

Chemical dependence of the structural position of OH groups in silicate glass: with implication for H₂O/OH measurements through IR spectroscopy

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Water drastically affects the physico-chemical properties of magmatic liquids, with in major influence on past and present magmatic activity of the Earth. Water may dissolve in magmas as H₂O molecules (H₂O_{mol}) and OH groups, with the OH groups bonded to the silicate network to form Si-OH or Al-OH bonds and perhaps alkali-OH and alkaline earth-OH complexes. A common procedure to obtain proportion of H₂O_{mol} and OH groups is to determine the intensities of the 5200 and 4500 cm⁻¹ IR bands, usually attributed to, respectively, (i) combination of stretching and bending vibrations of H₂O molecule and (ii) to combination of the Si-OH and fundamental OH stretching modes. By using this analytical protocol, the H₂O_{mol}/OH ratio seems to be nearly insensitive to the chemistry of glasses. However, important questions remain as to how bulk chemistry governs the link between the different OH groups and the silicate network, and, therefore, the H₂O_{mol}/OH ratio determined therefrom.

In order to obtain a quantitative assessment of bulk compositional effects on the speciation of water in quenched, hydrous silicate melt (glass), we analysed M₂Si₄O₉ glasses (M = Li, Na or K) containing different amounts of water (3.3 - 17.6 mol%) with the aid of ¹H and ²⁹Si MAS NMR, Raman and Infrared spectroscopy. Raman and infrared spectra of the silicate glasses display three different bands at ~ 2300, ~ 2800 and ~ 3600 cm⁻¹, assigned to O-H stretching from OH groups and from H₂O_{mol}. Those three bands seem related to different structural environments, as confirmed by ¹H NMR spectra. The OH distribution between those environments is affected by the size of the alkali element present within the silicate network.

These results question the real origin of the IR combination bands. By combining the 2300 and 2800 cm⁻¹ bands with the fundamental Si-OH stretching mode at 970 cm⁻¹ the resulting band will not contribute to the observed 4500 cm⁻¹ IR band, which arises mainly from the 970+3600 cm⁻¹ combination. Therefore, the use of the 4500 cm⁻¹ band in infrared spectra as a marker of total OH groups content may have introduced errors in our interpretation of the water speciation, maybe explaining why H₂O_{mol}/OH seem independent of glass chemistry.