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Exploring the structure of high temperature, iron-bearing liquids

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Abstract

This paper describes the direct measurements of the structure of iron-bearing liquids using a combination of containerless techniques and *in-situ* high energy x-ray diffraction. These capabilities provide data that is important to help model and optimize processes such as smelting, steel making, and controlling slag chemistry. A successful programme of liquid studies has been undertaken and the Advanced Photon Source using these combined techniques which include the provision of gas mixing and the control of pO_2 and the changing influence of mixed valance elements. It is possible to combine rapid image acquisition with quenching of liquids to obtain the full diffraction patterns of deeply supercooled liquids and the metastable supercooled liquid regime, where the liquid structures and viscosity change most dramatically, can also be explored.

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1. Introduction

For any liquid based process, the structure of the liquid will control the physical and chemical properties. These liquid structures reflect many different contributing phenomena including the temperature-dependent equilibria of liquid species, preferred bonding and density fluctuations, all of which will control the structure and structure-dependent processes such as crystallization and viscosity. Although glasses have often been used as a proxy for liquid, the vitrification process itself reflects a complicated, cooling rate-dependent process involving partial structural relaxation, emphasizing the need to determine the structures of liquids *in situ* and the requirement for careful structural modelling.

Containerless techniques such as aerodynamic levitation mean however that the contribution to the total scattered signal can be reduced and, when used in combination with X-rays or neutrons [1-3], diffraction data for a variety of metallic and oxide liquids

can be obtained. In liquids that contain redox variable elements the structure of the liquids is strongly influenced by the oxidation state of that element. Containerless methods can be adapted to control the partial pressure of oxygen and the structural changes that result from changing valance state determined. These capabilities provide the structural data that has potential to optimize processes such as smelting, steel making and the control of slag chemistry.

Combined high energy X-ray diffraction (HEXRD) and containerless measurements have been performed on a variety of refractory oxide liquids, including Y_2O_3-Al_2O_3[4], Al_2O_3-SiO_2 [5], CaO-Al_2O_3[6], MgO-SiO_2 [7] and CaO-SiO_2[8]. These data show changes in structure of the liquid both as a function of composition and on cooling, suggesting changes in the structure of the supercooled liquid than can be correlated with transport properties (viscosity)[8].

In this contribution we demonstrate the direct measurements of the structure of iron-bearing liquids by using these combined techniques. We will outline high energy X-ray diffraction studies for a range of iron bearing silicate liquids and show the changes in structure of these liquids as fO_2 is changed in both stable and supercooled liquids.

1.1 Aerodynamic levitation

Aerodynamic levitation is a containerless technique that has proved to be an extremely successful technique for *in situ* liquid study. A bead of ceramic precursor is levitated by a gas jet and laser heated to form a spherical liquid drop 2-3mm in diameter. The liquid drop is suspended in the purpose-designed and water-cooled nozzle and heated by a 240W continuous wave CO_2 laser to temperatures of up to 3000 K [2, 3, 9]. The absence of heterogeneous nucleation sites means that the liquids can be supercooled by several hundred degrees before crystallisation occurs and the metastable regime explored. Aerodynamic levitation furnaces can be incorporated into X-ray beamline infrastructure; the entire levitator is enclosed in a stainless steel chamber to allow operation under Class 1 conditions and Kapton® windows allow the sample environment to be operated in transmission mode. A video camera is used to monitor levitation and a pyrometer used to determine temperature (Figure 1). The laser path length is minimised to allow for more stable levitation and access to the supercooled regime.

1.2 High energy X-ray diffraction

High energy X-rays, with incident energies of 115keV have the advantage of acting as a bulk probe and scattering data for the liquid sample can be collected to high values of scattering vector with minimal correction for absorption and energy [10]. The entire liquid diffraction pattern can be collected using a 2D detector with a maximums value of scattering vector (Q) in excess of 20Å^{-1} ensuring good real space resolution. This diffraction technique has proved very useful in identifying the characteristics of medium range order (usually masked in neutron diffraction data for oxides). An aerodynamic levitation furnace has been integrated into the infrastructure of the high energy beamline, 6-ID-D at the Advanced Photon Source, Argonne National Laboratory. A recent development at the APS has been to use a Perkin Elmer amorphous silicon detector with rapid acquisition such that the entire pattern can be collected in 200ms. This rapid data collection can be synchronised with the laser heating and frames collected as the laser is blocked, meaning that structural changes in the metastable supercooled regime can be discerned and the crystallisation and vitrification processes observed [11].

