



Evolution of the uranium local environment during alteration of SON68 glass

Patrick Jollivet ^{a,*}, Christophe Den Auwer ^a, Eric Simoni ^b

^a Commissariat à l'Énergie Atomique (CEA), Rhone Valley Research Center, BP 17171, 30207 Bagnols-sur-Cèze cedex, France

^b Institut de Physique Nucléaire, Bâtiment 100, 91406 Orsay cedex, France

Received 27 July 2001; accepted 27 November 2001

Abstract

The speciation of uranium in SON68 glass specimens doped with 0.75–3.5 wt% uranium and in the gels formed by alteration of the specimens was investigated by X-ray absorption spectroscopy. In the glasses, uranium is present at oxidation state VI and coordination number 6 with the same average distances than those found in a UO₃ type environment. The U–O distances and uranium coordination numbers are identical throughout the uranium concentration range. During glass alteration the uranium remains at oxidation state VI in the gels, but was found in the uranyl form. An increase in the equatorial distances (from 2.20 and 2.32 Å in the glass to respectively 2.22 and 2.39 Å in the gel) and coordination numbers (to about 7 and 8, respectively) was observed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Aqueous alteration of SON68 high-level waste containment glass results in the formation of a surface alteration film, or 'gel', the nature of which depends on the leaching conditions. As they form, the gels incorporate some radionuclides, notably the transition metals, the rare earth elements and the actinides. From the perspective of geological waste disposal, this phenomenon significantly reduces the activity released by alteration of the glass package. The long-term conservation of these properties must be demonstrated, however, before radionuclide retention can be taken into account in safety analyses. Although a formal demonstration is impossible over very long time periods, observation under certain conditions can provide data to support (or contradict) this hypothesis. One such technique consists in studying the local environment of the radionuclides in the glass and in the alteration gel to determine whether they are in fact incorporated in the gel. Because of their long ra-

dioactive half-lives and their toxicity, the actinides have a major impact on the 'glass source term' depending on whether or not they are retained.

The behavior of uranium was investigated in this study. The uranium retention factors in the gel depend on the alteration conditions, and thus on the nature of the resulting gel. One of the most important parameters affecting uranium retention in a vitrified waste repository environment is the leaching solution flow rate. Glass specimens were therefore altered at two different flow rates to assess the influence of this parameter on the uranium local environment. Because the gels are primarily amorphous, the uranium environment was probed by X-ray absorption spectroscopy (XAS) at the uranium L_{III}-edge.

2. Experimental

2.1. Glass compositions

Three glass samples doped with different uranium concentrations were studied; the elemental and oxide weight compositions are indicated in Table 1. Glass samples G1, G2 and G5 were doped with 0.75%, 1.49%,

* Corresponding author. Tel.: +33-4 66 79 63 73; fax: +33-4 66 79 66 20.

E-mail address: jollivet@amandine.cea.fr (P. Jollivet).

Table 1
Uranium-doped glass compositions (wt%)

