

Kinetics of iron oxidation in silicate melts

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Abstract – High-temperature XANES experiments at the Fe K-edge have been used to study the kinetics of iron oxidation in a supercooled melt of Fe-bearing pyroxene composition. These experiments, made just above the glass transition between 600 and 700°C, show that variations in relative abundances of ferric and ferrous iron can be determined *in situ* at such temperatures. The kinetics of iron oxidation do not vary much with temperature down to the glass transition. This suggests that rate-limiting factor in this process is not oxygen diffusion, which is coupled to relaxation of the silicate network, but diffusion of network modifying cations along with a counter flux of electrons. To give a firmer basis to redox determinations made from XANES spectroscopy, the redox state of a series of samples was first determined from wet chemical, Mössbauer spectroscopy and electron microprobe analyses.

INTRODUCTION

Amorphous silicates being stripped of long distance order have an interesting capacity to incorporate many elements. So glasses especially borosilicate glasses seem to be the most adapted material for nuclear waste storage. Especially they allow to improve containment, reduce the volume of waste or to incorporate a larger range of elements. Glass matrix includes various multivalent elements as iron, whose redox states assign properties of glass during elaboration and that of final glass (rate of incorporation, chemical durability...).

Many studies carried out especially at CEA made it possible to better understand these reactions of oxydoreduction in glass melts and consequently to improve vitrification process. They related more particularly to the influence of oxydoreduction on glass properties, parameters influencing redox state, the establishment of a classification of redox couples, methods to regulate the redox state, the reduction of glass with addition of carbon [1],[2]. However kinetics of redox reactions remains still badly known. All authors describe the redox mechanisms as being limited by diffusion. Two theories are in opposition, oxygen diffusion [3], [4] or diffusion of cations being limiting [5], [6]. So our goal is to obtain kinetic information on iron redox reaction in silicate glasses in order to identify implied mechanisms. A better knowledge of

these mechanisms must allow to determine the methodology to control the redox of complex glass and thus to improve vitrification processes.

The major problem encountered in previous study was that the redox state of samples could not be investigated *in situ* during high-temperature experiments. In this preliminary study, our goal has been to determine whether this could be done through XRay Absorption Near Edge Structure (XANES) experiments. This technique has a two-fold potential advantage in that it allows not only to determine the redox state of iron but also to derive specific structural information on local environment around iron ions [7], [8].

In our study samples related to iron-bearing pyroxene melts have been investigated. They were examined as a function of both time and temperature just above the glass transition in temperature intervals where redox reactions are usually extremely sluggish.

EXPERIMENTAL PROCEDURE

Samples

The glass compositions investigated are listed in Table 1. A starting glass dubbed Pyrox was first prepared from a classis methodology, melted at 1600°C in air in a platinum crucible, and finally quenched in air. To get samples with different

redox state, part of the Pyrox material was annealed in the form of mm-size chunks under different conditions :

- Heating at 750 and 1200°C for 3 weeks in air in platinum crucible yielded the oxidized samples (Pyrox750, Pyrox1200).
- Melting in a graphite crucible during several times (5 or 17 min) in order to obtain strongly reduced samples (Pyrox5R, Pyrox17R).

TABLE I. Chemical composition, density, redox ratio

	Pyrox	Pyrox 17R	Pyrox 5R	Pyrox750	Pyrox1200
Mol%					
SiO ₂	50.21	50.34	50.25	50.32	50.22
MgO	17.05	17.05	16.96	17.07	16.55
CaO	17.43	17.37	17.34	17.47	16.90
Na ₂ O	5.05	5.07	5.12	5.02	5.50
FeO	10.26	10.17	10.32	10.12	10.82
Density	2.912	2.828	2.907	2.914	2.915
Redox ratio					
Wet chem.	0.752	0.094	0.624	0.985	0.903
Mossbauer	0.755	0.092	0.599	0.931	0.947
Microprobe	0.627	0.071	0.602	0.710	0.650
XANES		0		1	0.91

To determine the temperature range of the XANES measurements, the glass transition temperature of Pyrox glass was first determined from viscometry experiments, which yielded $T_g = 616^\circ\text{C}$ as defined by the temperature at which the melt viscosity is 10^{12} Pa.s. To give a firmer basis to redox determinations made from XANES spectroscopy, the redox state of a series of samples was first determined from wet chemical, Mössbauer spectroscopy and electron microprobe analyses.

