



Effect of oxygen fugacity on the coordination and oxidation state of iron in alkali bearing silicate melts



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ARTICLE INFO

Article history:

Received 16 March 2015

Received in revised form 22 June 2015

Accepted 3 July 2015

Available online 6 July 2015

Keywords:

Fe-oxidation state

Optical spectroscopy

XANES

Alkali silicate glasses

Fe-coordination

Oxygen fugacity

ABSTRACT

In this study the effect of oxygen fugacity (fO_2) on the oxidation state and coordination of Fe was investigated in different alkali trisilicate glasses ($Rb_2Si_3O_7 = RFS$, $K_2Si_3O_7 = KFS$; $Na_2Si_3O_7 = NFS$; $Li_2Si_3O_7 = LFS$) doped with ~5 wt.% of Fe_2O_3 with main focus on K- and Na-bearing compositions. Most of the experiments were conducted at ambient pressure in a gas mixing furnace at 1250 °C with controlled redox conditions ($\log fO_2/\text{bar}$: -0.68 to -16.18). The quenched glasses were analyzed using several methods. Analyses by a colorimetric wet chemistry method revealed a continuous increase in $Fe^{2+}/Fe_{\text{total}}$ towards more reducing conditions without reaching 100% Fe^{2+} even at extremely reducing conditions (range of $Fe^{2+}/Fe_{\text{total}}$: from 0.08 in air to 0.93 in H_2 atmosphere). X-ray absorption near edge structure (XANES) spectroscopy shows an increase of Fe coordination with decreasing ionic radius of the coexisting alkali, while the average coordination number seems to be independent on the oxidation state of iron aside from the largest studied alkali Rb, which seems to support lower coordinated Fe (tetrahedral) at more oxidizing conditions. The $Fe^{2+}/Fe_{\text{total}}$ ratios inferred by XANES, using an intensity ratio based calibration of Wilke et al. (2004), are systematically higher by 10% compared to the wet chemistry results of this study, which may be due to the different external $Fe^{2+}/Fe_{\text{total}}$ determination method (Mössbauer spectroscopy) used in their calibration. A new calibration curve based on wet chemistry and centroid positions is proposed for alkali silicate glasses. In optical spectroscopy, the position of the main Fe^{2+} -related peak shifts to lower wavenumbers with increasing ionic radius of the incorporated alkali and with increasing abundance of ferrous iron. Absorption coefficients $\epsilon_{Fe(II)}$ and $\epsilon_{Fe(III)}$ were calculated for the absorbance band at ~9000 and ~26,000 cm^{-1} , respectively. A decrease in $\epsilon_{Fe(II)}$ was detected with decreasing ionic radius of the incorporated alkalis ($\epsilon_{Fe(II)KFS} = 31.8 \pm 2.6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, $\epsilon_{Fe(II)NFS} = 30.7 \pm 2.3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and $\epsilon_{Fe(II)LFS} = 23.6 \pm 1.7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). Finally, the results of this study are compared with recent models, which predict fO_2 based on the knowledge of the $Fe^{2+}/Fe_{\text{total}}$ ratio. All models overestimate $Fe^{2+}/Fe_{\text{total}}$ in alkali silicate melts at very reducing conditions probably due to an unanticipated stabilization of Fe^{3+} by adjacent Fe^{2+} .

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1. Introduction

Iron is the most abundant transition metal in magmatic systems and the fourth most common element in the Earth's crust. For the comprehension of magmatic processes as well as for the understanding of the formation of iron-bearing technical glasses, the knowledge about the behavior of iron in the structure of glasses and melts is very important. Depending on the redox conditions during formation of either natural silicate melts or synthetic industrial glass melts, iron can appear in

different oxidation states (Fe^{3+} , Fe^{2+} and Fe^0). The Fe^{2+}/Fe^{3+} ratio is among others a function of oxygen fugacity, temperature and melt composition (e.g., Fudali, 1965; Sack et al., 1980; Kilinc et al., 1983; Mysen et al., 1985; Mysen, 1990; Borisov and Shapkin, 1990; Kress and Carmichael, 1991; Moore et al., 1995; Baker and Rutherford, 1996). Fe^{2+}/Fe^{3+} can significantly influence physical and chemical properties of silicate melts/glasses, e.g., viscosity, density, color, heat capacity and crystallization trends (e.g., Cuckierman and Uhlmann, 1974; Dingwell and Virgo, 1987; Lange and Carmichael, 1987; Toplis and Carroll, 1995; Liebske et al., 2002), due to the influence of ferrous and ferric iron on the local structure.

