



In situ high temperature investigation of cation environments in melts: links with mobilities and viscosities



Daniel R. Neuville¹, Laurent Cormier², Dominique de Ligny³, Jacques Roux¹, Anne-Marie Flank³, Pierre Lagarde³

¹ Physique des Minéraux et des Magmas, IPGP-CNRS, 4 place Jussieu, 75005 Paris

² Institut de Minéralogie et de Physique des Milieux Condensés, Universités Paris 6 et 7, IPGP, CNRS UMR 7590, 140 rue de Lourmel, 75015 Paris

⁴ LPCML, Université Claude Bernard Lyon, 12 rue Ampère, 69622 Villeurbanne

³ Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 48, 91192 Gif-sur-Yvette

INTRODUCTION

The knowledge of structures at high temperature is of fundamental importance for earth and material sciences. Aluminosilicates are major constituents in glass and ceramic industries and significant components of geological melts. Important efforts have been made to determine the structure of aluminosilicate glasses and melts. In peralkaline earth glasses, we have shown that Al K-edge XANES spectra exhibit remarkable structural variations with chemical composition [1]. The spectra of the glasses are compared to those of calcium aluminate crystals. The analysis reveals a correlation between some peaks and the degree of polymerization (Q^n) of the (AlO_4) tetrahedra. Al is distributed in Q^2 , Q^3 , and Q^4 species at low silica content and progressively enters only Q^4 as SiO_2 or Al_2O_3 content increases. This change can be related to some thermodynamical variations [2-4].

Temperature-induced changes in Al environment can contribute to the total configurational entropy of the system which has been correlated with viscosity of silicate magmas through the Adam-Gibbs theory [5]. Structural information at high temperature are thus required to provide atomic-level constraints in models of the mantle melting, and to better understand the configurational, thermodynamic and crystallization/nucleation properties. However, determination of the liquid structures at high temperature is a challenging endeavour, especially for refractory materials. NMR *in situ* measurements are possible to determine the Al environment in melts but are limited due to the quadrupolar broadening. XAS will be able to give us complementary information, regarding both the local and medium range organization. Furthermore, information on non-network forming elements, such as Ca, can be obtained and are essential to understand the structural modifications taking place in the liquid state.

EXPERIMENTAL PART

Our heating device consists in a Pt-Ir10% wire that can be heated from ambient up to more than 2000 K. This cell was already used on microbeam lines at LURE and ESRF and it is relatively easy to handle. A small chunk of glass ($<1mm^2$) is placed in the 1-mm hole drilled in the heating wire. We have verified the calibration, intensity-temperature of the Pt-cell in the vacuum chamber used to perform low energy experiments. Changes were observed in the $I=f(T)$ curves compare to air conditions. Figure 1 presents the furnace into the vacuum chamber with a sample heated at 1973 K. XANES spectra were acquired at the Swiss Light Synchrotron (SLS) on the LUCIA beamline in the fluorescence mode at the Al and Ca K-edges on aluminosilicate glasses and crystals which were heated up to the liquid state.