Xanes experiments

High temperature XANES spectra at the Fe K-edge were recorded in transmission mode on the D44 beam line of the LURE-DCI synchrotron radiation facility (Orsay, France). For measurements made on glasses, the samples were introduced as 20mg pellets in a cylindrical platinum tube and heated up in a horizontal tubular furnace. Spectra were successively recorded from 600°C , i.e., just below the estimated glass transition temperature of 616°C , up to 700°C .

Previous work has shown that $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios and oxygen coordination around iron ions in silicate minerals and glasses can be determined quantitatively from XANES spectroscopy [9],

[10], [11]. Specifically, there is a relationship between the redox and coordination states and the position and intensity of the pre-edge. After normalization and fitting of spectra, pre-edge features are extracted.

The pre-edges features of Fe^{2+} and Fe^{3+} appear at constant peak energies of 7111.5 and 7113.2 eV, respectively, but they overlap in a such a way that a mixture of both valences gives rise to two peaks whose intensities vary as a function of their relative proportion [10]. Several procedures are possible to determine quantitatively redox state from XANES pre-edges. In this work we used a linear combination of two pre-edge spectra corresponding to the most reduced (Pyrox17R) and most oxidized (Pyrox750) samples whose redox states were known from wet chemical, electron microprobe, and Mössbauer spectroscopy analyses.

RESULTS AND DISCUSSION

Redox analyses

The redox ratios determined from wet chemical, Mössbauer spectroscopy and electron microprobe analyses are listed in Table 1. A good agreement is observed between different techniques, especially Mössbauer spectroscopy and wet chemical data, as previously found [12]. The agreement with electron microprobe observations is less good, because significant iron reduction took place under electron beam. Overall, these methods nevertheless provide a good characterization of the redox state in our glasses, which can be compared with XANES results.

In Fig.1 are plotted the XANES spectra of Pyrox glasses obtained in air under ambient conditions. The pre-edge of Pyrox17R exhibits a strong contribution at low energy with a weak shoulder at higher energy, which indicates that this sample is mostly reduced. On the other hand, the pre-edge of Pyrox750 presents an intense contribution at high energy, which implies that iron in this sample is almost totally oxidized. These results agree with redox ratios obtained by wet chemical analyses (see Table1), where the value of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ is close to 0.09 and 0.99 for the most reduced glass (Pyrox17R) and the most oxidized sample (Pyrox750), respectively. The assumption that Pyrox17R and Pyrox750 can be used as characteristic pre-edges for Fe^{2+} and Fe^{3+} , respectively, thus is justified. An estimation of the redox ratio for the other glass compositions can be derived from the linear

relationship defined by these two XANES pre-edges. The redox ratio of an intermediate glass (Pyrox1200) was estimated in this way and compared to the results obtained with the other methods. The result is 0.910 ± 0.025 , whereas that determined by wet chemical analysis is 0.900 ± 0.005 . The good agreement found between these numbers supports the validity of the procedure.