Oxide	G1	G2	G5	Element	G1	G2	G5
SiO ₂	45.48	48.48	47.77	Si	21.26	22.66	22.33
Al ₂ O ₃	4.91	5.00	4.98	Al	2.60	2.65	2.64
B ₂ O ₃	14.02	14.66	13.80	B	4.35	4.55	4.29
Na ₂ O	9.86	9.47	10.45	Na	7.32	7.03	7.75
CaO	4.04	4.15	3.69	Ca	2.89	2.97	2.64
Li ₂ O	1.98	1.91	1.91	Li	0.92	0.89	0.89
ZnO	2.50	2.41	2.38	Zn	2.01	1.94	1.91
ZrO ₂	2.65	0.00	0.00	Zr	1.96	0.00	0.00
Fe ₂ O ₃	2.91	2.84	2.78	Fe	2.04	1.99	1.94
NiO	0.74	0.72	0.72	Ni	0.58	0.57	0.57
Cr ₂ O ₃	0.51	0.39	0.26	Cr	0.35	0.27	0.18
P ₂ O ₅	0.28	0.17	0.18	P	0.22	0.13	0.14
UO ₂	0.85	1.69	3.99	U	0.75	1.49	3.52
ThO ₂	0.00	0.00	0.00	Th	0.00	0.00	0.00
SrO	0.33	0.00	0.00	Sr	0.28	0.00	0.00
Y ₂ O ₃	0.00	0.00	0.00	Y	0.00	0.00	0.00
MoO ₃	1.70	2.08	1.68	Mo	1.13	1.39	1.12
MnO ₂	0.72	0.89	0.75	Mn	0.46	0.56	0.47
CoO	0.12	0.00	0.00	Co	0.09	0.00	0.00
Ag ₂ O	0.03	0.00	0.00	Ag	0.03	0.00	0.00
CdO	0.03	0.00	0.00	Cd	0.03	0.00	0.00
SnO ₂	0.02	0.00	0.00	Sn	0.02	0.00	0.00
Sb ₂ O ₃	0.01	0.00	0.00	Sb	0.01	0.00	0.00
TeO ₂	0.23	0.00	0.00	Te	0.18	0.00	0.00
Cs ₂ O	1.42	1.51	1.71	Cs	1.34	1.42	1.61
BaO	0.60	0.57	0.56	Ba	0.54	0.51	0.50
La ₂ O ₃	1.10	0.84	0.81	La	0.94	0.72	0.69
Ce ₂ O ₃	0.93	0.90	0.04	Ce	0.79	0.77	0.03
Pr ₂ O ₃	0.44	0.41	0.16	Pr	0.38	0.35	0.14
Nd ₂ O ₃	1.59	1.43	1.39	Nd	1.36	1.22	1.19
				O	45.20	46.46	45.47

and 3.52% U, respectively; their compositions were very similar to that of the French SON68 (R7T7-type) glass, even though oxides accounting for less than 0.1 wt% were not included in G2 and G5. In order to prevent interference with the uranium L_{III}-edge (17 167 eV), we eliminated Y (17 037 eV) and Th (16 300 eV) from all the samples. Because the EXAFS spectra were acquired over a 1000 eV range we also eliminated Zr (17 998 eV) and Sr (16 105 eV) from samples G2 and G5 to prevent even minor interference. Both of these elements were included in sample G1 for comparison purposes, since zirconium has a major role in cross-linking of the silicate network. The three glasses were melted for 3 h at 1200 °C in a platinum crucible, then annealed for 1 h at 520 °C in a graphite crucible.

2.2. Alteration gels

The gels were prepared by complete alteration of powder samples of glasses G1 (→ Gel1), G2 (→ Gel2 and Gel3) and G5 (→ Gel4 and Gel5) in pseudo-dynamic mode at 90 °C to obtain suitable gels within a reasonable time frame (about 1 year). Leaching solu-

tions were changed at the following renewal rates: a first series of gels (Gel2 and Gel4) was obtained with a high solution renewal rate (≈2 per day) and a second series (Gel1, Gel3 and Gel5) was obtained at a lower renewal rate (≈0.3 per day) under conditions slightly more representative of a geological repository (this rate of renewal is relatively low at the laboratory scale, but is nevertheless some 4–6 orders of magnitude higher than found in potential repository sites). We took 2 g of glass in 1000 cm³ of water for the first series and 2.5 g in 500 cm³ of water for the second series. At the end of the leaching of glasses, we recovered about 0.2 g of 1st series gels and 0.4 g of 2nd series gels.

The glass powder grain size was less than 20 μm, with a specific surface area of 0.93 m²g⁻¹ measured by the BET method using krypton. The samples were altered in ultrapure water (18 MΩ cm) under the conditions indicated in Table 2. The silicon concentrations in the leachate varied during alteration from 10 to 4 mg l⁻¹ for the 1st series gels, and from 40 to 10 mg l⁻¹ for the 2nd series gels. The pH at 90 °C ranged from 8.4 to 8 for the 1st series gels, and from 9 to 8 for the 2nd series gels.