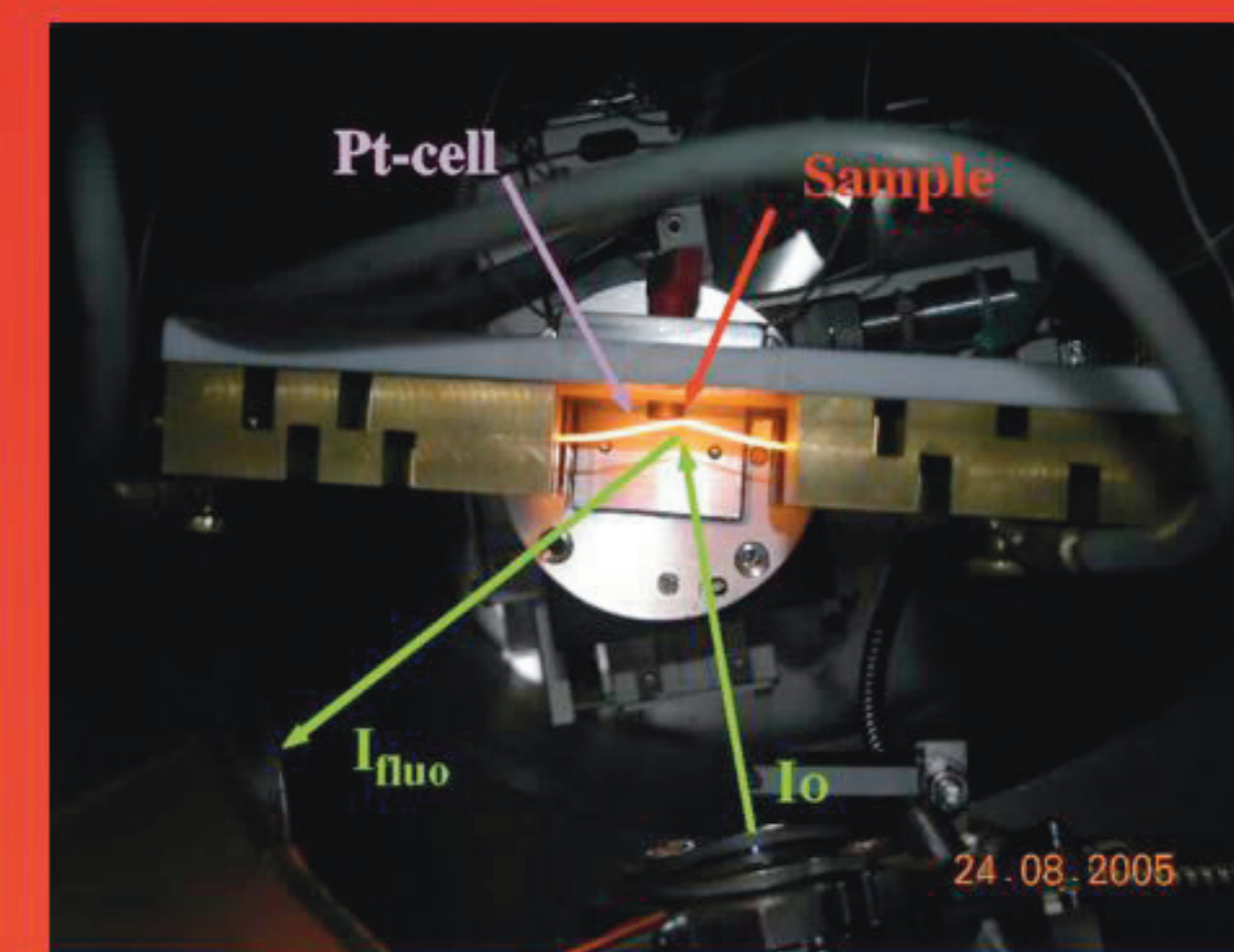


Figure 1: Furnace into the vacuum chamber with a sample heated at 1973 K.

Al K edge

XANES spectra of two crystal phases CA ($CaO-Al_2O_3$) and C3A ($3CaO-Al_2O_3$) were acquired using a KTP monochromator and are reported in figures 2 and 3 as a function of temperature, up to the liquid state.

The spectra at room temperature are similar with those obtained on the SA32 beamline (SUPER-ACO, LURE) [2,3] but the resolution has improved in the present experiment. In both crystals, Al is present in a tetrahedral site but in distinct polymerized species. Al is in Q^4 position for CA and in Q^2 position for C3A [2,3]. A first intense peak *a* is observed for the CA crystal that rapidly decreases in intensity as the temperature increases. This peak is smaller than peak *b* in the liquid state. The peak *c* almost vanishes in the liquid state. These changes can be attributed to an increase of the distortion of the Al site between crystal and liquid and/or modification at medium range order (opening of the ring structure).