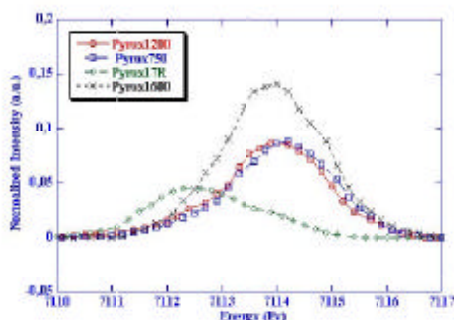


Fig 1. Fe K-edges XANES spectra for the four studied glasses

Temperature dependence of XANES spectra

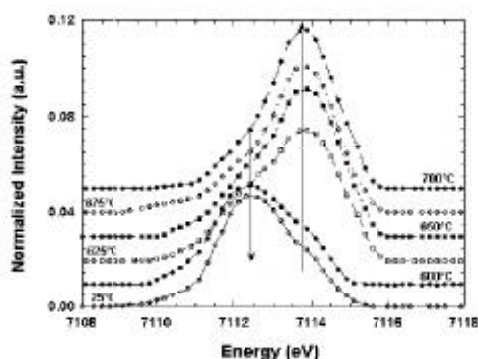


Fig 2. Pre-edges of Pyrox17R extracted from XANES spectra recorded at the indicated

The evolution of the pre-edge peak with temperature for Pyrox17R heated in air is shown in Fig. 2 from 25 to 700°C where are plotted the first isothermal spectra recorded at each temperature. There is little difference between the spectra recorded at room temperature and at 600°C. The pre-edge is made up of a strong band near 7112 eV along with a weaker shoulder near 7114 eV. Important changes then take place at temperatures higher than T_g whereby the initial high-energy shoulder overwhelms the band at lower energy. The evolution is almost complete

in the 700°C spectrum where the low-energy shoulder has nearly disappeared.

As expected, the two variable components of the spectra are found at the same energies as the single peaks observed for essentially pure Fe^{2+} and Fe^{3+} . These changes indicate that iron oxidation took place in response to the high oxygen fugacity of air. From a linear combination, we observed that starting with a sample with a $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of 0.1, we end up in this way with a value of 0.85, i.e., with predominantly ferric iron.

Time dependence of XANES spectra and kinetics of the redox reaction

In Fig. 3, we have selected a temperature of 600°C to show how the kinetics of the oxidation reaction close to T_g affect XANES spectra. As already shown in Fig. 2, the first spectrum at 600°C ($t = 0$) is similar to that recorded at 25°C but differs from that obtained at 625°C. With time, oxidation of iron is again signaled by spectral changes similar to those described in previous section. Although the kinetics of the redox reaction is significant at such low temperature, equilibrium could not be achieved in such short experiments. After a total of 90 min at 600°C, the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio had reached a value of only 0.2.

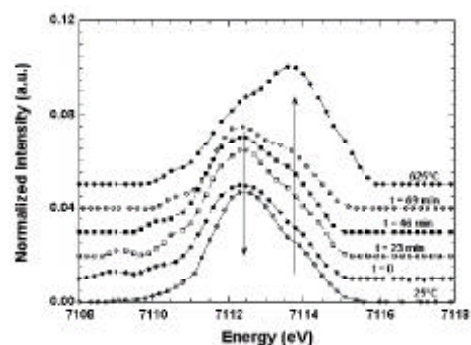


Fig 3. Pre-edges of Pyrox17R extracted from XANES spectra recorded at 600°C after various lengths of time.

The results of analogous series of experiments made at higher temperatures are summarized in Fig. 4 where the observations made during the heating periods are distinguished from those made isothermally. Thanks to higher temperatures, the kinetics appear to speed up a little bit. Interestingly, however, within

experimental errors the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio follows a single curve that levels off at a constant value of about 0.85.

