes de fundido estimados a partir de imágenes de electrones retrodispersados de los resultados experimentales y contenidos en agua: inicial (de los vertidos de partida) y final (en los fundidos experimentales).

700 °C. Experimental results are summarised in Table 2. All these experiments are above the *solidus* for these conditions. Estimations of the water contents of the generated melts are made with the following assumptions:

a) Back-scattered electronic images of the experimental results are used to quantify the volumetrical proportion of melt in equilibrium with the mineral phases. As the initial water content of the starting glass is known, and all the phases crystallised from the melt are anhydrous (or only up to 2 vol% biotite in some cases), we assume that the melt has dissolved all the initial water content, being then inversely proportional to the final volume of melt.

b) Loss of water in the gold capsule during the experiment is minimum for the chosen experimental conditions (Patiño Douce & Beard 1994).

c) Formation of occasional bubbles in the melts has to be due to quenching, and may not influence the water solubility value estimated.

Water solubility has been expressed as mole fraction of the H₂O component on a one-oxygen mole basis, X_{H₂O}, following Behrens and Jantos (2001), in

order to compare the measured experimental solubility data with the calculated values using the anhydrous melt composition and the expression proposed by these authors for 5 kbar:

$$X_{H_2O} = 0.1681 \times (1 + 0.13 \times \{[(MCLNK - A)/O] - 0.5\}^2) \quad (1)$$

This expression gives the mole fraction of water as a function of the anhydrous composition of the melt, being the anhydrous-melt parameter as follows:

$$(MCLNK - A)/O = 100 \times (2Mg + 2Ca + Li + Na + K - Al)/O \quad (2)$$

in concentrations of oxide in mol/g (erratum published Behrens & Jantos, 2001)

Experimental glasses (melts) were analysed using LINK-ISIS energy-dispersive spectrometer mounted on a scanning electron microscope (JEOL-JSM65410) at the University of Huelva. These analyses were used to get the anhydrous-melt parameter using expression (2).

Water solubility in melts was experimentally determined by Behrens & Jantos (2001) to obtain expression (1) using natural glasses of different compositions and added water exceeding

an expected solubility value. In contrast, we have chosen an initial water content independent of any expected solubility value. If this value is below the real solubility value for any P / T condition, crystallisation of melt may occur, to attain equilibrium with the exact water content for the new melt composition.

Figure 1 shows X_{H₂O} of the experimentally generated melts for both, the calculated method using the expression (1) mentioned above, and the estimation using the measured melt volume. It can be seen the difference between both measured and calculated solubility values for the different starting materials.

We would like to emphasize the non-linear behaviour of the X_{H₂O} curve with temperature, with two maximum values for the temperatures 900 °C and 750 °C, corresponding to two minimum melt proportions for these temperatures, in the three different starting materials. These maximum values are not expected using classical water solubility models (Burham and Nekvasil 1986, Holtz et al. 1995, Moore et al. 1998, Yamashita 1999, Mysen & Wheeler 2000). However, it can be observed how the model proposed by Behrens & Jantos (2001) predicts these inflexions at 750 °C for the three different starting materials.

These maxima in the X_{H₂O} curve may be due to increases in water solubility in melts with temperature. Paillat et al. (1992) found a similar behaviour in NaAlSi₃O₈ melts at moderate pressures (~5 kbar) and they explain this inflexion as a consequence of a change in the solubility curve from retrograde (solubility decreases with T at constant P) to prograde with temperature. This is so for a simple binary model: silicate-H₂O, and can be more complex in a natural system as the one we are dealing with.

Curves of X_{H₂O}/T show some differences of the order of 10% of X_{H₂O} between measured and calculated data, but similar pattern as mentioned above.

Low resolution of the analytical method used for the generated hydrous melts can explain the low correlation of calculated and measured water contents in some cases, nevertheless this is better approach than the low-pressure water solubility models for minimum melt composition. These models seem to

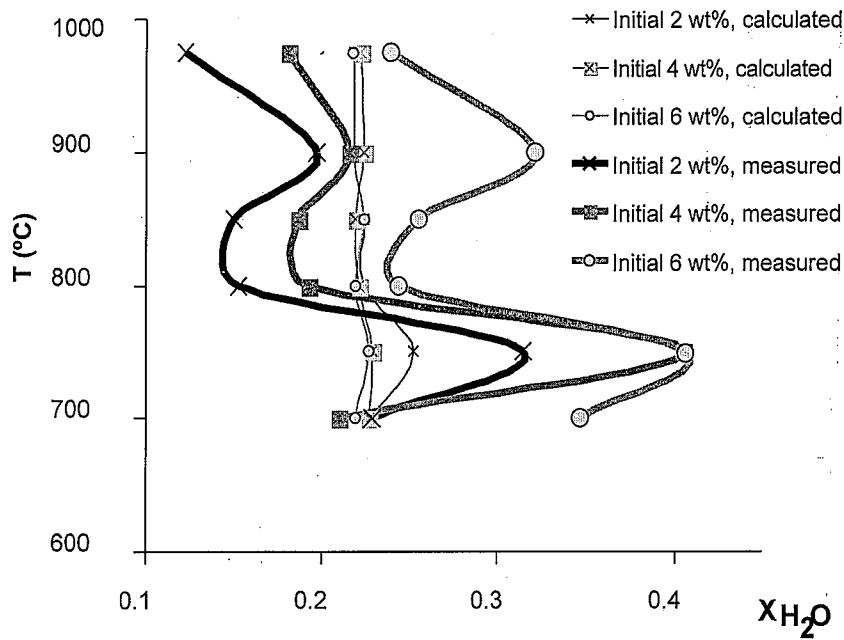


Fig. 1.- X_{H_2O}/T curves at 6 kbar. Calculated using analytical data of our experimental melts with expressions given by Behrens & Jantos (2001), and measured from estimated melt volume as explained in the text.

Fig. 1.- Curvas X_{H_2O}/T para 6 Kb. Calculadas utilizando los datos analíticos de nuestros fundidos experimentales con las expresiones propuestas por Behrens & Jantos (2001), y medidas a partir de las estimaciones de volumen de fundido, explicadas en el texto.

be far from real solubility behaviour values for natural granitic systems in which elements such as calcium, magnesium and iron may play an important role in the structure of melts, modifying water solubility at

the same time. This compositional factor, together with the critical behaviour of water at moderate pressures may explain the "non-linear" water solubility found in our experimental results.

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