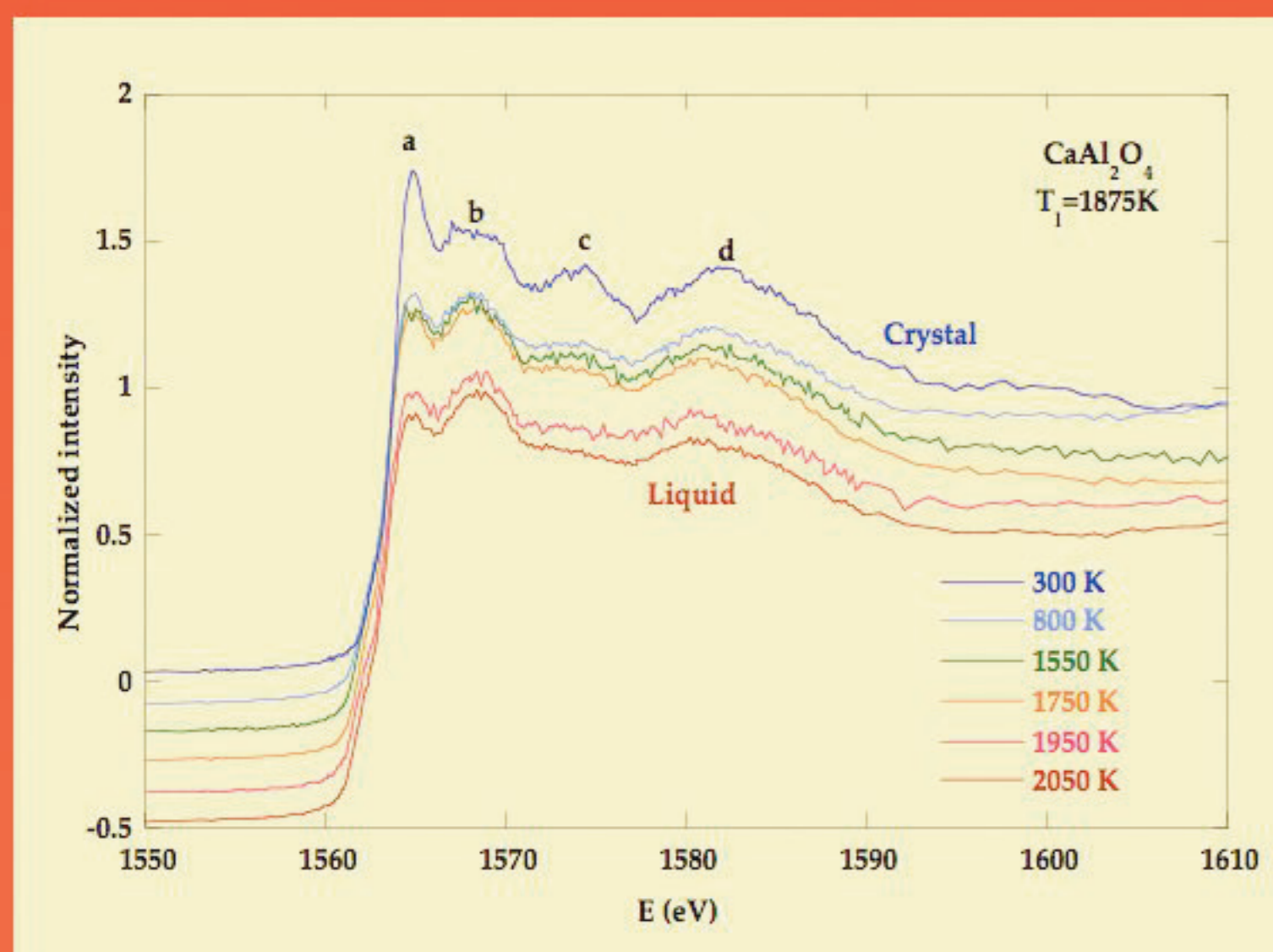


Figure 2: XANES spectra at the Al K-edge for Ca ($CaAl_2O_4$) crystal and liquid.

