

LOCAL ENVIRONMENT OF ZIRCONIUM IN NUCLEAR GELS STUDIED BY XAS

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FR0203220

7NIS - FR - 1509

ABSTRACT

During lixiviation experiments, nuclear gels are formed and heavy metals are retained. In order to understand this retardation mechanisms, we performed an analysis of the local environment of Zr in parent glasses and derived alteration gels both at the Zr-L_{II,III} and Zr-K edges. Calibration of the method was conducted through the analysis of model compounds with known coordination number (CN): catapleite Na₂ZrSi₃O₉·2H₂O (CN=6), baddeleyite ZrO₂ (CN=7) and zircon SiZrO₄ (CN=8). Nuclear glasses (R7T7, and a simplified nuclear glass V1) and gels obtained at 90°C, with leaching times from 7 to 12 months and with solution renewal were also investigated (GR7T7R and GV1). Zr-L_{II,III} XANES spectra evidenced that zirconium is 6-fold coordinated in R7T7 and V1 nuclear glasses. For GR7T7R and GV1 gels, Zr local environment is significantly changed, and a mixture of CN (6 and 7) has been evidenced. Quantitative structural results were derived from EXAFS analysis at Zr-K edge. In parent glasses, derived Zr-O distance is 2.10 ± 0.01 Å, and is in the range Zr-O distances for octahedral coordination in model compounds. In both gels studied, Zr-O distances increase significantly up to 2.15 ± 0.01 Å. This distance is close to that known in baddeleyite (2.158 Å). A better understanding of the Zr retention mechanism has to be made by studying the second neighbors contributions.

INTRODUCTION

In France, high level nuclear wastes are incorporated in boron silicate glass (R7T7). The long term stability of this glass in a deep geological site is crucial to avoid radionuclides spread in the geosphere. Many chemical studies have been performed on the behavior of elements during lixiviation experiments. Modeling of alteration kinetics are usually based on released elements in solution. During these lixiviation experiments, the glass surface is transformed and a "gel" like phase [1] has been described which incorporates cations such as zirconium [2], and may retain radionuclides [3]. To determine the influence of gel on glass alteration and radionuclides trapping, the mechanisms of the gel formation must be understood. Zr is a particularly fitting element to study glass alteration since it probes glass matrix [4], it is retained in the alteration gel [2], and it is a

radionuclide. With this end in view, the structural environment of zirconium in nuclear glasses and gels was studied by using Zr-L_{II,III} XANES and Zr-K EXAFS.

L-edge absorption is dominated by dipole-allowed transition from 2p core levels to empty 4d levels, while K-edge absorption is due to 1s → p empty states. L-edge XANES structures are better resolved than K-edge ones, because the core-hole lifetime broadening is 3-4 times smaller, 3p_{3/2} and 3p_{1/2} spectral parts are clearly separated by the core-hole spin-orbit interaction [5].

MATERIALS

Three kinds of samples were studied:

- three crystalline model compounds with known Zr coordination number (CN): catapleite Na₂ZrSi₃O₉·2H₂O (CN=6), baddeleyite ZrO₂ (CN=7), and zircon ZrSiO₄ (CN=8);
- two nuclear glasses: R7T7 and a simplified nuclear glass V1. Nuclear glasses R7T7 and V1 [6] were cast at 1150°C;
- two alteration products of parent-glasses: GR7T7R, GV1. Gel GR7T7R [6] was obtained after pseudo-dynamic alteration of a 400 kg-block of R7T7 glass, at 90°C for a period of 1 year. Gel GV1 [6] was obtained after pseudo-dynamic alteration of a powder of V1 glass (grain size 20 μm), at 90°C during 7 months.

Chemical compositions of samples studied are reported in Table 1.

