Earth alkaline elements a probe to understand redox and nucleation processes

DANIEL R. NEUVILLE[1] AND MARIA RITA CICCONI[2]

[1]IPGP CNRS-USPC, 1, rue Jussieu 75005 Paris, France.

[2] Department Werkstoffwissenschaften, Universität Erlangen-Nürnberg. Martensstrasse 5, D-91058 Erlangen

Calcium can be a network modifier or a charge compensator of $AlO4^-$ in aluminosilicate glasses and melts. As a function of its role, density, molar volume, viscosity, liquidus and glass transition temperature and more generally, macroscopic properties can change significantly. But how evaluate or prove this change of role? Recently, Helhen and Neuville (2014) have show by comparing Raman in VV and VH polarization, that a new band appears in the VH Raman spectra when the role of Ca changes from charge compensator to network modifier. Furthermore, we have shown in the XANES spectra at the Ca K-edge, an important change in the Ca pre-edge peaks as a function of this same change of role.

Application to redox processes: in the case of an Fe^{2+}/Fe^{3+} silicate, like window glass or natural lava, Fe^{3+} can be consider playing same role than Al^{3+} following result on viscosity (Dingwell, 1991). By looking Ca pre-edge peaks, in window glasses, is possible to follow a change in the role of Ca as a function of redox, similar at those observe with or without Al. This variation of the role of Ca is associated with the need of Fe^{3+} to be compensated, and it proved that Fe^{3+} acts in the network former as Al^{3+}. Furthermore, the large variations of the oxygen distribution around Ca could explain the large variations of the redox mechanisms in silicate melts.

Application to nucleation processes: Ca environment can be a key to understand nucleation process. Indeed the nucleation process is very difficult to follow and needs highly sensitive tools. In fact, Ca is expected to move at lower temperatures than atoms involved in the glass network, in agreement with observation on relaxation processes (Gruener et al. 2001). As a consequence, Ca environment should be quickly modified in case of nucleation. Neuville et al. (2008) observed that, in a diopside composition, Ca pre-edge peak was modified and associated it with a change of Ca site from an “amorphous” one, to a “pre-nucleus” one. The quantitative approach of the Ca pre-edge XANES spectra, presented here, has the sensitivity required to further study nucleation.

To conclude, by looking the role of alkaline earth element in glass and melts, it is possible have a better knowledge of the structure of glass and melts, but also to better understand redox and nucleation processes.