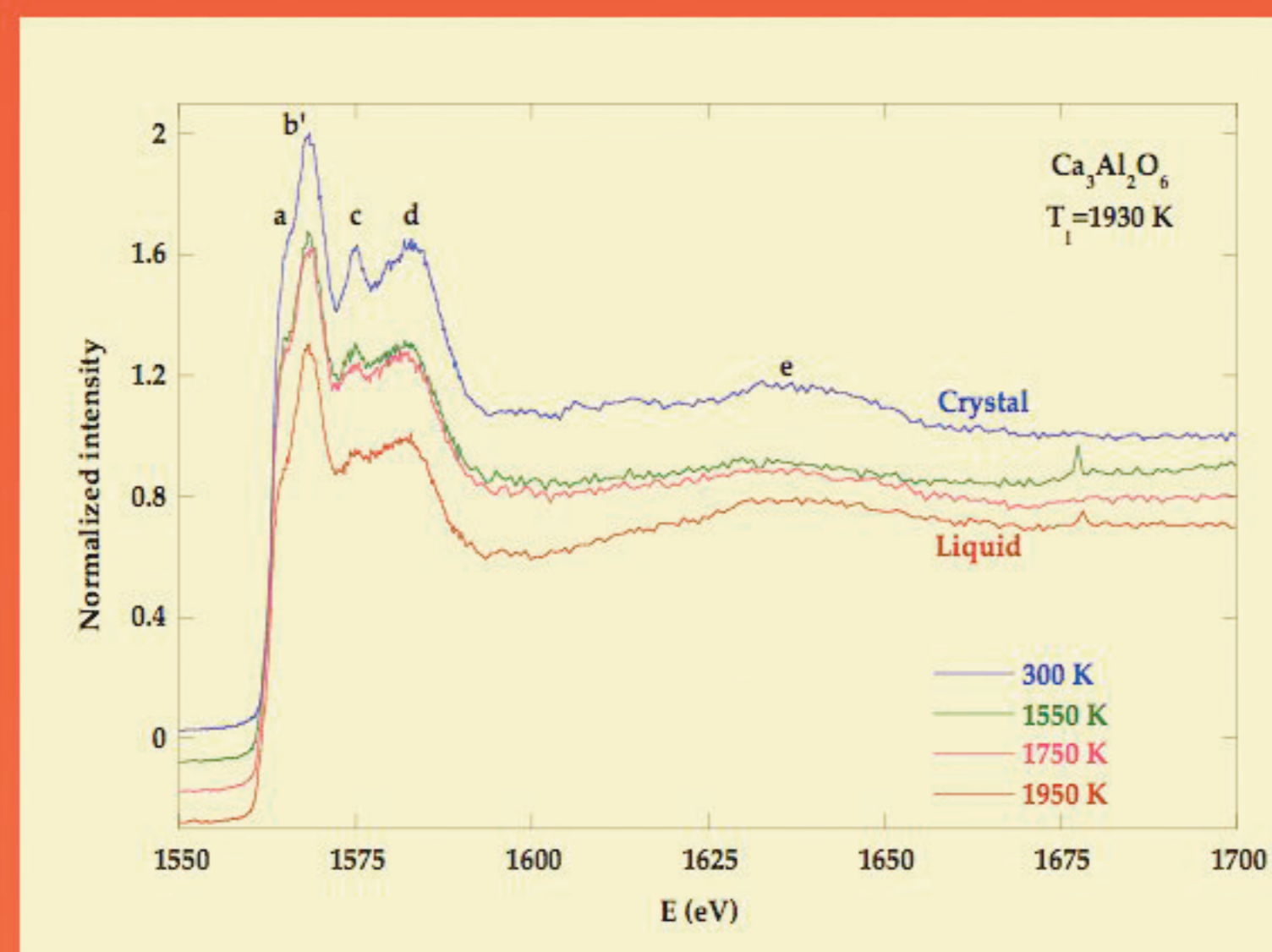


Figure 3: XANES spectra at the Al K-edge for C3A ($Ca_3Al_2O_4$) crystal and liquid.

There is, qualitatively, a striking resemblance in the evolution of XANES features of liquid and crystals with compositions. Therefore, we can consider that the Al environment in these two liquids is similar to the Al environment in the corresponding crystals. These results indicate that Al K-edge XANES spectra are sensitive to the local geometry and to its connection with other AlO_4 tetrahedra though other contributions such as mean Al-O bond length and intertetrahedral angle can also modify the XANES shape.