Table 2
Glass alteration conditions to obtain gels

Parameter	Gel1	Gel2	Gel3	Gel4	Gel5
Glass mass (g)	2.49	1.96	2.52	1.95	2.49
Leachate volume (l)	≈0.5	≈1.0	≈0.5	≈1.0	≈0.5
S/V (cm ⁻¹)	≈20	≈18	≈47	≈18	≈46
Renewal rate (per day)	≈0.3	≈2	≈0.3	≈2	≈0.3
Si retention factor	0.19	0.14	0.13	0.15	0.15
U retention factor	0.88	0.82	0.92	0.92	0.94

The gels have been recovered from the leaching solution and dried in an oven for 2 days at 90 °C. At this temperature, the free water inside the pores of the gels is drained off but the structure water is kept inside the gels. After drying, the gels are compacted with a press and coated in Kapton.

The elemental weight compositions of the gels (Table 3) were determined from the elemental concentrations measured in the leachate. The low renewal rate led to a slower leaching of the less soluble species (Al, transition metals and rare earth elements) and therefore to their

Table 3
Uranium-doped gel compositions (wt%)

Element	Gel1	Gel2	Gel3	Gel4	Gel5
Si	13.5	23.7	12.9	23.2	14.0
Al	4.6	4.0	6.8	4.0	6.1
B	0.7	0.0	1.0	0.0	0.5
Na	0.7	0.0	0.9	0.0	0.0
Ca	4.9	3.2	2.2	3.2	2.5
Li	0.0	0.0	0.1	0.0	0.0
Zn	7.0	5.8	7.6	5.6	7.2
Zr	6.7	0.0	0.0	0.0	0.0
Fe	7.1	5.9	7.8	5.7	7.3
Ni	2.0	1.7	2.2	1.6	2.1
Cr	1.2	0.8	1.0	0.8	0.7
P	0.5	0.7	0.3	0.7	0.3
U	2.4	3.7	6.0	8.3	13.9
Th	0.0	0.0	0.0	0.0	0.0
Sr	0.3	0.0	0.0	0.0	0.0
Y	0.0	0.0	0.0	0.0	0.0
Mo	0.2	0.0	0.2	0.0	0.1
Mn	1.5	1.3	1.9	1.3	1.8
Co	0.2	0.0	0.0	0.0	0.0
Ag	0.0	0.0	0.0	0.0	0.0
Cd	0.0	0.0	0.0	0.0	0.0
Sn	0.0	0.0	0.0	0.0	0.0
Sb	0.0	0.0	0.0	0.0	0.0
Te	0.2	0.0	0.0	0.0	0.0
Cs	0.0	0.0	0.2	0.0	0.1
Ba	0.9	0.5	0.4	0.5	0.5
La	2.6	2.0	3.1	2.0	2.9
Ce	2.6	2.3	3.4	0.0	0.1
Pr	1.2	1.0	1.5	0.4	0.6
Nd	4.8	3.6	5.3	3.5	5.0
O	34.2	39.8	35.2	39.2	34.3

enrichment in the gels (see Gel1, Gel3 and Gel5). The variation in the silicon concentration was attributable to the different leaching solution renewal rates because of different enrichment rates of less soluble elements, and the uranium variation was due to the different enrichment values in the glass samples. The silicon retention factor in the gels was about 0.15, and ranged from 0.82 to 0.94 for uranium (Table 2).

2.3. XAS model compounds

Uranium model compounds at formal oxidation states IV and VI were selected for the XAS studies:

- UO₂ (space group = Fm3m and uranium point symmetry = O_h) [1] to model uranium oxidation state IV,
- U₃O₈ α phase (space group = C2mn and deformed pentagonal bipyramidal U sites with different U–O distances) [2] as the uranium starting phase in the glass composition,
- UO₃ γ phase (space group = I4₁/amd and 2 uranium sites with different U–O distances in a distorted octahedron U(2) and a distorted dodecahedron U(1)) [3] to model oxidation state VI,
- UO₂(OH)₂ α phase (space group = Cmca and deformed hexagonal bipyramidal U sites) [4] to model the uranyl (VI) cation,
- cuprosklodowskite Cu[(UO₂)₂(SiO₃OH)₂].6H₂O (space group = P-1 and deformed pentagonal bipyramidal uranium site) [5] to model the uranyl cation in a silicate network. Cuprosklodowskite is a natural silicate compound.

