AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY

The effect of the [Na/(Na+K)] ratio on Fe speciation in phonolitic glasses†

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ABSTRACT

Natural iron-bearing sodic phonolitic melts represent an extreme compositional range of the effect of the [Na/(Na+K)] ratio on the geochemical behavior of Fe in volcanic systems. Yet phonolitic melts have not been well investigated. The glasses studied here have been synthesized from liquids equilibrated over a range of oxygen fugacity conditions [log$_{10}$($f_{O_2}$)] from −0.68 to −11 to elucidate the role of the alkali ratio in influencing the local environment around both divalent and trivalent Fe. In this study, the Fe K-edge XAS spectra (XANES and EXAFS) have been employed, to constrain the Fe structural role (oxidation state, coordination number, bond distances) in phonolitic glasses as a function of synthesis temperature (T), [Na/(Na+K)] ratio (0.0, 0.25, 0.5, 0.75, 1.0) and redox state. We verify that at constant oxygen fugacity, the [Na/(Na+K)] ratio has a strong effect on the Fe$^{2+}$/ (Fe$^{3+}$+Fe$^{2+}$) ratio. The results obtained are parameterized and discussed in terms of the contrasting effects of T, $f_{O_2}$, and alkali ratio.

Keywords: Alkalis, iron, oxidation state, phonolitic glasses, XAS

INTRODUCTION

The speciation of iron in magmatic systems influences both phase equilibria and physical properties of magma. This speciation is known to depend significantly on temperature, redox state, and chemical composition (e.g., Mysen and Richet 2005). Ultimately, sufficiently robust and comprehensive characterization of Fe redox and coordination states may provide the data necessary for constructing thermodynamic models of the role of reduced and oxidized iron in both volcanic and technologically significant systems that is so badly needed.

Iron can be found in a variety of oxidation states and coordination geometries in both melts and crystals. The common Fe species interpreted from investigations of silicate melts and glasses include $^{56}$Fe$^{2+}$, $^{57}$Fe$^{2+}$, $^{58}$Fe$^{3+}$, and $^{59}$Fe$^{3+}$ (see Wilke et al. 2001; Giulì et al. 2002, 2011, 2012a; Jackson et al. 2005; Mérich et al. 2006; Rossano et al. 2008). The presence of $^{57}$Fe$^{2+}$ (e.g., Calas and Petiau 1983; Virgo and Mysen 1985; Dingwell and Virgo 1987) and a minor presence of $^{58}$Fe$^{3+}$ (Wilke et al. 2007) have been reported. Variation of the relative proportions of these species influences the <Fe-O> distances and bond strengths, thus likely affecting all aspects of glass/melt structure, including melt polymerization, basicity, as well as melt properties; such as density and viscosity (e.g., Dingwell and Virgo 1987; Dingwell 1991; Lieske et al. 2003).

The Fe$^{2+}$/Fe$^{3+}$ ratio is also widely used as a monitor of the redox conditions of magmatic systems (e.g., Fudali 1965; Carmichael 1991). Several empirical and theoretical models have been proposed (e.g., Kilinc et al. 1983; Kress and Carmichael 1988, 1991; Ottolengo et al. 2001), and most of them assume a linear dependence of log (Fe$^{2+}$/Fe$^{3+}$) on the mole fractions of the main components of the silicate melts. However, some differences have been observed for alkali- and alkali-earth-bearing materials. In particular, it has been verified that the different ionization potential (Z/r) of cations influences the Fe redox ratio (e.g., Paul and Douglas 1965) and the iron-oxygen coordination geometry (e.g., Mysen 2006). These effects have been related to the steric factors associated with charge-balance of Fe$^{3+}$ in fourfold coordination (Mysen 2006). In particular, several studies suggest a stabilization of $^{58}$Fe$^{2+}$ by charge-balancing K$_2$O (Sack et al. 1980; Kilinc et al. 1983; Dickenson and Hess 1981; Kress and Carmichael 1988). In contrast, Tangeman et al. (2001) observed that in very Fe-rich K$_2$O-FeO-SiO$_2$ glasses an increase of K$_2$O leads to an increase of the ferrous iron.

It follows from the above that a full understanding of the parameters that influence Fe coordination and oxidation state in silicate melts should be a research priority. Alkali content is one of the melt chemical parameters that exhibits a very strong influence on melt structure and properties. It is known to affect virtually all glass properties (Isard 1969) as well as the Fe oxidation state itself in silicate melts (see Dickenson and Hess 1981; Duffy 1993; Moretti and Ottolengo 2003 and references therein). It also exerts a first-order effect on the viscosity of silicate liquids at high temperatures (Giordano et al. 2008). Nevertheless few data are available to assess quantitatively to which extent the Na/(Na+K) ratio can modify the Fe structural role in multicomponent glasses and melts. Le Losq and Neuvillé (2013) have recently studied the effect of Na/K ratio on the structure and rheology of silica-rich glasses, proposing the occurrence of two sub-networks in mixed alkali tectosilicate glasses. In previous experiments on

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