PANTELLERITIC MAGMAS: EXPERIMENTAL STUDY ON THE EFFECT OF [Na/(Na+K)] RATIO AND fO$_2$ ON IRON REDOX AND VISCOSITY

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INTRODUCTION

The knowledge of iron oxidation state in silicate melts represents an important key for the comprehension of magmatic processes as well as for the understanding of the formation of iron-bearing glasses. In fact, iron is the most abundant element occurring in more than one oxidation state in natural silicate melts (mainly as Fe^{2+} and Fe^{3+}) and, depending on this, it can influence physical and chemical properties such as melt structure and viscosity (*e.g.* Liebske *et al.*, 2003; Jayasuriya *et al.*, 2004; Giordano *et al.*, 2008).

The goal of the present study is to investigate the iron speciation in glasses depending on the redox conditions, temperature and alkali ratio as well as to address the role of iron redox and alkali ratio on viscosity of pantelleritic glasses. These are analogues of natural pantelleritic composition of Kenya Rift Valley, corresponding to the Ebu-1 composition in Scaillet & MacDonald (2006), used for studying sulphur solubility in melts. Several sets of synthesis were performed on glasses with a nominal iron content of 5.2 wt.% and with distinctive [Na/(Na+K)] ratio (= 0, 0.69, and 1) in a gas mixing furnace at ambient pressure and three temperatures (1110, 1250, and 1400 °C). Different oxygen fugacities (from air to IW buffer) were imposed using simply gas (air, CO_2, O_2) or gas mixtures (93%Ar/7% H_2, Ar/H_2/H_2O).

fO$_2$ DEPENDENCE ON IRON STRUCTURAL ENVIRONMENT

The preliminary study of Fe reduction kinetics at low oxygen fugacity (near IW buffer conditions) allowed to ascertain that equilibrium of the iron redox ratio is attained wi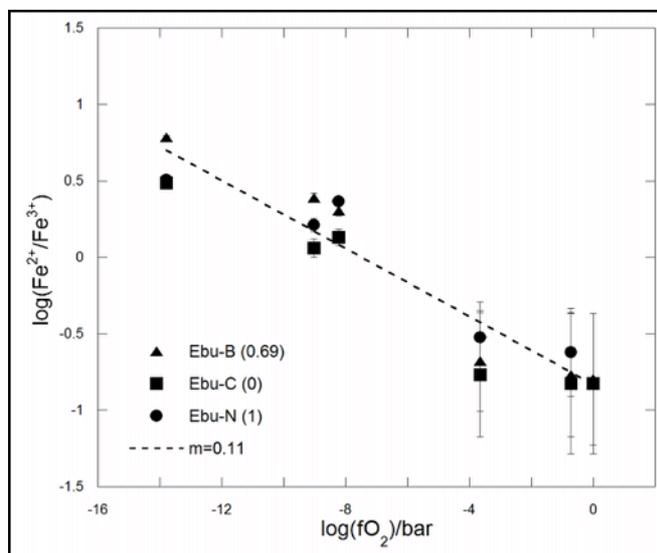thin 20 hours at 1250 °C for the pantelleritic melts. The Fe^{2+}/Fe^{3+} of the glasses were determined by a colorimetric wet chemistry method after Wilson (1960) modified by Schuessler *et al.* (2008). Analyses revealed a continuous increase in ferrous iron towards more reducing conditions (from -0.72 to -13.8 $\log fO_2$/bar), with Fe^{2+}/Fe_{tot} ratio covering a range of values from *i*) 0.12 to 0.86 (±0.03) for the Ebu-B, *ii*) from 0.11 to 0.76 (±0.03) for Ebu-C, and *iii*) from 0.16 to 0.76 (±0.03), for Ebu-N. A roughly linear correlation between $\log$ (Fe^{2+}/Fe^{3+}) and $\log$ (fO_2/$_{bar}$) was observed for all the compositions (Fig. 1).