2.4. XAS data acquisition

XANES and EXAFS spectra were recorded at the LURE synchrotron facility of Orsay University (France), using experimental station D44 of the DCI ring. Double crystal Si(311) monochromator was used. The spectra were acquired in transmission mode at the uranium L_{III}-edge using three ionization chambers, the third one being used to calibrate the absorption spectra using an yttrium foil (17 052 eV). The measurements were performed using argon-filled ionization chambers at current intensities of about 0.30–0.35 nA. The overall energy resolution at the uranium L_{III}-edge was of 7 eV.

2.5. XAS data treatment

2.5.1. EXAFS data

Pre-edge removal was carried out by linear function and Lengeler normalization. All EXAFS oscillations were extracted from the atomic adsorption spectra by simulating the atomic absorption using a 6th order

polynomial function (EXAFS98 code [6]). Fourier transform (FT) of the EXAFS data was achieved in the k^3 weighting mode using a Kaiser window ($\tau = 2.5$) between 2.9 and 12.2 \AA^{-1} .

Data were adjusted using *Round Midnight* code after back Fourier transformation of the FT peak from ≈ 0.8 to ≈ 1.9 \AA (distances not phase shift corrected) corresponding to the uranium first coordination sphere. Adjustments were carried out with a weight of $1/s(k)^2$, where $s(k)$ is the standard deviation of the k . $\chi(k)$ data calculated by EXAFSTAT code [6].

The simulation of the EXAFS spectrum of γ - UO_3 using FEFF7.02 [7] code gave satisfactory agreement with the experimental spectrum. Electronic parameters (inelastic losses $S_0(k)$, electron mean free path $\lambda(k)$, backscattering phases $\Phi(k, 2\pi)$ and amplitudes $f(k, 2\pi)$) extracted from this calculation were used in *Round-Midnight* code [6] for all compounds.

As a check, adjustment of the filtered EXAFS spectrum of γ - UO_3 with its own calculated electronic parameters ($e_0 = -3.4$ eV) gave a satisfactory agreement with the crystallographic data (Table 4). The U(1) site (dodecahedron) in γ - UO_3 is seen by EXAFS as an octahedron (four equatorial oxygens instead of six) because of the boundaries taken for the back FT (the oxygens at ≈ 3 \AA cannot be seen). In all other adjustments of this study, e_0 was kept constant and equal to -3.4 eV. Since there are two crystallographic sites in γ - UO_3 (with occupancy equal to 0.5), the EXAFS data fitting has been carried out with three oxygen shells accounting for the average contributions of the two sites.

2.5.2. XANES data

All XANES data were normalized using a linear pre-edge removal (*Galaad* code [6]) and normalization to absorption value equal to 1 in the middle of the first EXAFS oscillation.

Energy calibration of the XANES data was achieved using the reference Y foil (17 052 eV at the absorption

edge maximum) positioned after the second ionization chamber.

3. Oxidation state and uranium site in the glasses and gels

The uranium L_{III} -edge XANES spectra of the reference compounds are shown in Fig. 1 and characteristic features are given in Table 5. Both white line shape and position for UO_2 (a compound in which uranium is found at formal oxidation state IV in an octahedral site) are very different from those of the other compounds (in which uranium is at formal oxidation state VI). The white line maximum for U(IV) is about 3 eV lower than for U(VI) and this is in agreement with the general rule associating the high energy shift of the absorption edge with an increase of the absorbing atom oxidation state. Among the U(VI) reference compounds, the spectra of cuprosklodowskite, UO_3 and $\text{UO}_2(\text{OH})_2$ are similar, while the signature of U_3O_8 is significantly different.

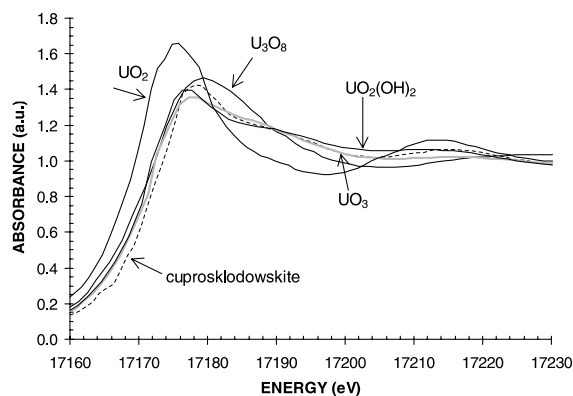


Fig. 1. Uranium L_{III} -edge XANES spectra of reference compounds.