By investigating silicate minerals, glasses and liquids, systematic correlations have been noted between the Al K-edge XANES, the polymerization and the mobility of the aluminosilicate framework. The evolution of the XANES spectra of CA liquids are consistent with an increase of the AlO_5 content upon temperature. Stebbins and Farnan [7] have shown that, to ensure mobility of Si in a silicate melts at high temperature, a mechanism must involve rapid exchange of NBOs and the formation of a transient high coordinated silicon, $[^5Si]$. Similarly, it can be proposed that $[^5Al]$ species are required to induce the mobility of the fully-polymerized tetrahedral network on a within the aluminosilicate melts at high temperature. Stebbins and Farnan [7] show that that to ensure mobility at high temperature between Q^3 and Q^4 species, high coordinated silicon, $[^5Si]$, are needed to create this mobility. This observation of AlO_5 at high temperature agrees with previous studies on magnesium and calcium aluminate [8].

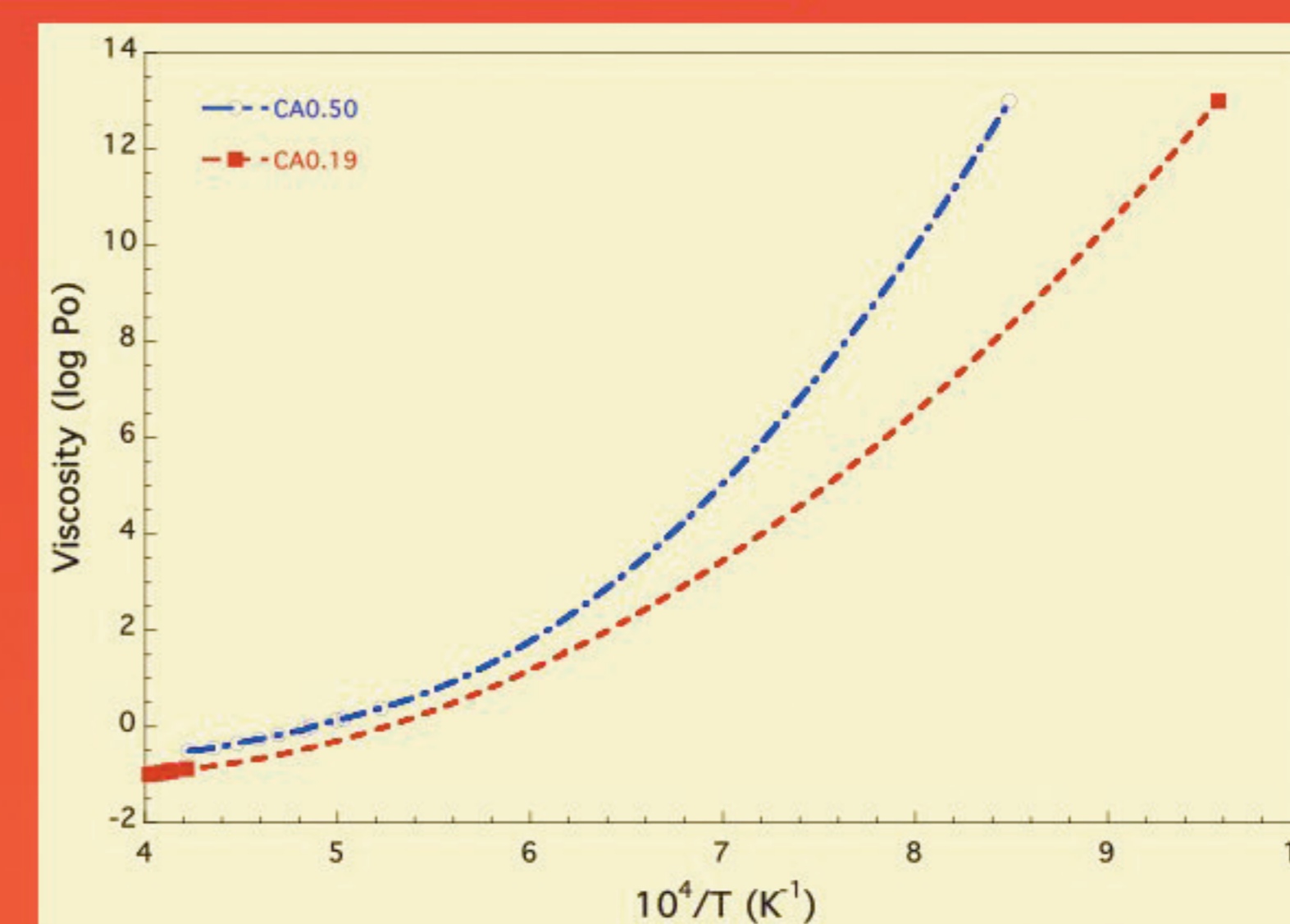


Figure 4: Viscosity versus $1/T$; high temperature measurements are from Urbain [9, 10] and T_g measurements are unpublished data determined by DSC experiments.

C3A melts correspond to a depolymerized aluminate network with a large fraction of NBOs. Therefore, mobility at high temperature can involve relative motion of large molecular units (e.g. rings, chains) without breaking Al-O bonds. Five-fold coordinated Al atoms are thus not required to allow structural rearrangement in the liquid state.

These differences of behavior between depolymerized aluminate, C3A, and fully polymerized compositions (CA and $CaAl_2Si_2O_8$), are also visible in term of viscosity and glass transition temperatures. In Fig. 4, we have summarized viscosity measurements at high temperature for calcium aluminate and alumina liquids, respectively [9, 10]. The CA0.19 glass sample close than to the C3A glass composition investigated in this study is always less viscous than the calcium aluminate (CA0.50) melt, even at high temperature. This is in relation with the more depolymerized aluminate network in C3A