1.3 Controlled atmosphere

The aerodynamic levitator is totally and enclosed and different gas mixtures can be used as a levitation gas. Previous measurements have used argon or oxygen as a levitation gas, however we have now begun to explore a range of oxidation conditions by using mixtures of CO and CO_2 in the levitation gas. This added dimension allows a range of liquids to be explored as a function of composition, temperature and fO_2.

2 Experimental methodology

The liquids studied in the MgO-SiO_2 system ranging from orthosilicate and an inosilicate (pyroxene) compositions and are used as a basis for the set of experiments used to evaluate the structural role of iron. The study of three FeO-MgO-SiO_2 composition liquids is discussed here with the ratio of FeO/(FeO+MgO) is fixed to 0.50. The starting material was prepared by grinding the appropriate amounts of iron, magnesium and silicon oxides together and pressing to form a pellet that was then sintered at 1573K in air to form a hard ceramic. Three compositions were studied the orthosilicate ($(Fe,Mg)_2SiO_2$. 33 mole % SiO_2) and pyroxene ($(Fe,Mg)SiO_3$, 50 mole % SiO_2) compositions and one intermediate (42 mole % SiO_2). Beads of approximately 2-3mm (~40mg) were made by fusing this ceramic material on a copper hearth. The precursor bead of sintered ceramic material is levitated in the aerodynamic levitation furnace installed as part of the X-ray beam line infrastructure and heated until a drop is formed.

X-ray measurements were made at 6–ID-D using X-rays of incident energy 100.25 keV (wavelength, λ=0.1237 Å). 2D

diffraction patterns were obtained for stable liquids with 0.5 second exposure for each image; each measurement of the stable liquid is the sum of 100 frames. The supercooled liquids were studied by collecting 30 frames of 200ms as the liquid is quenched. The first five frames are held in the detector buffer and when quenched these five frames are averaged to represent the stable liquid diffraction pattern; the remaining 25 frames reflect the changing structure as the sample is cooled. The temperature of the cooling drop is measured by pyrometer.

Each diffraction pattern is a 2D image that is then processed using the FIT2D package and a one dimensional pattern obtained by integrating over all pixels in the two dimensional array [12]. CeO_2 is used to calibrate the detector for the detector to sample distance and other detector parameters. The total structure factor (S(Q)) (where $Q = \frac{4\pi}{\lambda}\sin\theta$)for each composition was obtained using PDFgetX2 [13]. As reported by other authors, the advantage of using HEXRD is that corrections for absorption and attenuation are minimised since the X-rays act as a bulk probe. The total structure factor can be obtained straightforwardly by subtracting background (empty instrument) contributions and by correcting for the Q-dependence of the X-ray form factors and Compton scattering, normalising to self-scattering at high Q.

Four different levitation mixtures were used, with the gas mixtures are controlled by mass flow controller. The levitation gas is formed by mixing 5% CO-Ar and 5% CO_2-Ar gases in the ratios 4:1, 3:2, 2:3 and 3:2. The samples were recovered following each experiment to determine weight loss and for chemical analysis. The range of temperature and fO_2 explored as part of this study is shown in figure 2 the fraction of is shown, based on thermodynamic calculations and Mössbauer studies of iron in silicate liquids.

Figure 1: The aerodynamic levitation furnace installed at beamline 6 ID D (advanced photon source). Incident X-rays are correlated and emerge from the brass tube the amorphous silicon detector is behind the furnace. Temperature is monitored by a pyrometer and the video camera is used to monitor sample positon.
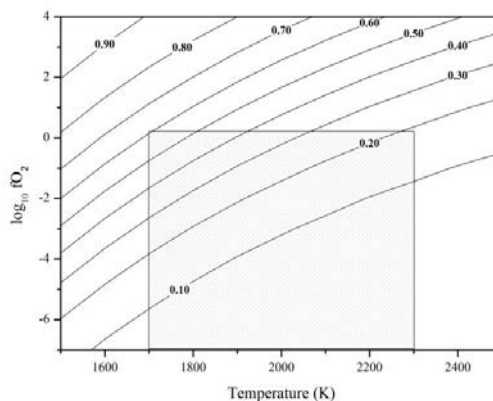