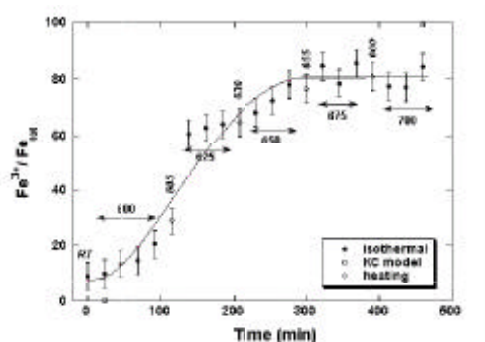


Fig 4. Time evolution of the redox ratio obtained from XANES spectra

In our case, thin pellets through which air could circulate have been investigated. If diffusion were rate limiting in these experiments, it was only at the scale of single grains whose size was typically a few tens of μm . As embodied by Eyring's relationship, oxygen diffusion and relaxation of the silicate network are closely related [13]. Hence, the kinetics would be vanishing near the glass transition range if they were controlled by oxygen diffusion. This is inconsistent with our observations. We thus conclude that another mechanism was operating under our experimental conditions. In view of the decoupling between relaxation times for rearrangement of the silicate network (and oxygen diffusion) and for hopping of network-modifying cations [14], our observations are instead consistent with diffusion of network-modifying cations, along with a counter flux of electrons, as previously proposed [5]. Especially relevant is the fact that calcium diffusivity decreases much less than viscosity and oxygen diffusivity and, in addition, is not strongly affected by the glass transition [14].

CONCLUSIONS

Our results thus show that XANES experiments make it possible to measure variations of redox state at temperatures much lower than previously made. For instance, this is only a preliminary study where a simple composition was studied. Composition could have an important role on these kinetics and dominating mechanism. So it seems to be interesting to observe the influence of alcalin element (network modifier), the effect

of the coupling Fe/Al and to investigate the influence of Boron (network former) in more complex composition. The aim is to determine dominating mechanism and redox kinetic in a borosilicate glass using for nuclear waste storage.

REFERENCES

1. C. DI NARDO, *Etude et contrôle des réactions d'oxydoréduction au cours de l'élaboration des matrices vitreuses de confinements des déchets nucléaires*, thèse de l'université de Montpellier, (2002).
2. O. PINET, C. DI NARDO, Proc. 101th Meet. Am. Ceram. Soc., *Electroch. Mater. and Devices, Ceramics Transactions*, **109**, 367 (1999).
3. H.D. SCHREIBER, S.J. KOZAK, A.L. FRITCHMAN, D.S. GOLDMAN, H.A. SCHAEFFER, *Phys. Chem Glasses*, **27**, 152 (1986).
4. R.F. WENDLANDT, *Contrib Mineral Petrology*, **108**, 463 (1991).
5. G.B. COOK, R.F. COOPER, *J. Non-Crystal Solids*, **120**, 207 (1990).
6. D.J.M. BURKHARD, *J. Petrology*, **42**, 507 (2001).
7. L. GALOISY, G. CALAS, ARRIO. M.A., *Chem Geol*, **174**, 307 (2001).
8. M. WILKE, F. FARGES, P.E. PETIT, G.E. BROWN Jr, F. MARTIN, *Americ Mineral*, **86**, 714 (2001).
9. S. BAJT, S.R. SUTTON, J.S. DELANEY, *Geochim Cosmo Acta*, **58**, 5209 (1994).
10. M. BONNIN-MOSBAH, A.S. SIMIONOVICI, N. METRICH, J.P. DURAUD, D. MASSARE, P. DILLMANN, *J. Non-Crystal Solids*, **288**, 103 (2001).
11. A.J. BERRY, H.St.C.O'NEILL, K.D. JAYASURIYA, S.J. CAMPBELL, G.J. FORAN, *Americ Mineral*, **88**, 967 (2003).
12. B.O. MYSEN, D. VIRGO, E-R. NEUMANN, F.A. SEIFERT, *Americ Mineral*, **70**, 317 (1985).
13. J.E. REID, B.T. POE, D.C. RUBIE, N. ZOTOV, M. WIEDENBECK, *Chem Geol*, **174**, 77 (2001).
14. G. GRUENER, P. ODIER, D. DE SOUSA MENESES, P. FLORIAN, P. RICHET, *Phys Rev*, **B64**, 024206,1 (2001).