ESRF	**Experiment title:** **Structural origin of the stability of glasses and alteration gels: the role of zirconium in simplified waste glasses**	**Experiment number**: EC400
Beamline: BM 29	**Date of experiment**: from: 18/2/2009 to: 24/02/2009	**Date of report**: 21/04/2009
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Report:

During the geological repository of the High Level Nuclear Waste, the alteration of the vitreous matrix by the water will be one of the main mechanisms of the release of the radionucleides. During the leaching of the glass, an amorphous layer (the "gel") is formed and can play the role of a protective barrier toward further alteration of the pristine glass.

Leaching experiments showed the effect of zirconium on the glass ability to resist to alteration. The addition of zirconium in the glass composition lowers the intial alteration rate, slows down the kinetic drop due to the apparition of the gel and may influence the long term durability of the protective gel. Zirconium effect on the porosity of the gel has been investigated for many years but few studies observed the evolution of the environment of zirconium in the alteration gels as compare to glass.

Zirconium is 6-fold coordinated in the nuclear glass and behaves as a reticulating element in the glass structure. A direct chemical consequence of the presence of octahedral Zr, is the need of charge compensation by alkaline or alkaline-earth elements. During the alteration, zirconium is retained in the alteration gel whereas the alkaline and alkaline-earth elements are released in the solution.

During this experiment we investigated the zirconium environment in four simplified borosilicate glasses (5-oxides) with a simplified composition as compare to R7T7 glass and their respective alteration gels. The glass powders were totally leached in three different conditions (pH1, pH7, pH9). We determined the local environment around zirconium by acquiring XAS spectra at the zirconium K-edge using a cryostat at 30K in transmission mode. The ESRF ring operated at 6 GeV with typical currents of 170-200mA. The beam was monochromatized using Si (1 1 1) crystals and scans were set up to record the preedge with 5

eV step (1s per step), the edge region with a 0.5eV step and the post edge region with an energy mesh constant in the k-space. The EXAFS region was acquired up to 29 A^{-1} in aim to improve the extraction of the EXAFS signal, that gives a total acquisition time of around 25 minutes. We collected 3 spectra per sample except for the glass containing 1mol% of ZrO_2 that required 9 spectra.

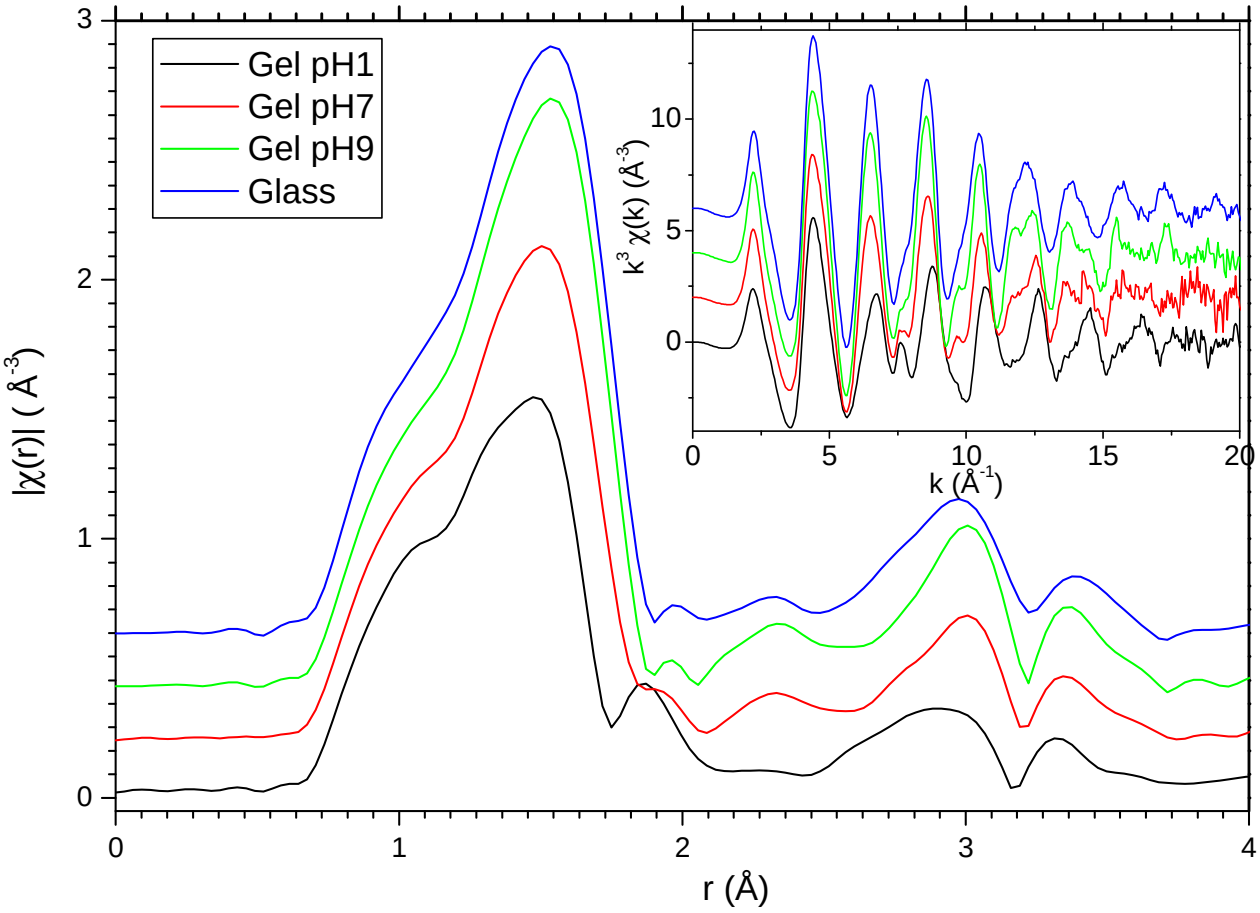

Figure 1: Zr K edge EXAFS spectra of a glass containing 8 mol% of ZrO_2 and its alteration gels obtained at pH 1, pH 7, and pH 9.

Figure 1 presents the Zr K edge spectra of the glass containing 8 mol% of Zr and Ca and its related alteration gels. In the glass, the first shell of coordination around Zr includes 6.4±0.3 atom of oxygen at an average distance of 2.08±0.01Å. These values are consistent with those observed for the R7T7 glass [*Galoisy L et al. (1999) J. Am. Ceram. Soc. (82)2219-2224*].
Our first data extraction does not reveal a significant evolution of the Zr environment with the increase of the Ca content in the various glasses.
In the alteration gels obtained at pH 9, the first shell around Zr is very similar to the first shell in the pristine glass (see fig. 1), but the second neigthbour shell seems more ordered in the gel than in the glass.
The first shell around Zr is modified for the two alteration gels obtained at pH 7 and in acidic conditions. More over one should note that the Zr environment in the alteration gel obtained at pH 7 seems to be sensitive to the composition of the initial glass.
While we are currently making progress in analysing the data, we can still remark the importance of the very good signal to noise ratio that characterizes BM 29 to observe the evolution of the second shell around Zr in those very disordered materials.