Complex IR spectra of OH\textsuperscript{-} groups in silicate glasses: Implications for the use of the 4500 cm\textsuperscript{-1} IR peak as a marker of OH\textsuperscript{-} groups concentration

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ABSTRACT

Previous studies of hydrous glasses and melts with infrared spectroscopy have led to the conclusion that the IR combination peaks near 4500 and 5200 cm\textsuperscript{-1} reflect the existence of OH\textsuperscript{-} (hydroxy) groups and H\textsubscript{2}O\textsubscript{mol} water molecules in those materials. Here, we show that the glass chemical composition can impact profoundly the intensities and frequencies of the fundamental O-H stretching signal and, therefore, potentially those of the 4500 and 5200 cm\textsuperscript{-1} combination peaks. In alkali silicate glasses, compositional effects can give rise to peaks assigned to fundamental O-H stretching at frequencies as low as 2300 cm\textsuperscript{-1}. This expanded range of Raman intensity assigned to O-H stretch is increasingly important as the ionic radius of the alkali metal increases. As a result, the combination of the fundamental O-H stretch in OH\textsuperscript{-} groups with the Si-O-H stretch located near 910 cm\textsuperscript{-1} gives rise to a complex combination signal that can extend to frequencies much lower than 4200 cm\textsuperscript{-1}. This combination signal then becomes unresolvable from the high-frequency limb of the band assigned to fundamental O-H stretch vibration in the infrared spectra. It follows that, when O-H stretch signals from OH\textsuperscript{-} groups extend to below 3000 cm\textsuperscript{-1}, the 4500 cm\textsuperscript{-1} peak does not represent the total OH\textsuperscript{-} signal. Under such circumstances, this infrared peak may not be a good proxy for determining the concentration of OH\textsuperscript{-} hydroxyl groups for glassy silicate materials.

Keywords: Water speciation, FTIR spectroscopy, O-H stretch signal, silicate glasses

INTRODUCTION

Water dramatically affects the physical properties of silicate melts and glasses (see the review by Mysen and Richet 2005), and, as a result, is of key importance in both industrial and geologic processes. An important feature of water dissolved in glassy and molten silicate materials is that it exists both as molecules (H\textsubscript{2}O\textsubscript{mol}) and as hydroxyl groups (OH\textsuperscript{-}) bonded to the silicate network. It has often been stated that these two different species give rise to IR combination peaks at \textasciitilde5200 and \textasciitilde4500 cm\textsuperscript{-1}, respectively (Davis and Tomozawa 1996; Efimov and Pogareva 2006; Malfait 2009; Scholtze 1960; Stolper 1982). The OH\textsuperscript{-} groups are bonded to the tetrahedral network of silicate glasses and melts, forming Si-OH and Al-OH bonds by breakage of bridging oxygen bonds (Si-O-Si, Al-O-Al, and Si-O-Al) (see for instance Moulson and Roberts 1961; Scholtze 1960; Stolten and Walrafen 1976; Stolper 1982). This solution mechanism results in depolymerization of the silicate network (see for instance the study of Mysen and Cody 2005). In contrast, water dissolved in the form of H\textsubscript{2}O\textsubscript{mol} species does not change melt polymerization. As a result, the dissolution of water as OH\textsuperscript{-} groups or as H\textsubscript{2}O\textsubscript{mol} species has different effects on the polymerization and hence properties of hydrous silicate amorphous materials. These differences are reflected in transport properties of hydrous melts, glass transition temperature (see for instance Deubener et al. 2003), solidus temperatures, melt/mineral phase equilibria, and element partitioning (see for a review Mysen and Richet 2005).

The water speciation, in terms of H\textsubscript{2}O\textsubscript{mol} species and OH\textsuperscript{-} groups, varies with total water concentration and temperature (Behrens and Yamashita 2008; Nowak and Behrens 1995; Stolper 1982). It also depends on composition (Deubener et al. 2003; Moretti et al. 2014). However, it is not known how temperature effects vary with bulk composition, and how bulk compositional variables govern solution mechanisms and solubility.

FTIR spectroscopy may be used to examine such effects by using the combination peaks often located near 4500 and 5200 cm\textsuperscript{-1} in the spectra. However, as a first step, it is necessary to ascertain exactly what governs the frequency and integrated intensity of the 4500 and 5200 cm\textsuperscript{-1} combination peaks in the IR spectra of hydrous silicate glasses (and melts). An example of this is the recent work of Malfait (2009) who concluded that the 4500 cm\textsuperscript{-1} IR peak is formed by the combination of the fundamental O-H stretching mode at \textasciitilde3600 cm\textsuperscript{-1} with the Si-O-H, and presumed Al-O-H, stretching vibrational mode. The Al-O-H vibrational mode can occur near 800 cm\textsuperscript{-1}, whereas the Si-O-H is near 920 cm\textsuperscript{-1}. Combined with the fundamental O-H stretching mode at 3600 cm\textsuperscript{-1} in simple aluminosilicate glasses, the exact frequency of the 4500 cm\textsuperscript{-1} would be somewhat correlated, therefore, with the Al/Si of the glass. Concerning the 5200 cm\textsuperscript{-1} peak, it is attributed to arise from the combination of the 3600 cm\textsuperscript{-1} stretching and 1630 cm\textsuperscript{-1} bending modes of H\textsubscript{2}O\textsubscript{mol} species (Scholtze 1960; Stolper 1982).

The infrared signal assigned to O-H stretch in OH\textsuperscript{-} and H\textsubscript{2}O\textsubscript{mol} species, usually characterized by an asymmetric band centered near 3600 cm\textsuperscript{-1}, can have a complex shape in some silicate glasses, where broad bands extend into the 2000–3000 cm\textsuperscript{-1}...