



	Experiment title: Evolution of lanthanum local environment upon glass alteration	Experiment number: ME-736
Beamline: BM29	Date of experiment: from: 1/10/03 to: 4/10/03	Date of report: february 6 th 2004
Shifts: 9	Local contact(s): Dr P.L. SOLARI	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): JOLLIVET Patrick , CEA Marcoule / LCLT DEN AUWER Christophe , CEA MARcoule / LCAM CACHIA Jean-Nicolas , CEA MARcoule / LMPA		

Report:

In the frame of the study of geological disposal of high-level waste containment glasses, it is necessary to know the mechanisms of radionuclides retention in the layer formed during glass aqueous alteration. During glass leaching, a surface layer called gel is formed, incorporating a large number of radionuclides—notably the transition metals, the rare earth elements and the actinides. The gels formed from glass leaching are amorphous.

We investigated the behavior of lanthanum during leaching of simplified SON68-type glasses with 9 constituent elements (instead of about 30). A glass sample was doped with 4 wt% La_2O_3 and another one with 4 wt% La_2O_3 and 1.8wt% P_2O_5 (2 P atoms for 1 La atom). The lanthanum retention factors in the gels depend on the glass alteration conditions and on the nature of the resulting gels. One of the most important parameters of glass alteration in a geological repository is the leaching solution renewal rate. Glass samples were altered with two leachate renewal rates to determine the influence of this parameter on the local environment of lanthanum.

The spectra were acquired at the lanthanum K-edge at 70 Kelvin in transmission mode. In a first approximation, Lanthanum is found in a silicate environment ($\text{La}_2\text{Si}_2\text{O}_7$ like structure) in glass G1 (without phosphorus). The first shell around lanthanum atoms includes 7.1 ± 2 oxygen atoms at an average distance of $2.62 \pm 0.02 \text{ \AA}$. The FT modulus of glass G1 shows (figure 2) a signal due to the second neighbours at about

2.9 Å (non phase shift corrected). After treatment, this signal can be attributed to a shell composed of 2.2 ± 1 silicon atoms at an average distance of 3.45 ± 0.02 Å.

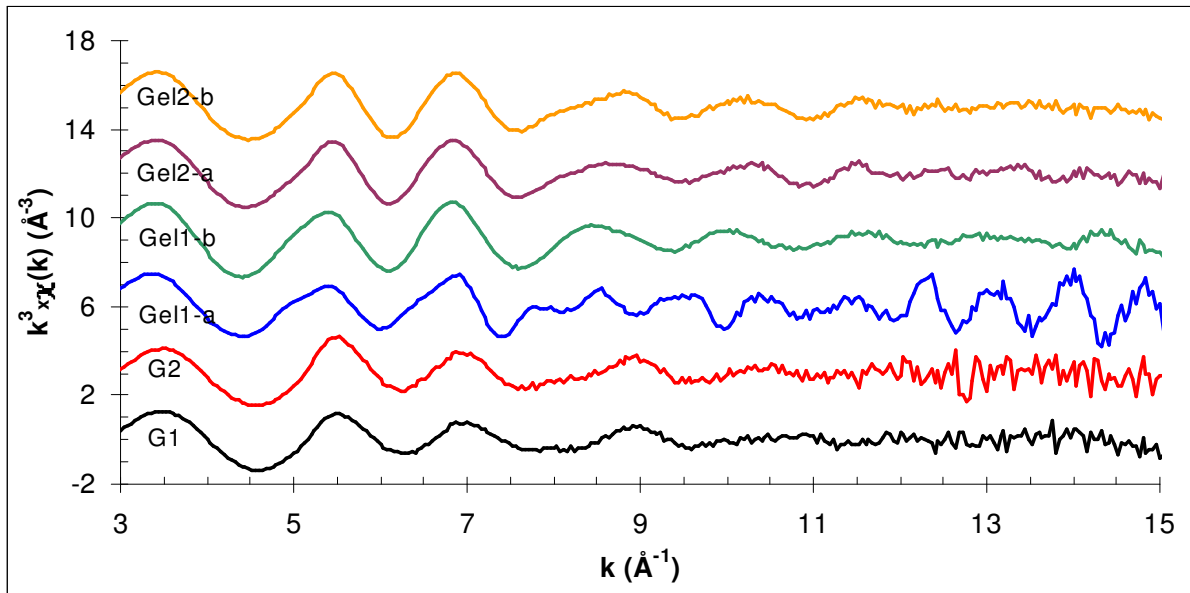


Fig. 1: EXAFS spectra of glasses and gels at lanthanum K-edge.