All the investigated compositions, including Ebu-C and Ebu-N, regardless the opposing [Na/(Na+K)] ratio (0 and 1, respectively), present a similar slope and can be well represented by the average value of 0.11. Such value differs from the ideal slope of 0.25 resulting from the assumption of the ideal Fe^{2+} and Fe^{3+} mixing. This may be explained by the

Fig. 1- Redox state of iron as function of oxygen fugacity for glasses synthesized at 1250 °C. Data can be described by Fe^{2+}- Fe^{3+} non-ideal mixing in the melt (dashed line), *i.e.* average slope of 0.11 for all the Ebu. *Notes*: (0.69), (0), and (1) refers to the [Na/(Na+K)] ratio in Ebu-B, Ebu-C and EBu-N, respectively.

presence of aluminium in the structure of the silicate network that acted, as Fe^{3+}, as network former in the melt, stabilizing more ferric iron at the expense of ferrous iron in the system.

The structural study was performed by X-ray absorption near edge structure (XANES) spectroscopy at the Fe K-edge, and provided structural information of the iron environment in the glasses, *i.e.*, Fe oxidation state and average coordination number. The XANES spectra of Fe-bearing glasses and model compounds were collected at ESRF (European Synchrotron Radiation Facility, Grenoble, France) in order to obtain the needed structural information.

An example of normalized Fe K-edge XANES spectra is shown in Fig. 2, where Ebu-B pantelleritic glasses, synthesized at 1250 °C, are arranged in order of increasing oxygen fugacity (ranging from -13.8 to -0.72 $logfO_2$/bar) from top to the bottom. It appears evident a shift of the absorption edge from higher to lower energies when decreasing the oxygen fugacity, as well as in the shape of the pre-edge peak (P) (*e.g.*, passing from Ebu-B MT to Ebu-B H_2/Ar in Fig. 2). The pre-edge peaks have been fitted with two components with energies of 7112.5 eV and 7114.3 eV, which are ascribed to contributions from Fe^{2+} and Fe^{3+}, respectively.

The integrated intensities of the pre-edge peaks *vs.* their centroid energies for all the studied glasses are plotted in Fig. 3 along with the data of Fe model compounds included in the shaded ellipse (Farges, 2001; Wilke *et al.*, 2001; Giuli *et al.*, 2002). In terms of coordination number, Fe^{3+} is present in tetrahedral coordination in all the glasses, whereas Fe^{2+} displays an higher coordination number, possibly resulting from the presence of $^{[4]}Fe^{2+}$, $^{[5]}Fe^{2+}$ and $^{[6]}Fe^{2+}$ contributions.

EFFECT OF TEMPERATURE AND ALKALI RATIO ON IRON REDOX

Data for the three series of glasses Ebu-B, Ebu-C, and Ebu-N ([Na/(Na+K)] ratios of 0.69, 0, and 1, respectively) melted in air at three different temperatures (1100 °C-LT, 1250 °C-MT, and 1400 °C-HT) are plotted against the reciprocal T in Fig. 4. It is evident that divalent iron increases with increasing temperature, and according to the ionization potential (K < Na). The temperature dependence of the Fe redox is described employing linear equations with slope varying from -0.10 to -0.07 (±0.02) for [Na/(Na+K)] ratios ranging
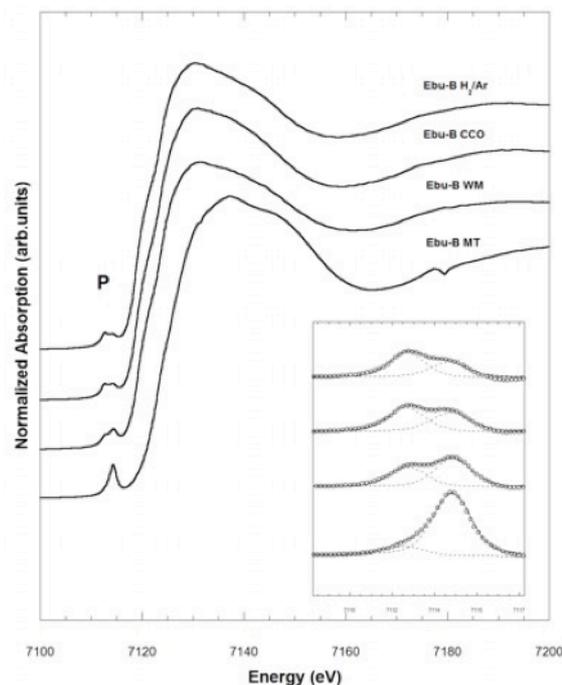

