Solubility and solution mechanism of H_2O in alkali silicate melts at high pressue

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The solubility behavior of H_2O in melts in the system Na_2O-SiO_2-H_2O were determined by Raman and NMR methods in the 0.8-2 GPa and 1000˚-1300˚C pressure and temperature range. The NBO/Si-range of the melts (0-1) was chosen to cover that of most natural magmatic liquids.

The H_2O solubility (X_w) ranges between 18 and 45 mol% (O=1) with $(\partial X_w/\partial P)_T$~14-18 mol% H_2O/GPa. The $(\partial X_w/\partial P)_T$ is negatively correlated with NBO/Si (=Na/Si) of the melt. The $(\partial X_w/\partial T)_P$ is in the –0.03 - +0.05 mol% H_2O/˚C range, and is negatively correlated with NBO/Si. Melts with NBO/Si similar to basaltic liquids show $(\partial X_w/\partial T)_P<0$, whereas more polymerized melts exhibit $(\partial X_w/\partial T)_P>0$. The $[\partial X_w/\partial(NBO/Si)]_{P,T}$ is in the -3 - -8 mol% H_2O/(NBO/Si) range. Complete miscibility between hydrous melt and aqueous fluid occurs in the 0.8-2 GPa pressure range for melts with NBO/Si≤0.5 at T>1100˚C. Miscibility occurs at lower pressure the more polymerized the melt. From the solubility data, the partial molar volume of H_2O in the melts, V_w^m, ranges between 10 and 13 cm^3/mol with $(\partial V_w^m/\partial T)_P$ ranging between 0 and –0.01/˚C.

Results from ^1H-^{29}Si CP MAS and ^1H NMR and Raman spectroscopy of quenched melts (glass) with ~20 mol% H_2O indicate the formation of Si-OH and Na-OH groups in addition to molecular H_2O. In quenched SiO_2-H_2O melts, protons are associated with Q^3-species (ie, $1H^+$/Si). In less polymerized melts (Na/Si = 0.25-1), protons are associated with both Q^3 and Q^2 structural units ($1H^+$/Si and $2H^+$/Si). In the most depolymerized melts (Na/Si>0.5), protons were also associated with Q^1 structural units ($3H^+$/Si). Evidence for Na-OH groups was observed in all Na-bearing melts.

Relations between abundance of Q^n-pecies (n=0, 1, 2, and 3) and H_2O content are consistent with formation of OH-groups via H_2O-solution mechanisms such as (in addition to molecular H_2O):

$$2Q^4 + H_2O \Leftrightarrow 2Q^3(H) \quad (1)$$

$$Q^4 + H_2O \Leftrightarrow Q^2(H), \quad (2)$$

$$2Q^3(Na) + 3H_2O \Leftrightarrow 2Q^2(H) + 2NaOH, \quad (3)$$

$$Q^3(Na) + 2H_2O \Leftrightarrow Q^1(H) + 2NaOH. \quad (4)$$

Reactions (1-3) dominate in felsic liquids (NBO/Si<0.5), whereas (3-4) is the predominant solution mechanism for less polymerized melts (NBO/Si>0.5). These solution mechanisms help explain the melt composition dependent H_2O solubility and partial molar volume of H_2O in these alkali silicate melts.