In glass G2, lanthanum is found in a phosphate environment (LaPO_4 like structure), although the Si/P ratio in this glass is 20. The first shell is composed of 6.1 ± 1.2 oxygen atoms at an average distance of 2.41 ± 0.02 Å. The difference of distance La-O for the first shell in the glasses G1 and G2 is 0.21 Å; this value is greater than the difference of bond lengths in SiO_2 and PO_4 tetraedra (~ 0.05 Å). The FT modulus of glass G2 (fig. 2) shows a contribution due to 2nd neighbours. After fitting, this second shell is composed of 1.0 ± 0.5 phosphorus atoms at an average distance of 3.23 ± 0.02 Å. In spite of the Si/P ratio of 20, lanthanum is surrounded by phosphate sites, and these results show the very high affinity of La atoms for phosphate environment instead of silicate when phosphorus is present in the glasses.

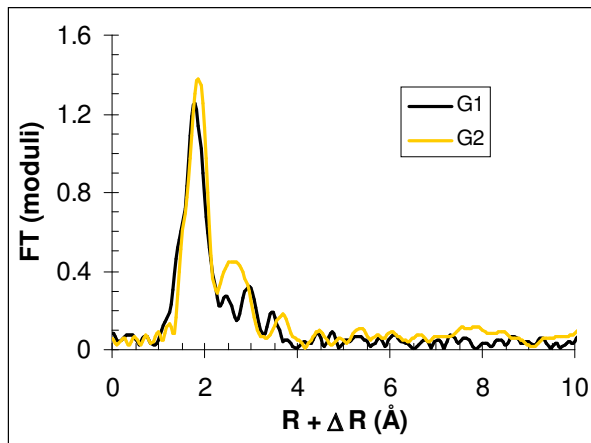


Fig. 2: FTs of glasses without P (G1) and with P (G2)

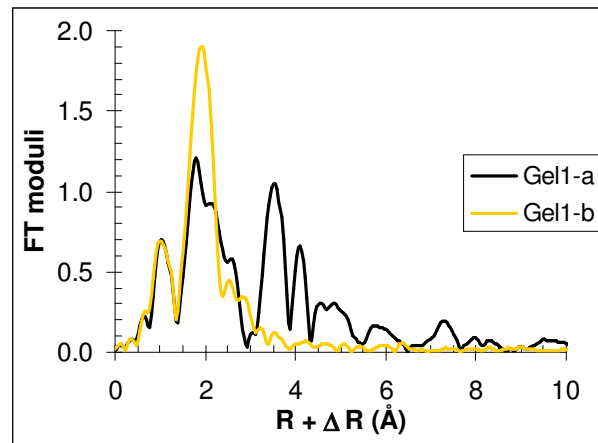


Fig. 3: FTs of gels without P for 2 flow rates.

The EXAFS spectra of gel1-a and gel1-b, obtained by full alteration of glass G1 at a renewal rate of 2/day and 2/week, are different beyond 7 Å^{-1} (fig. 1). On the contrary, the spectra of gel2-a and gel2-b, formed in the same conditions than gel1-a,b but by alteration of glass G2 (with phosphorus), are almost identical. This suggests that the gels that include phosphorus are much less sensitive towards the renewal rate of the leachate than the gels without phosphorus. That is confirmed by FT moduli of the gels, as indicated in figures 3 and 4; the FT moduli of gel2-a and gel2-b do not show any difference.

