



## **Kinetics of iron oxidation in silicate glasses : A XANES study**

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Silicate melts are generally complex materials with more than ten oxydes. The presence of multivalent elements, as iron, within the glass compositions can significantly affect physical properties of glasses. Understanding redox reactions is thus necessary to control vitrification processes for nuclear waste storage and the way in which the structure of melts could change with temperature during magmatic processes.

Many studies have been undertaken to characterize redox reactions in iron-rich silicates, especially for thermodynamic purposes (models to predict redox ratios according to composition, fugacity and temperature...). Nevertheless few studies on kinetics aspect. All authors describe redox mechanisms as being limited by diffusion : either by oxygen diffusion or by migration of divalent cations (Schreiber et al., 1986; Wendlandt, 1991; Cook and Cooper, 1990; Cooper et al., 1996).

However a kinetic study of redox equilibrium is required in order to identify limiting mechanisms and to improve vitrification processes.

Because XANES spectroscopy allows to determine redox state and to derive structural information about iron (Galoisy et al., 2001; Wilke et al., 2001), our goal was to follow the evolution of redox state with time and temperature through XANES experiments. Many compositions (various alumin rates) were studied at Fe-K edge on several temperature stages around T<sub>g</sub>. Furthermore, to assess the validity of the method, we have also determined Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios of a set of samples at room temperature through

other techniques, namely, wet chemical, Mossbauer spectroscopy and electron microprobe analyses. Our results are in good agreement with previous studies (Wilke et al, 2001) or results from other methods. A shift of the pre-edge position towards the contribution of  $\text{Fe}^{3+}$  was observed as a function of time and temperature, representing the oxidation of our samples. Significant redox changes around  $T_g$  suggest that rate-limiting factor is not oxygen diffusion (coupled to network relaxation) but diffusion of network modifying cations (Magnien et al, 2004). Besides alkalin elements make redox reactions faster, especially in the case of lithium. To complete those conclusions, new experiments should be performed to show the effect of the rates of alumina or iron on redox kinetics.

References :

1. H.D. SCHREIBER, S.J. KOZAK, A.L. FRITCHMAN, D.S. GOLDMAN, H.A. SCHAEFFER, *Phys. Chem Glasses*, **27**, 152-177 (1986).
2. R.F. WENDLANDT, *Contrib Mineral Petrology*, **108**, 463-471 (1991).
3. G.B. COOK, R.F. COOPER, *J. Non-Crystal Solids*, **120**, 207-222 (1990).
4. R.F. COOPER, J.B. FANSELOW and D.B. POKER, *Geochim. Cosmochim. Acta* **60**, 3253-3265 (1996).
5. L. GALOISY, G. CALAS, ARRIO. M.A., *Chem Geol*, **174**, 307-319 (2001).
6. M. WILKE, F. FARGES, P.E. PETIT, G.E. BROWN Jr, F. MARTIN, *Americ Mineral*, **86**, 714-730 (2001).
7. V. MAGNIEN, D.R. NEUVILLE, L.CORMIER, B.O. MYSEN, V. BRIOIS, S. BELIN, O. PINET and P. RICHET, *Chem. Geol*, **213**, issues 1-3, 253-263 (2004)