Table 1: Chemical composition of R7T7, V1, GR7T7R and GV1 samples (moles % of element) (for R7T7, only elements > 1 mole% were considered) (data from [6])

Si	B	Na	Al	Ca	Li	Fe	Zn	Zr	Total	
R7T7	38.66	20.58	16.25	4.92	3.68	6.79	1.85	1.57	1.10	95.4
GR7T7R	33.80	0.00	0.00	16.40	2.10	0.00	13.90	15.80	8.40	99.8
V1	41.91	22.08	17.92	4.89	0.00	7.67	2.69	0.00	1.45	99.9
GV1	54.30	0.00	0.00	11.40	0.00	0.00	18.60	0.00	8.10	99.9

EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

Zr-L_{II,III} XANES, and Zr-K EXAFS spectra were collected on the SA32, and D44 lines at the LURE/SUPERACO LURE/DCI facilities (Orsay, France), using double-crystal Si(111) and Si(311) monochromator respectively. On SA32, the X-ray beam was focused on the sample thanks to a toroidal mirror, and the experimental energy resolution was approximately 0.2 eV at 2000 eV. On D44 beam line, energy resolution was 3.5 eV at 18000 eV. Samples were prepared as powders collected on Millipore filters, or powders sandwiched between two Kapton layers. Data were collected in transmission mode at Zr-

L and K edges. Energy calibration was performed with a Zr foil at the Zr-K edge (17998 eV), and with ZnS powder at the S edge (2473 eV) for the Zr-L_{II,III} edges. The Zr-L_{II,III} XANES were linearly background fitted so that the pre-edge regions are relatively flat. EXAFS analysis was conducted by using phase-shift and amplitude functions calculated, with Feff6 code [7], from catapleite structure [8].

RESULTS

Fig.1 displays Zr-L_{II,III} XANES spectra of model compounds with known Zr-CN, and Table 2 summarizes the energy positions of the resonances as well as the mean Zr-O distances derived from structure calculation. For catapleite, where CN=6, both L_{III} and L_{II} XANES spectra yield 2 well-resolved resonances (2eV wide): (A) and (B) at 2229.4 and 2226.4 eV respectively (Zr-L_{III}), and (C) and (D) at 2310.6 and 2313.8 eV respectively (Zr-L_{II}). For baddeleyite (CN=7), L_{III} and L_{II} XANES spectra are broader than those for catapleite, but two resonances are still observed both at L_{II} and L_{III} edges. (A) and (C) resonances are at the same energy positions as those found in catapleite, whereas both (B) and (D) resonances are shifted to 1.2 eV lower energy, at 2228.2 and 2311.6 eV respectively. In baddeleyite, the broadness of the spectra could be related to the large distribution of Zr-O distances (from 2.05 to 2.25 Å) [9] in comparison with the quite similar Zr-O distances of the two subshells found in catapleite (2.07 and 2.08Å). For zircon (CN=8), L_{III} and L_{II} XANES spectra yield only one broad resonance at 2228.0 and 2312.0 eV respectively, with ill-defined shoulders at lower energy for L_{III} edge and at higher energy for L_{II} edge. The energy shift between main resonances and their change in apparent width, related to 6, 7 and 8-fold Zr, makes Zr-L_{II,III} XANES a fingerprint method for the determination of Zr-CN.

