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Names and affiliations of applicants (* indicates experimentalists):

*Pelegrin Emmanuele, CEA- Valrho /SCD, Marcoule

*Rossano Stephanie, University of Cambridge, Earth Sciences Department

*Ildefonse Philippe, Universite Paris 6, Laboratoire de Mineralogie Cristallographie Paris

*Allard Thierry, CNRS, , Laboratoire de Mineralogie Cristallographie Paris

Report:

XANES and EXAFS data at Zr- and Fe-K edges were recorded at room temperature in fluorescence mode using Si-photodiodes and quick-EXAFS software. The excellent quality of the data attests for the capabilities of ID26 for studying chemically complex materials with heavy matrix. Two kinds of samples were studied: 3 powders of fully altered glass (GV1, HP1 and HP5), and a R7T7 glass (29 oxides) monolith altered 1 day, in static mode, with deionized water. HP1 and HP5 were obtained by alteration of R7T7 powders after 9 months of lixiviation at 90°C, under dynamic flow, with an increasing silicon content of the leaching solution. GV1 is an alteration product of a simplified glass (8 oxides) at 90°C, under pseudo-dynamic flow (1 renewal/day), with deionized water. SEXAFS data at Fe- and Zr-K edges were recorded with grazing incidence on the glass monolith. Only SEXAFS measurements at Fe-K edge were successful. At Zr-K edge, the probed volume was too large to get valuable information on the surface transformation of the pristine glass.

Fe EXAFS data (Fig.1a,) indicate that, in all powder samples studied, Fe³⁺ octahedra (Fe-O=2,00Å) are mainly edge-connected (Fe-Fe= 3.10Å). A small contribution of corner sharing octahedra was also identified (Fe-Fe =3.50 Å). This local environment is close to that known in natural hydrated ferric oxides (Ildefonse and Calas, 1997). Measurements in grazing incidence

on glass monolith indicate that Fe is very reactive (Fig. 2) because in one day of alteration, this local environment was evidenced both by XANES and SEXAFS at the surface.

Zr EXAFS (Fig. 1b) data indicate that, in the three powder samples studied, Zr experiences significant changes in comparison to pristine glass where Zr is octahedrally coordinated to oxygens (Zr-O= 2.09 Å). Two Zr-O distances are observed. Second neighbor contributions increase in amplitude, and the kind of backscatterers change. Average Zr-2nd neighbor distance was calculated at 3.45 Å. This local environment of Zr is closed to that obtained for XRD amorphous Zr-oxides synthesized by sol-gel (Zeng et al., 1993).

3. Conclusion

These results complete Zr- and Fe-L_{2,3} XANES experiments obtained at LURE/SuperACO (Pelegrin et al., 1997) which showed that, whatever the alteration conditions were, Fe and Zr coordination number increase in the alteration products obtained with deionised water. On the contrary, the silicon content of the alteration solution controls the behavior of Zr because no structural modification of Zr was observed with Si-bearing solutions. In the same way, no change was observed for Zr when pristine glass is still present.

In conclusion, one can say that Zr and Fe seem to have different structural reactivity during alteration of nuclear glass. In all cases, for Fe, no connection to the silicon network has been evidenced at the all alteration products scale. The structural comportement of Zr is more complex. Our results let suppose a stabilizing effect of a sufficient silicon content diffusing through the altered layer (from the solution or from the glass). Do Fe and Zr present local environment heterogeneities not evidenced by this study? Does the presence of pristine glass really stabilize Zr in a glass-like structure? Some microXANES experiments at Zr- and Fe-K edges along a cross cutting of a glass altered sequence could answer to these questions.

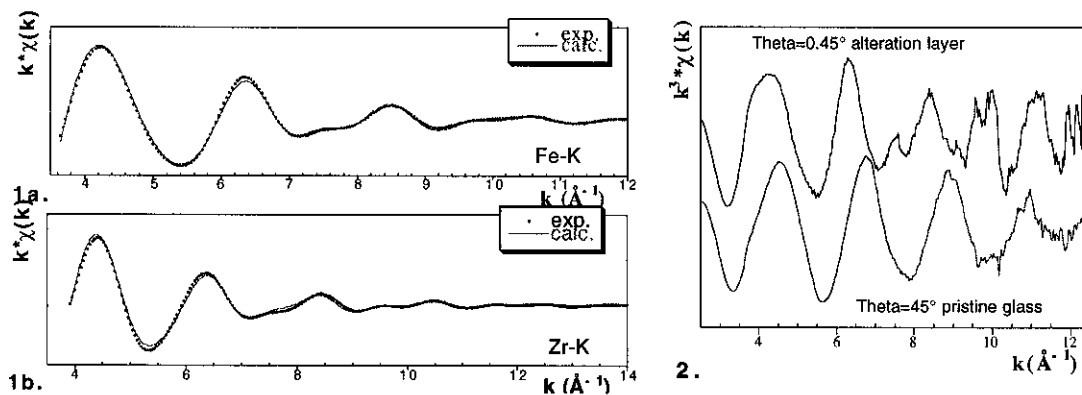


Fig.1a, b. Simulations of the inverse fourier transform of the 1st and 2nd neighbor at Fe and Zr-K edges respectively of GV1. Fig.2. EXAFS spectra at Fe-K edge of the altered monolith at theta=0,45° (grazing incidence) and theta=45°.

Reference:

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