Figure 2 The range of fO_2 sampled (pattern) in the experiments discussed below, the contours are the fraction of $Fe^{3+}/\Sigma Fe$

The total structure factor ($S(Q)$) for the $(Fe,Mg)SiO_3$ composition is shown in figure 3 for the four gas mixtures. As with most liquid diffraction data the $S(Q)$ comprises a series of broad peaks that represent the partial contributions of atom pairs which are damped to high Q. There are two prominent peaks at low Q at 2.1 and 4.7 Å^{-1}. These two features are the sum of each partial contribution and do not correspond to specific features in real space. Nevertheless the changes with position and intensity with changing CO/CO_2 indicate changes in the liquid structure. In figure 4 the pair distribution function for the $(Fe,Mg)SiO_3$ liquid is shown, obtained by Fourier transform of the $S(Q)$. This also comprises a series of overlapping partial contributions, the main structural unit in silicates is the SiO4 tetrahedron and this is reflected in an approximately Gaussian feature centered on the Si-O distance of 1.65Å, this peak apparently changes in intensity as a function of $CO:CO_2$ although is due to the overlap between Mg-O and Fe-contributions. Since magnesium scatters X-rays weakly the differences in intensity and position indicate the changing local environment surrounding iron, this does not however vary systematically with changing fO_2. Iron can adopt two configurations in the liquid, octahedral (FeO_6) and tetrahedral (FeO_4) units [14], these have Fe-O distances that depend on the valance state of iron. The amount of ferric iron is expected to change as a function of $CO:CO_2$, the range of fO_2. sampled (Figure 2) would indicate that in the most oxidizing compositions the fraction of will be 0.2 however the changes in structure do not show a simple equilibrium between FeO_4 and FeO_6 units and the changes in intensity and position of the Fe-O peaks do not very systematically with Fe^{3+} /ΣFe, the peaks are broader for the 2:3 and 3:2 mixtures for example and would suggest the structures are complicated by interactions between Fe^{2+} and Fe^{3+} even at low Fe^{3+} concentrations.
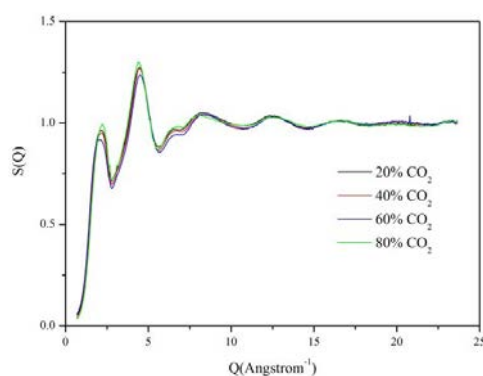

Figure 3. The total structure factor for an $(Fe,Mg)SiO_3$ composition liquid as a function of gas mixture. There are clear changes in the structure of this liquid, evidenced by the changes in the first and second dominant peaks.
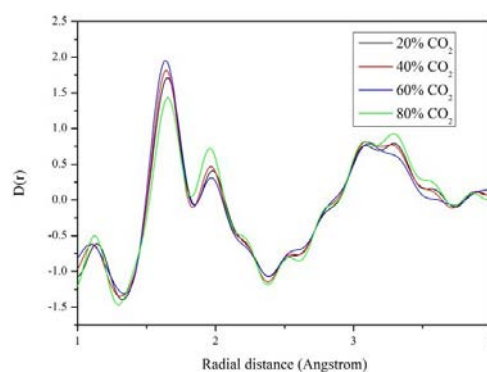
Figure 4. The real space transform of the $S(Q)$ data shown in figure 3. The first peak in this pair correlation function is the Si-O correlation, centred at 1.6 Å. This overlaps with Fe-O and mg-O correlations and these change with fO_2. Although the most oxidised composition has a stronger correlation the other gas mixtures show a range of Fe-O local environments.

The viscosity of silicate (and other liquids) depends on temperate and more subtly on the temperature-dependence of the melt structure, formalised for example in the Adam-Gibbs model of structural relaxation [15]. These changes occur in the metastable supercooled regime which can be accessed by rapid data acquisition, as demonstrated for $CaSiO_3$ liquids [8]. Interpretation of the structural changes that occur is difficult but an indication of the structural change can be made by evaluating the changes in peak-height or integration between common (isosbestic) points in the diffraction pattern. The quenched liquid data for these iron-bearing silicates varies as a function of both silica content and as the ratio of $CO:CO_2$ is changed. In figures 5 and 6 the temperature dependence of the $(Fe,Mg)SiO_3$ liquid is shown for two gas mixtures together with the patterns for the glasses produced as these liquids are quenched. As well as an expected sharpening of the main correlations on quenching there are changes in position and intensity that suggest structural changes on cooling and this differ depending on the fO_2 and according the Fe^{3+}/ΣFe.