Fig. 2 - Example of experimental Fe K-edge XANES spectra of the studied glasses Ebu-B synthesized at 1250 °C. In the inset: background subtracted pre-edge peaks of the studied glasses Ebu-B (empty circles) along with pseudo-Voigt component used in the fitting procedures (dotted lines), and pseudo-Voigt sums (solid lines).
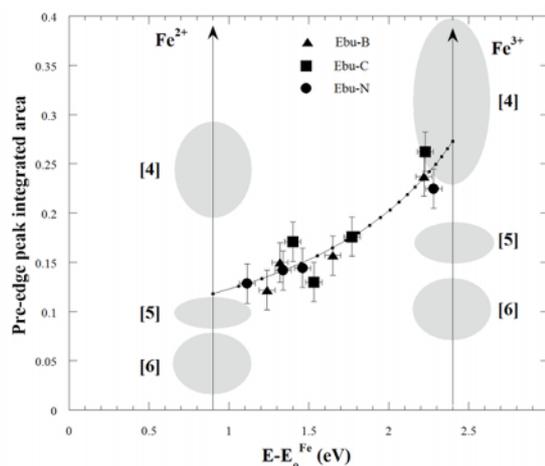

Fig. 3 - Plot of the pre-edge peak integrated intensity *vs.* centroid energy position of all the glasses synthesized at 1250 °C and 1 atm. The small circles joined by the dotted lines represent the mixing lines between the pre-edge peaks.

from 0 to 1. It is absent any significant slope dependence on alkali ratio for these compositions, however the [Na(/Na+K)] ratio strongly affects the Fe redox.

Under oxidizing conditions, in fact, low [Na/(Na+K)] ratios stabilizes more Fe^{3+} in the melt; the association of tetrahedral Fe^{3+} with charge compensating cations is strongest for K^+, which is consistent with the lower ferrous ferric iron ratios observed in the K-bearing glasses (Ebu-C).

INFLUENCE OF IRON REDOX STATE AND ALKALIS ON VISCOSITY

The micro-penetration technique has been used to determine shear viscosity in the range of 10^9 - 10^{14} Pa s (*e.g.*, Douglas *et al.*, 1965; Bruckner & Demharter, 1975) on the produced glass discs (1.5 mm in thickness and 5 mm in diameter).

Fig. 5 shows that an increase of Fe^{2+}/Fe_{tot} and [Na/(Na+K)] ratio reduces the viscosity. For instance, the difference in viscosity between the oxidized sample Ebu-B (Fe^{2+}/Fe_{tot} = 0.18) and the reduced sample Ebu- B-red (Fe^{2+}/Fe_{tot} = 0.84) was found to be 0.71 log units at 876 K. In the oxidized sample Ebu-N (Fe^{2+}/Fe_{tot} = 0.15) and the reduced Ebu-N-red (Fe^{2+}/Fe_{tot} = 0.76) the change in viscosity was 1.02 log units at 901 K. The oxidized sample Ebu-C (Fe^{2+}/Fe_{tot} = 0.19) and the reduced Ebu-C-red (Fe^{2+}/Fe_{tot} = 0.76) showed a difference in viscosity of 0.79 log units at 976 K.

The viscosity behaviour depending on the iron redox reflects the iron structural environment in these glasses. Trivalent Fe was here present mainly in 4-fold coordination, with <Fe^{3+}-O> = 1.86 Å, whereas divalent Fe was clearly present in a different coordination that was intermediate between 4- and 5-fold with <Fe-O>= 2.00 Å. This means that the oxidation of Fe produced an increase in the polymerization as well as shorter (and stronger) Fe-O bonds in these pantelleritic glasses.

