

## Structure of hydrous aluminosilicate melts (glasses): New insights from advanced one- and two-dimensional $^1\text{H}$ and $^{27}\text{Al}$ NMR

Xianyu Xue[1]; # Masami Kanzaki[1]

[1] ISEI, Okayama Univ.

<http://www.misasa.okayama-u.ac.jp/~xianyu/xianyu.shtml>

Water is among the most important volatile components that significantly affect the physical and thermodynamic properties of silicate melts and glasses. Understanding the dissolution mechanisms of water is important because the formation of different water species may have contrasting effects on melt properties. For Al-free silicate compositions, water speciation in the form of SiOH and molecular H<sub>2</sub>O are well known. The formation of SiOH is considered to play a major role in the reduction of melt polymerization and viscosity by water dissolution. More recently, another OH species, free OH (OH bonded only to metal cations, such as Mg and Ca), was also confirmed, and was found to be important for depolymerized silicate melts (glasses) containing metal cations of large field strength, such as Ca and Mg (Xue and Kanzaki, 2004). The formation of free OH, in contrast to SiOH, may cause an increase in the melt polymerization and viscosity.

Although most natural magmas contain Al as a major component, the dissolution mechanisms of water in Al-bearing silicate melts (glasses) remained controversial until recently. This was largely due to the non-uniqueness of spectral interpretations for simple one-dimensional (1D) NMR and Raman data when Al is present. Recently, we have made much progress in unraveling the dissolution mechanisms of water in aluminosilicate glasses of both polymerized and depolymerized compositions by taking full advantage of the rich information provided by advanced two-dimensional, double-resonance NMR (Xue and Kanzaki, 2006, 2007). Here we summarize some of these results.

Samples studied include quenched melts (glasses) containing 0-2 wt% H<sub>2</sub>O in the Na<sub>2</sub>O- SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O, K<sub>2</sub>O- SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O and CaO-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O systems with a range of NBO/T and Al/Si ratios. A variety of advanced NMR techniques, ranging from 1D  $^1\text{H}$  and  $^{27}\text{Al}$  MAS NMR and  $^{27}\text{Al}$ - $^1\text{H}$  CP-MAS NMR, to 2D  $^1\text{H}$  NOESY and DQ (double quantum) MAS NMR,  $^{27}\text{Al}$  3Q (triple quantum) MAS NMR, and  $^1\text{H}$ - $^{27}\text{Al}$  HETCOR (heteronuclear correlation) and 3QMAS/HETCOR NMR, have been applied. These data clearly revealed that for fully polymerized K-, Na- and Ca- aluminosilicate compositions, both SiOH and AlOH are present, in addition to molecular H<sub>2</sub>O. For depolymerized Ca- and Mg- aluminosilicate glasses, free OH, SiOH, AlOH and molecular H<sub>2</sub>O are all present, with the proportion of free OH increasing with decreasing degree of polymerization. Whereas Al is solely in tetrahedral coordination for Na- and K- aluminosilicate compositions, four-, five- and six-coordinate Al coexist for Ca- and Mg- aluminosilicate compositions. These results suggest that the dissolution mechanisms of water in aluminosilicate melts/glasses are in general similar to those in Al-free compositions, with two competing mechanisms, formation of SiOH/AlOH and depolymerization of the network structure, and formation of free OH and polymerization of the network structure, operating. One unique aspect for the alkaline earth aluminosilicate system is the rich variety of Al coordination, which may enhance water dissolution in the melts under high pressure.

### References:

Xue, X., and Kanzaki, M. (2004) Dissolution mechanisms of water in depolymerized silicate melts: Constraints from  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectroscopy and ab initio calculations. *Geochim. Cosmochim. Acta*, 68, 5027-5057.

Xue, X., and Kanzaki, M. (2006) Depolymerization effect of water in aluminosilicate glasses: direct evidence from  $^1\text{H}$ - $^{27}\text{Al}$  heteronuclear correlation NMR. *Am. Mineral.*, 91, 1922-1926.

Xue, X., and Kanzaki, M. (2007) Al coordination and water speciation in hydrous aluminosilicate glasses: direct evidence from high-resolution heteronuclear  $^1\text{H}$  -  $^{27}\text{Al}$  correlation NMR. *Solid State Nucl. Magn. Reson.*, 31, 10-27.