4   Future work

The examples presented here are restricted to a series of iron-bearing magnesium silicates, however there is potential to explore a variety of liquid compositions of relevance to the steel industry. These include oxide systems such as CaO-MgO-Al_2O_3-SiO_2 with iron or other transition metals added [16, 17]. The role of individual oxide components can be explored by traverses across phase diagrams and complements other studies on the same systems such as viscosity and thermodynamic measurements and

measurements of the activity on iron. From the limited data presented above the liquid structures and by extension the physical and chemical properties of these liquids do not vary linearly with either temperature or fO_2 and accordingly provides a fertile area for future study. We have presented data on iron bearing liquids but liquids with other transition metals or combinations of transition metals can also be explored, for example data have been recently collected on cobalt-bearing silicates and studies of nickel and titanium-bearing systems can be easily undertaken. Combinations of components such as iron and titanium and their response to fO_2 can be studied. The role of oxides (e.g. P_2O_5 [18]) which are known to have a dramatic effect on the $Fe^{3+}/\Sigma Fe$ can be explored over a range of compositions and their partial structural role and specific role in slag compositions explored. Although refractory oxide liquids have only been discussed here, the combined HEXRD and levitation studies can be extended to of metallic systems and studies of metallic liquids as they are progressively oxidized are possible. Similarly there are no restrictions on the composition of the levitating gas, we report the CO/CO_2 mixtures but more reducing conditions can be provided (H_2/CO_2) and the role of sulphur, for example, explored.
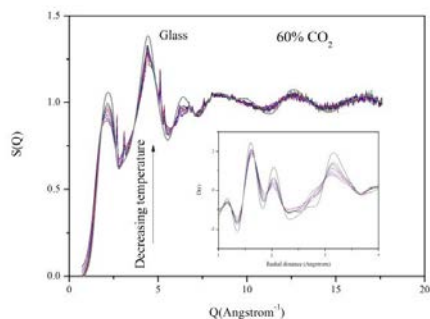

Figure 5 The temperature-dependent total structure factor for (FeMg)SiO$_3$ composition liquids quenched to form a glass, the inset is changes in the pair correlation function (D(r)), the levitation gas was CO:CO$_2$ mixture of 2:3, glasses could not be produced in more oxidising conditions. Note the small crystal peaks at high temperature; these are not present in the glass.
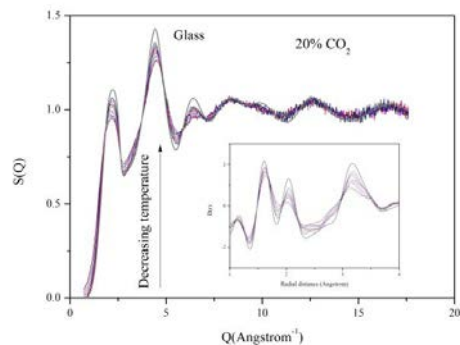
Figure 6 The temperature-dependent total structure factor for the (FeMg)SiO$_3$ composition under more reducing conditions (was CO:CO$_2$ mixture of 4:1), again the inset is the D(r).

5 Summary

We have shown that levitation experiments can be combined with high energy X-ray diffraction to determine the liquid structure for refractory systems including iron-bearing silicates. Containerless techniques further provide the opportunity to control the redox state of iron and other transition metals by gas mixing and by using a mixture of CO and CO_2 in the levitation gas a range of fO_2 conditions can be explored. The results for a series of iron-bearing silicate liquids show that by controlling the fO_2 of the levitation gas different Fe^{2+}/Fe^{3+} mixtures can be achieved which strongly influence the liquid structure. When rapid quenching is combined with fast data acquisition the structural changes during the vitrification process can also be studies and these also show significant variation with the partial pressure of oxygen. These capabilities can be used to provide data that is important to help model and optimize processes such as smelting, steel making, and the control of slag chemistry.

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