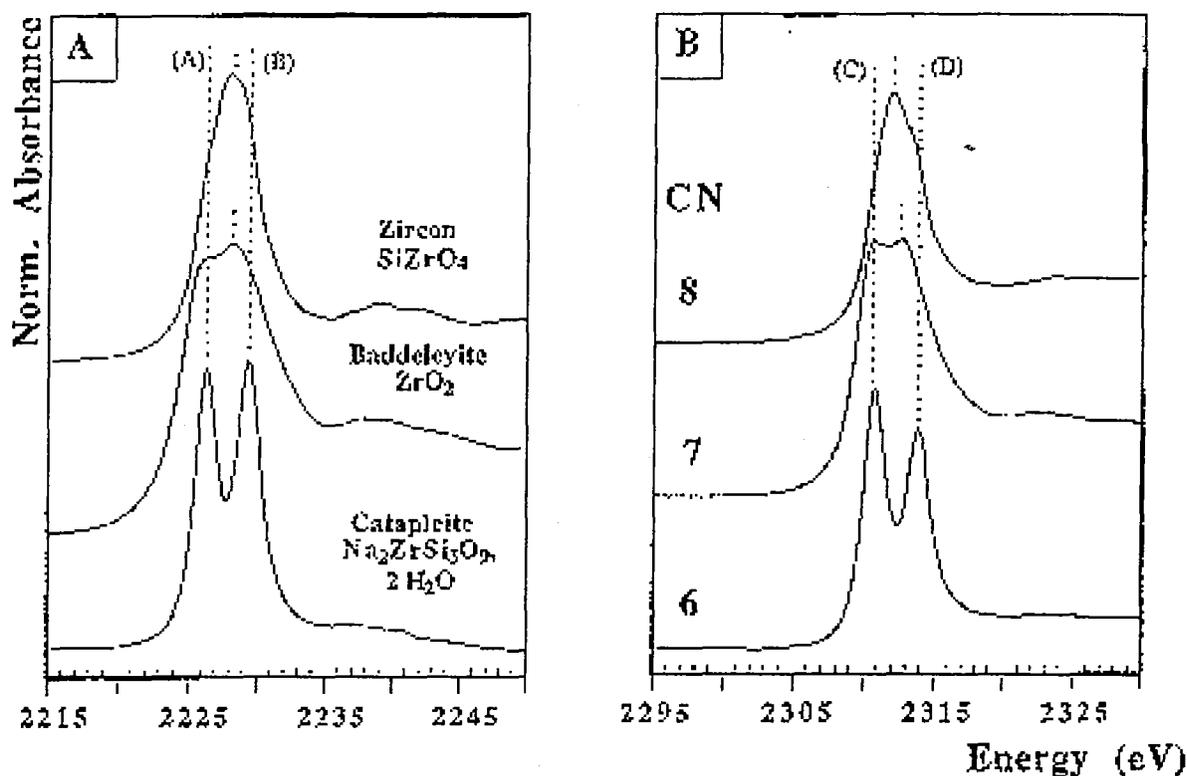


Figure 1: Zr-L_{III} (A) and L_{II} (B) XANES spectra of crystallized model compounds

Table 2: Positions in energy of Zr-L_{I,III} edges structures in XANES spectra, average Zr-O distances in crystalline compounds [8, 9, 10], and EXAFS-derived Zr-O distances in unknown compounds.

A	B	C	D	Zr-O (Å)	
Catapleite	2226.4	2229.4	2310.6	2313.8	2.073
Baddeleyite	2226.4	2228.2	2310.6	2312.6	2.158
Zircon		2228.0		2312.0	2.200
R7T7, V1	2226.4	2229.4	2310.6	2313.6	2.10-2.09
GR7T7, GV1	2226.4	2228.6	2310.6	2313.0	2.15

Fig.2 displays Zr-L_{I,III} XANES spectra of nuclear glasses and of their alteration products. For R7T7 and V1 glasses, both L_{III} and L_I XANES spectra yield 2 well-resolved resonances (2eV wide) at the same energy position as those found in catapleite, but feature D at 2313.6 eV (Tab.2). Thus, Zr is 6-fold coordinated to oxygens in the parent glasses studied.

For GR7T7 and GV1 gels, two well resolved resonances are observed both on L_{III} and L_I XANES spectra: (A) and (C) resonances are found at the same energy positions as those in glasses (Tab. 2). On the contrary, (B) and (D) resonances are shifted 0.8 eV to lower energy by comparison to parent glasses, and pointed at 2228.6 and 2313.0 eV. These energy positions are closer to that found in baddeleyite than those found in catapleite.