than in CA. In Fig. 4, we can also observe the strong non-arrhenian behavior between C3A and CA compositions. The important difference in viscosity at low temperature indicates that activation energies are higher for CA than for C3A because an important local reorganization is required around Al in CA in order to allow Q^3 - Q^4 exchange and the formation of AlO_5 species. Such a requirement for local rearrangements is not the strongest process of viscous flow in the C3A composition, and mobilities of atomic species are thus enhanced at low temperature compared to CA.

CONCLUSIONS

We have demonstrated the possibility to measure XANES spectra at Al and Ca K-edges up to temperatures as high as 2100 K, using a home-made Pt-furnace and the micro beam available at the LUCIA beamline. We have shown important modifications of the XANES spectra between crystals and glasses at room temperature and melts above the liquidus temperature. Such experiments will be used to characterize refractory materials and investigate the structural modifications between glasses, crystals and melts at high temperature.

Neuville D.R., Cormier L., de Ligny, D., Roux, J., Flank A.M., Lagarde P. (2008) American Mineralogist, 93 228.

References:

- [1] Neuville D.R., Cormier L., Flank A.M., Lagarde P., Massiot D., (2004) Chemical Geology, 213 153.
- [2] Neuville D.R., Cormier L., Massiot D., (2004) Geochim. Cosmochim. Acta, 68 5071.
- [3] Neuville D.R. (1992) Propriétés thermodynamiques et rhéologiques des silicates liquides. Thèse U. Paris 7.
- [4] Cormier L., Ghaleb D., Neuville D.R., Delage J.M., Calas G., (2003) J. Non-Crystal. Solids, 332 255.
- [5] Cormier L., Neuville D.R. Calas G., (2005) Journal of the American Ceramic Society., 88 2292.
- [6] Richet P., (1984) Geochim. Cosmochim. Acta, 48 471.
- [7] Cormier L., Neuville D.R., (2004) Chemical Geology, 213 103.
- [8] Stebbins J. and Farnan I (1992) Science 255, 586-589,
- [9] Poe, B.T., McMillan, P.F., Coté, B., Masiot, D., and Coutures, J.P. (1994) J. Amer. Ceram. Soc, 77, 1832.
- [10] Urbain, (1982) Rev. Int. Hautes Temp. Refrac., 19, 55.
- [11] Urbain (1983) Rev. Int. Hautes Temp. Refrac., 20, 135.