The oxidation state of iron in natural glasses can be used as sensitive probe for the redox conditions during rock formation (Kress and Carmichael, 1988; Moretti, 2005; Métrich et al., 2006). In technical

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applications the redox state of iron in glasses is important for e.g. colorization of container glass, protection from UV rays in glass windows and reduction of heat-load by absorption of IR-rays in cars and buildings (Uchino et al., 2000; Lefrere, 2002; Falcone et al., 2011).

In general, ferric iron is assumed to act in silicate structures similar to Al^{3+} , i.e. as network former with tetrahedral site geometry. However, Lange and Navrotsky (1993), Tangeman and Lange (1998) and Tangeman et al. (2001) have inferred also contributions by higher coordinated ferric iron based on heat capacity measurements. This interpretation is supported by X-ray absorption near edge structure (XANES) spectroscopy (Farges et al., 2004). In contrast, ferrous iron acts in most cases as network modifier with variable site symmetry. Cuckierman and Uhlmann (1974) proposed a mix of octahedral and tetrahedral sites, while more recent studies found evidence of fivefold coordinated Fe^{2+} being the dominating geometrical site along with fourfold coordinated iron (Rossano et al., 2000; Farges et al., 2004; Wilke et al., 2004; Jackson et al., 2005).

To provide a more definite description of the speciation of iron in silicate melts depending on the redox conditions and composition, this study investigated the effect of oxygen fugacity (fO_2) on the oxidation state and coordination of iron in alkali trisilicate glasses, which were synthesized at well-defined conditions. A colorimetric wet chemistry method after Wilson (1960) modified by Schuessler et al. (2008) was used to determine the Fe^{2+}/Fe_{total} ratios. These data were used to calibrate the absorption coefficients ϵ of Fe^{2+} and Fe^{3+} related bands in optical spectra. This method allows getting quantitative information about the concentration of common metal ions through the entire volume of a sample in contrast to near-surface analyses such as XPS (X-ray photoelectron spectroscopy) (Rossman, 2014). Additionally, XANES spectroscopy provides ferrous to ferric iron ratio as well as the average coordination numbers of Fe-species in the glasses (Galoisy et al., 2001; Berry et al., 2003; Wilke et al., 2004, 2005; Cottrell et al., 2009; Henderson et al., 2014). Implications for the thermodynamics of iron-bearing silicate melts are discussed.

2. Experiments

2.1. Starting materials

To understand the effect of the different alkalis (Rb, K, Na, Li) on the incorporation of iron in silicate melts, four different trisilicate glasses ($Rb_2Si_3O_7 = RFS$, $K_2Si_3O_7 = KFS$; $Na_2Si_3O_7 = NFS$; $Li_2Si_3O_7 = LFS$) were synthesized as starting material, containing ca. 5 mol% FeO (2.25 mol% Fe_2O_3). Alkali carbonates, quartz powder and hematite powder were mixed by hand before melting in a Pt-crucible for 2 h at 1500 °C in a chamber furnace (Nabertherm P310). Afterwards the melt was quenched to glass on a brass plate. For better homogenization the glass was crushed by a steel mortar, melted for a second time for 2 h at 1500 °C and quenched on a brass plate. The Rb-trisilicate glass was synthesized in air at 1400 °C as described in Wilke et al. (2007a).

To reduce internal stress, the quenched glasses were relaxed by annealing for 15 min near the glass transition (NFS at 430 °C and KFS at 440 °C, LFS at 420 °C) and subsequently cooled at a rate of 2 K/min to room temperature.

2.2. Reduction experiments

The experiments with KFS, NFS and LFS were carried out in a horizontal gas mixing furnace at 1250 °C and ambient pressure. The tube furnace (Nabertherm P330) has a large region with roughly constant temperature (variation by less than 2 °C at 1250 °C over 10 cm). A wide range of oxygen fugacities was adjusted using gases (air, Ar, H_2) or gas mixtures (93% Ar/7% H_2 , Ar/ H_2/H_2O). Different H_2/H_2O ratios were established by bubbling 93% Ar/7% H_2 gas through a water reservoir in a thermostat bath before streaming the gas into the furnace. An oxygen sensor (Econox, Type: ZRO2 C700 OXYGEN SENSOR) is placed in

the furnace to control EMF (electromotive force) about 2 cm in front of the ceramic boat in which open noble metal container with the melt were loaded. Oxygen partial pressure was calculated by the following equation (Eq. (1)).

$$pO_2 = pO_{2(ref)} \cdot \exp \frac{EMF \cdot n \cdot F}{R \cdot T} \quad (1)$$

Here, $pO_{2(ref)}$ is the reference partial pressure of oxygen, which is in our case dry air at ambient pressure (0.20950 atm), EMF is the electromotive force, n is the number of exchanging electrons ($n = 4$ in the case of O_2 exchange), F is the Faraday constant (96,500 C/mol), R is the gas constant (8.314 J/mol K) and T is the experimental temperature (K). As all experiments were carried out at ambient pressure, pO_2 can be equalized to fO_2 . The measured fO_2 of each experiment is listed in Table 1.