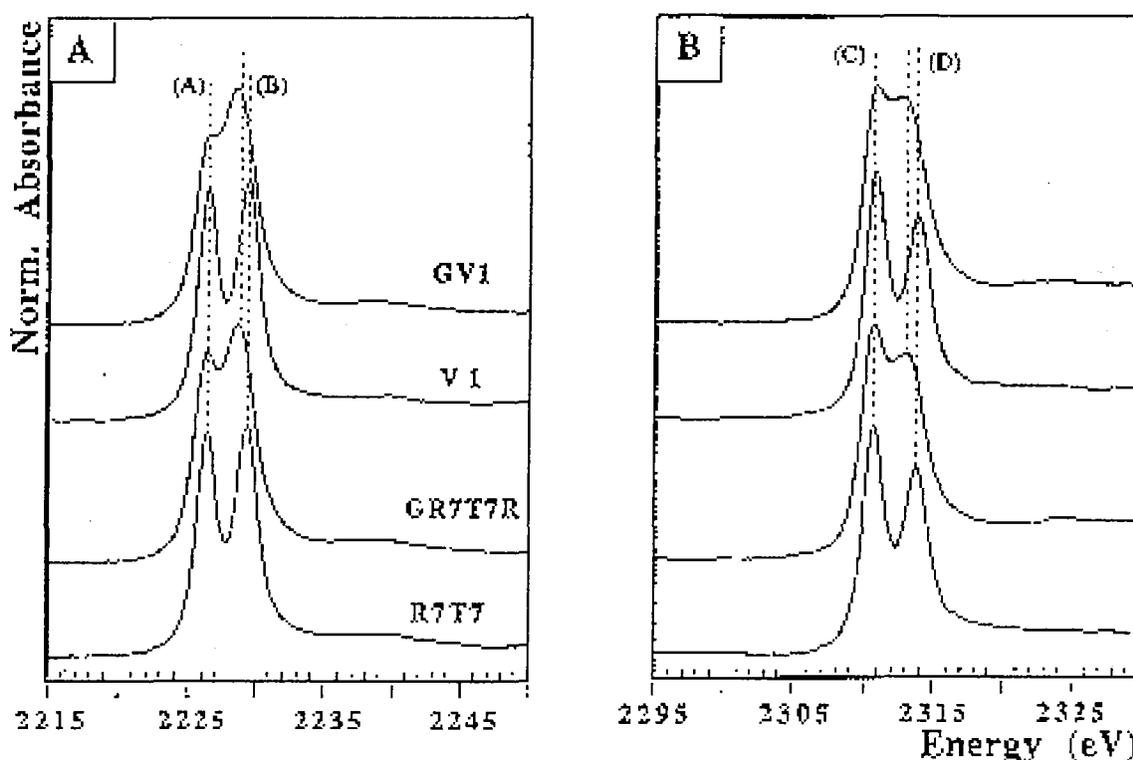


Figure 2: Zr-L_{III} (A) and L_I (B) XANES spectra of nuclear glasses (R7T7 and V1), and gels (GR7T7R and GV1)

Nevertheless, the general shape of L_{III} and L_{II} XANES spectra in gels is intermediate between those of glasses/catapleite and baddeleyite.

Zr-K EXAFS performed on parent glasses and alteration gels evidenced significant changes of the Zr local environment. Fitted data show that Zr-O distances increase significantly in gels ($2.15 \pm 0.01 \text{ \AA}$) with respect to those calculated in glasses ($2.10 \pm 0.01 \text{ \AA}$). The short distances in glasses are related to octahedral Zr, whereas the long ones in gels are very close to the average Zr-O distance in baddeleyite (2.158 \AA , Tab. 2).

CONCLUSION

During alteration of nuclear glasses, Zr local environment experienced significant changes. Both Zr- $L_{II,III}$ XANES and Zr-K EXAFS data demonstrate that (i) Zr is octahedrally coordinated to oxygens in parent glasses, and (ii) Zr CN is close to 7 in alteration gels. A mixture of CN=6 and CN=7 cannot be ruled out when taking into account the $L_{II,III}$ XANES data. Improvement of the crystal chemistry of Zr in these complex materials needs more quantitative data. This will be done in the future by simulating $L_{II,III}$ XANES spectra, and by fitting the second neighbors contribution detected on EXAFS spectra. These quantitative structural data will help in a better understanding of the Zr retention mechanisms during nuclear glass lixiviation.

ACKNOWLEDGMENTS

This work is supported by CEA/DCC and ANDRA.

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