

Alkali influence on the water speciation and the environment of protons in silicate glasses revealed by ^1H MAS NMR spectroscopy

CHARLES LE LOSQ^{1,*}, GEORGE D. CODY¹ AND BJORN O. MYSEN¹

¹Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, D.C. 20015, U.S.A.

ABSTRACT

Water can form different chemical bonds with the ionic entities composing silicate melts. Because of that, its influence on the physico-chemical properties of magmas can vary with silicate composition and water content, temperature, and pressure. To further our understanding of how silicate chemical composition governs proton distribution in magmas, the environment of protons in hydrous alkali (Li, Na, K) silicate glasses was varied as a function of the type of alkali metal and total water content. From ^1H MAS NMR spectroscopy, H^+ are distributed among five different structural environments in alkali silicate glasses. One of these environments is in the form of H_2O molecules ($\text{H}_2\text{O}_{\text{mol}}$). The four others are the proton environments associated with Si-OH bonding, and perhaps also with M-OH bonding (with $M = \text{Li, Na, or K}$). Those environments differ in their O-O distance and extent of hydrogen bonding. $\text{H}_2\text{O}_{\text{mol}}$ species are located in an environment with an O-O distance of ~ 290 pm. OH^- groups are in environments with O-O distances from 240 to 305 pm. The ionic radius of the alkalis, and hence their ionic field strength, determines the fraction of water dissolved as $\text{H}_2\text{O}_{\text{mol}}$ and OH^- groups, as well as the distribution of protons in the various OH^- environments. The mean volume of the H^+ oxygen coordination sphere was calculated using the $^1\text{H}^+$ NMR signal intensity and the mean O-O distance around H^+ . Increasing ionic radius of the alkali metal in silicate glasses results in a decrease of this mean volume. The partial molar volume of water in the corresponding melts determined through other technics seems to vary in a comparable way. Therefore, the chemical composition of silicate melts may control the partial molar volume of dissolved water because of its influence on the structural environment of protons. This probably also plays a role in determining water solubility.

Keywords: Water, silicate glasses, proton solid-state NMR, proton environment