Glass plates with a height of 2 mm (200–300 mg) were loaded into noble metal container (base area $10 \times 10 \text{ mm}^2$, side walls 5 mm high) prepared by folding foil with ca. 0.2 mm thickness. Rhenium foil was used under very reducing conditions owing to its low iron solubility compared to noble metals like e.g. Pt (Borisov and Jones, 1999). However, at more oxidizing conditions ($> QFM-1$, means one log unit above fO_2 controlled by the quartz–fayalite–magnetite buffer) rhenium tends to form volatile Re-oxides at high temperatures. Therefore, to minimize

Table 1

Experimental conditions and results of density determination and wet chemical analysis.

Sample	Gas	$T_{furnace}$ (°C)	T_{bath} (°C)	Time (h)	$\log fO_2 / \text{bar}^a$	Density [g/L]	Fe^{2+} / Fe_{total}
LFS-14 ^b	Ar/ H_2	1250	–	20	–9.43	–	0.91
LFS-7	Ar/ H_2/H_2O	1250	92.43	20.00	–7.59	–	0.76
LFS-3	Ar	1250	–	20	–3.07	–	0.28
LFS-1	Air	1250	–	20	–0.89 ^c	–	0.10
LFS-St	Air	1500	–	2 + 2	–	2409 (2)	0.21
NFS-15	H_2	1250	–	5	–14.84	–	0.93
NFS-14	Ar/ H_2	1250	–	20	–13.80	2453 (5)	0.91
NFS-14a	Ar/ H_2	1250	–	0.167	–13.24	–	0.30
NFS-14b	Ar/ H_2	1250	–	1	–14.18	–	0.62
NFS-14c	Ar/ H_2	1250	–	6	–15.58	–	0.93
NFS-11	Ar/ H_2/H_2O	1250	31.00	20	–11.24	2478 (7)	0.83
NFS-10	Ar/ H_2/H_2O	1250	51.55	20	–10.30	2483 (11)	0.84
NFS-9	Ar/ H_2/H_2O	1250	76.20	20	–9.08	2480 (7)	0.79
NFS-8.4	Ar/ H_2/H_2O	1250	85.70	20	–8.40	2503 (3)	0.81
NFS-7.7	Ar/ H_2/H_2O	1250	92.43	20	–7.69	2502 (2)	0.76
NFS-3	Ar	1250	–	20	–2.97	2501 (3)	0.20
NFS-1	Air	1250	–	20	–0.72 ^c	2507 (2)	0.09
NFS-St	Air	1500	–	2 + 2	–	2502 (25)	0.17
KFS-15	H_2	1250	–	5	–16.18	–	0.92
KFS-14	Ar/ H_2	1250	–	20	–13.80	2425 (5)	0.90
KFS-14a	Ar/ H_2	1250	–	0.167	^d	–	0.31
KFS-14b	Ar/ H_2	1250	–	1	^d	–	0.78
KFS-14c	Ar/ H_2	1250	–	6	^d	–	0.92
KFS-11	Ar/ H_2/H_2O	1250	31.00	20	–11.24	2458 (20)	0.86
KFS-10	Ar/ H_2/H_2O	1250	51.55	20	–10.30	2448 (4)	0.84
KFS-9	Ar/ H_2/H_2O	1250	76.20	20	–9.08	2457 (14)	0.80
KFS-8.4	Ar/ H_2/H_2O	1250	85.70	20	–8.40	2458 (2)	0.80
KFS-7.7	Ar/ H_2/H_2O	1250	92.43	20	–7.69	2449 (2)	0.77
KFS-3	Ar	1250	–	20	–2.97	2460 (2)	0.17
KFS-1	Air	1250	–	20	–0.72 ^c	2461 (2)	0.08
KFS-St	Air	1500	–	2 + 2	–	2460 (25)	0.15

Notes. a, b, and c in sample names refer to kinetic experiments, i.e. runs with short duration. Error of wet chemical Fe^{2+}/Fe_{total} analysis is ± 0.02 . Other errors are given in parentheses.

Ar/ H_2 is composed of 93.5% Ar and 6.5% H_2 . T_{bath} refers to the temperature adjusted in the thermostat to fix the water vapor pressure.

No analyses are available for RFS.

^a Calculated from measured EMF.

^b fO_2 probably incorrect, colorimetry indicates more reduced conditions, consistent with other experiments in Ar/ H_2 .

^c Measured EMF differs slightly from theoretical fO_2 value in air ($\log fO_2 = -0.68/\text{bar}$), which was used for calculations.

^d Measured EMF was not stable (ranged between 0.89 and 1.08 V).

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