The FT of gel1-a, formed with a high renewal rate, indicates clearly that the first shell of oxygen atoms is composed of 3 distances (fig. 3). To fit this 1st shell, it is necessary to take into account 2 kinds of sites: a $\text{La}_2\text{Si}_2\text{O}_7$ like structure and a LaOHCO_3 like structure site. For the silicate site, we found 4.9 ± 1 atoms at 2.64 ± 0.02 Å and 4.3 ± 1 atoms at 2.77 ± 0.02 Å and for the hydroxycarbonate site, 2.1 ± 0.54 atoms at 3.12

± 0.02 Å. On the contrary, to fit the spectrum of gel1-b, formed with a low renewal rate, we used only a $\text{La}_2\text{Si}_2\text{O}_7$ site. The result of the fit leads to 10.0 ± 2.0 oxygen atoms at 2.70 ± 0.02 Å. The second shell is composed of 2.9 ± 1 silicon atoms at 3.37 ± 0.02 Å. These values in gel1-b are very close from those in glass G1. With a low renewal rate, the lanthanum local environment is weakly modified during glass alteration, except the coordination number that increases by 3 units with regard to the glass, but the La-O distances are almost the same. With a higher renewal rate, the lanthanum local environment is strongly modified (gel1-a) because the total coordination number of La increases. The La-O distances also increase and the second shell is composed of La atoms. These two gels show that the mechanisms of retention of lanthanum in the gels are different according to the renewal rate. With a high flow rate, the lanthanum is trapped in the gel by a dissolution and precipitation mechanism while with a low flow rate, the mechanism is an in situ reorganisation of glass with the hydration of the La atoms.

For the gels including phosphorus, we used only one site (LaPO_4 like structure) to fit the spectra. For gel2-a, we found 5.4 ± 1 oxygen atoms at 2.44 ± 0.02 Å for the 1st shell and 1.2 ± 0.2 phosphorus atom at 3.22 ± 0.02 Å for the 2nd shell. For the gel2-b, formed under a renewal rate of 2/week, the 1st shell is composed of 6.0 ± 1.2 oxygen atoms at 2.44 ± 0.02 Å and the 2nd of 1.6 ± 0.3 phosphorus atom at 3.24 ± 0.02 Å. These results show that the lanthanum local environment in the gels including phosphorus is independent of the renewal rate. More, the sites occupied by the lanthanum atoms in the gels are similar to that of the glass G2. It appears that lanthanum in a phosphate site is not modified by leaching.

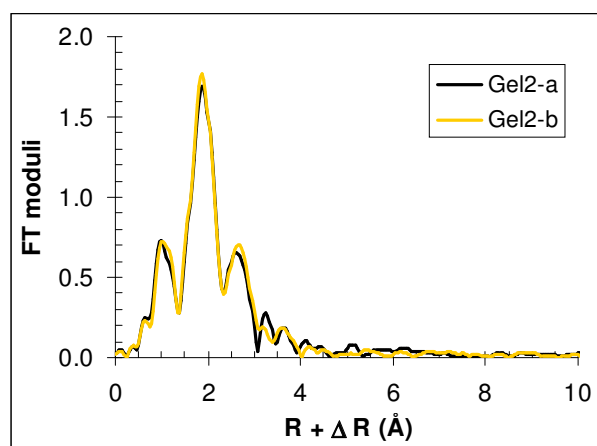


Fig. 4: FTs of gels with P for 2 flow rates.

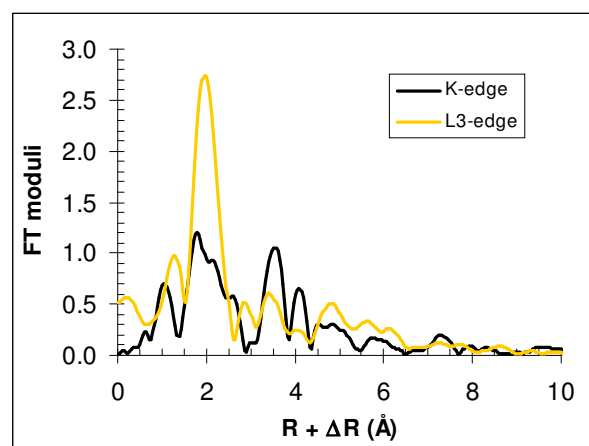


Fig. 5: FTs of gel1-a at K- and L_{III}-edge.

These first results show how the EXAFS spectra at the lanthanum K-edge provide many informations on the sites occupied by the rare earth element in glasses and how these sites are modified upon leaching. We can obtain also information on the mechanisms of retention of lanthanum in the gels. K-edge spectra give unique information compares to L₃-edge, as indicated by figure 5 (1st shell composed of three distances La-O at K-edge instead of one at L₃-edge). It would be very interesting to carry out similar measurements with cerium and neodymium because the L₃-edge study has shown a different behavior during leaching for these two rare earth elements.