

The effect of water on the solubility and speciation of CO₂ in aluminosilicate glasses along the join SiO₂-NaAlO₂

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Introduction

CO₂ and H₂O are the most important volatiles in the majority of magmatic systems and although the CO₂ is usually subordinate in concentration, it is often the first component to reach saturation due to the much higher solubility of water in the melt. CO₂ vesiculation can therefore be the driving force in many eruptive situations and it is important to investigate quantitatively the effect that varying amounts of water have on CO₂ saturation.

A number of previous studies have suggested that the solubility of CO₂ is greater in hydrous melts than in the anhydrous equivalents. This effect has been observed for a variety of polymerized and depolymerized compositions at high pressures (e.g. Brey and Green, 1975; Mysen, 1976). For albite and other simple sodium aluminosilicates, Mysen (1976) suggested that there is a maximum in the solubility as a function of the molar CO₂/CO₂ + H₂O ratio in the capsule. In contrast, Blank *et al.* (1993), studying the solubility of CO₂ in rhyolite at much lower pressures and temperatures found that the solubility of CO₂ was not enhanced by the presence of water.

The aim of this study is to examine the effect of water on the solubility and speciation of CO₂ in albite and jadeite melts. The speciation information is important if changes in the physical properties of magmas under such conditions are to be predicted. Albite is the main composition studied as there is considerable data available on the solubility and speciation of the pure components (e.g. Stolper *et al.*, 1987; Kohn *et al.*, 1989; Silver and Stolper, 1989) as well as theoretical predictions of solubility mechanisms. In addition, our data will provide a direct test of the conclusions of Mysen (1976).

Experimental methods

Samples were prepared in a piston cylinder apparatus at 1600–1625°C and 2.0–2.5 GPa. The

design of the NaCl/Pyrex solid media assembly has allowed the use of single platinum capsules rather than the double buffered arrangement used by previous workers. The assembly is designed to limit diffusion of furnace carbon into the capsule (Brooker *et al.*, in prep), as early experiments showed evidence of reduction to CO and graphite. Carbon diffusion appears to be the process responsible for reduction in these experiments, rather than hydrogen diffusion (as previously supposed). Starting materials were SiO₂, Al₂O₃ and Na₂¹²CO₃ or Na₂¹³CO₃. ¹³C MAS NMR spectra were acquired in the Department of Physics, University of Warwick, using a Bruker MSL 360 spectrometer operating at 90.56 MHz and a home-made probe based on a Doty Scientific 5 mm high speed spinning assembly. Micro-FTIR spectra were also obtained.

Results and discussion

Albite. Whilst the infrared spectra allow measurement of the abundance of molecular CO₂, there is an interference between the carbonate doublet and the molecular water bending motion, which limits the quantitative information which may be obtained by this technique. ¹³C MAS NMR has the advantage of providing complete information on all carbon species (Kohn *et al.*, 1991). The ¹³C MAS NMR spectra shown in Figure 1 show peaks at 124–125 ppm, due to molecular CO₂, and a multi-component feature at 170–155 ppm due to a variety of carbonate groups. Two main effects can be observed: (i) CO₂/CO₂ + CO₃²⁻ shows a maximum as a function of the dissolved water concentration (Figure 2) and (ii) the relative abundances of the different CO₃²⁻ species change, the more distorted carbonate, with a shift of about 160 ppm, becoming dominant at water concentrations above about 1 wt%. It should be noted that the glasses with higher water concentrations will have lower glass transition temperatures (Dingwell