Following the finding that the Fe redox state plays an important role on melt viscosity in different silicate melts (Toplis *et al.*, 1994; Liebske *et al.*, 2003; Vetere *et al.*, 2008; Giordano *et al.*, 2008; Giuli *et al.*, 2011; Duan, 2014), this study aims to account the effect of iron oxidation
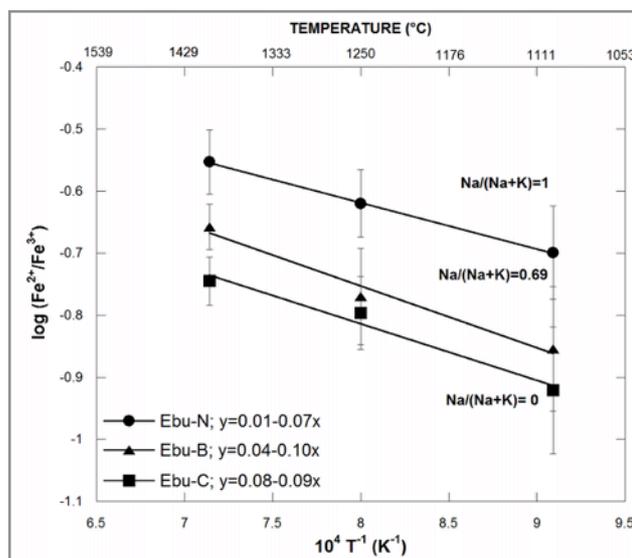

Fig. 4 - Effect of alkali type on T driven change in Fe redox state. Temperature dependence of the iron redox state for samples Ebu-B, Ebu-C and Ebu-N synthesized at three different temperatures (1100 °C-LT, 1250 °C-MT and 1400 °C-HT). *Notes*: Reported iron redox ratios are the ones obtained by wet chemical analysis.
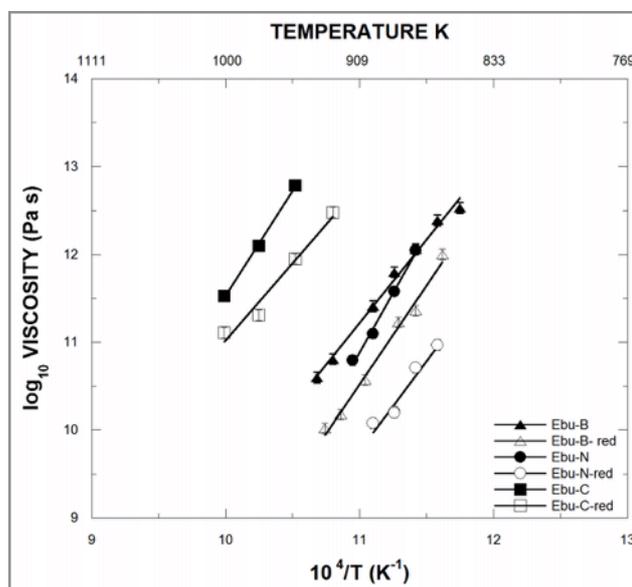

Fig. 5 - Log viscosity *vs.* reciprocal temperature for Ebu pantelleritic glasses. The error in viscosity, based upon the precision and accuracy of previous calibrations (Webb *et al.*, 2004), is ± 0.06 log units. Filled and empty symbols represent samples synthesized at oxidizing and reducing conditions, respectively, which present different [Na/(Na+K)] ratios (1 for Ebu-N and EBu-N-red, 0.74 for Ebu-B and Ebu-B-red and 0 for Ebu-C and Ebu-C-red).

state on viscosity of pantellerites, which is not so far investigated. It is worth to remark that this study is of particular interest since scarce literature data on the influence of all these different parameters (redox conditions, alkalis, temperature) on iron redox are available for the investigated compositions, yet. Moreover, these data are important to implement actual viscosity predicting models that still do not take in consideration the influence of iron redox state on viscosity.

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