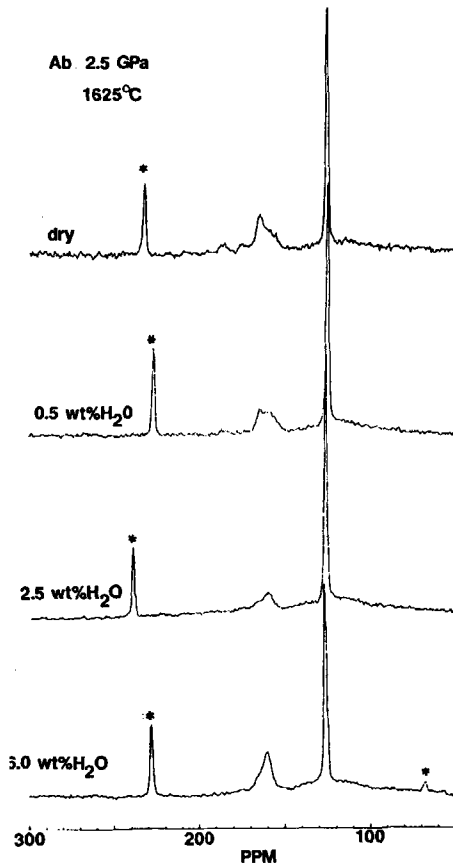


FIG. 1. ^{13}C MAS NMR spectra for CO_2 -bearing glasses. The range of shifts shown includes the centre-bands for molecular CO_2 (125 ppm) and carbonate groups (155–170 ppm), and spinning sidebands of molecular CO_2 (Marked with a *). The variation in the position of the spinning sideband is due to different spinning speeds. The peak at 185 ppm may be due to dissolved molecular CO , which was present in some early experiments.

and Webb, 1990; Romano *et al.*, 1993); thus, if the speciation is temperature dependent, the changes observed with increasing water concentration could represent the speciation at the lower glass transition temperature.

Measurements of the effect of water on solubility of CO_2 in these samples are in progress, but preliminary results suggest that the solubilities are lower than those reported by Mysen (1976) using the beta track autoradiography technique. This is consistent with the suggestion that beta track autoradiography overestimates the CO_2 solubility in albite melts (Tingle and Aines, 1988).

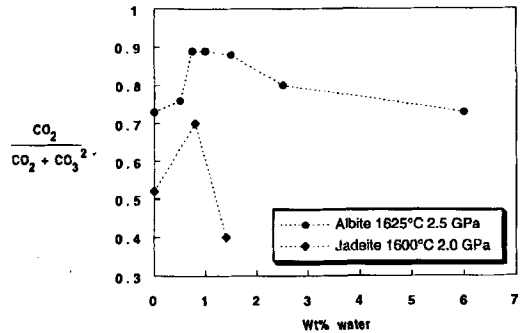


Figure 2. The $\text{CO}_2/\text{CO}_2 + \text{CO}_3^{2-}$ ratio in glasses quenched from CO_2 saturated melts, as a function of H_2O concentration in the melt.

Jadeite. The ^{13}C NMR spectra of jadeite glasses differ from those of albite in that; (i) the $\text{CO}_2/\text{CO}_2 + \text{CO}_3^{2-}$ ratio is smaller and (ii) the shape of the carbonate resonance is different, presumably due mainly to the relative abundances of the different types of carbonate group. Otherwise the changes observed as a function of increasing water concentration are the same in that there appears to be a maximum in the $\text{CO}_2/\text{CO}_2 + \text{CO}_3^{2-}$ ratio at around 1 wt% dissolved H_2O , and the shift of the most abundant carbonate species changes from 164 ppm to 160 ppm.

References

- Blank, J.G., Stolper, E.M. and Carroll, M.R. (1993) *Earth Planet. Sci. Lett.*, **119**, 27–36
- Brey, G. and Green, D.H. (1975) *Contrib. Mineral. Petrol.*, **49**, 93–103.
- Brooker, R.A., Holloway, J.R. and Hervig, R.L. (in prep) The diffusion of carbon in to platinum capsules in piston cylinder experiments.
- Dingwell, D.B. and Webb, S.L. (1990) *Eur. J. Min.*, **2**, 427–49.
- Kohn, S.C., Dupree, R. and Smith, M.E. (1989) *Geochim. Cosmochim. Acta*, **53**, 2925–35
- Kohn, S.C., Brooker, R.A. and Dupree, R. (1991) *Geochim. Cosmochim. Acta*, **55**, 3879–84.
- Mysen, B.O. (1976) *Amer. J. Sci.*, **276**, 969–96.
- Romano, C., Dingwell, D.B. and Sterner, S.M. (1993) *EOS, Trans. Am. Geophys. Union 1993 Fall Meeting*, **74**, 631.
- Silver, L. and Stolper, E. (1989) *J. Petrol.*, **30**, 667–709
- Stolper, E., Fine, G., Johnson, T. and Newman, S. (1987) *Amer. Mineral.*, **72**, 1071–85.
- Tingle, T.N. and Aines, R.D. (1988) *Contrib. Mineral. Petrol.*, **100**, 222–5.