Table 4

Best fit parameters of the uranium L_{III} -edge EXAFS spectrum and distances in the two sites occupied by uranium in γ - UO_3 (EXAFS and crystallographic data)

Material	N_i	R_i (\AA)	σ_i (\AA)	r factor
UO_3	2.0	1.80 ± 0.01	0.0746 ± 0.0007	8.04×10^{-4}
	2.0	2.22 ± 0.01	0.0656 ± 0.0013	
EXAFS data	2.0	2.33 ± 0.01	0.0974 ± 0.0008	
	Site 1		Site 2	
EXAFS data	$N_{\text{ax}} = 2.0$	$R_{\text{ax}} = 1.80$	$N_{\text{ax}} = 2.0$	$R_{\text{ax}} = 1.80$
	$N_{\text{eq}} = 4.0$	$R_{\text{eq}} = 2.22$	$N_{\text{eq}} = 4.0$	$R_{\text{eq}} = 2.33$
Crystallographic data (average)	$N_{\text{ax}} = 2.0$	$R_{\text{ax}} = 1.82$	$N_{\text{ax}} = 2.0$	$R_{\text{ax}} = 1.82$
	$N_{\text{eq}} = 4.0$	$R_{\text{eq}} = 2.21$	$N_{\text{eq}} = 4.0$	$R_{\text{eq}} = 2.31$

Table 5
White line (E_A) maximum energy and resonances due to axial oxygen (E_{ax}) and equatorial oxygen (E_{eq})

Com- pounds	E_A (± 0.8) (eV)	E_{ax} (± 1.5) (eV)	E_{eq} (± 1.0) (eV)	ΔE_{ax} (± 2.3) (eV)	ΔE_{eq} (± 1.8) (eV)
UO ₂	17175.3				
Cuprosklo- dowskite	17178.4	17192	17215	14	37
U ₃ O ₈	17179.4				
UO ₃	17177.9	17185	17216	7	38
UO ₂ (OH) ₂	17177.2	17187	17211	10	34
G1	17178.2	17188	17219	10	41
G2	17178.5	17185	17217	7	39
G5	17179.2	17187	17218	8	39
Gel1	17178.4	17190	17214	12	36
Gel2	17177.1	17185	17212	8	32
Gel3	17177.4	17188	17212	10	35
Gel4	17177.5	17186	17214	9	36
Gel5	17177.5	17186	17215	8	37

All XANES spectra of the glass samples G1 (0.75 wt% U), G2 (1.5%) and G5 (3.5%) are at similar energy position (Fig. 2: the absorbance of each spectrum is offset by 0.1 unit in the figure for clarity). This position indicates that the uranium atom is at the same oxidation state, and no major changes in the uranium local environment occurred at concentrations of up to 3.5 wt% U. The uranium L_{III}-edge XANES spectra for the gels (Fig. 2) are also identical: uranium is at the same oxidation state in all the gels (the position of Gel1 is 1 eV out of range and seems to represent a singular point in the series).

In all the reference compounds except UO₂, uranium is coordinated to two axial oxygen atoms and generally to 4–6 oxygen atoms in the equatorial plane depending

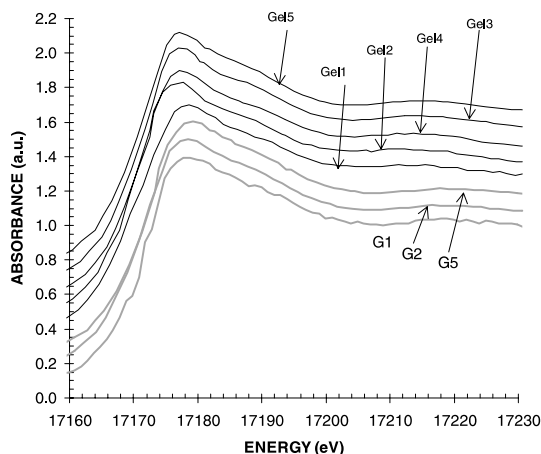


Fig. 2. Uranium L_{III}-edge XANES spectra of glasses and gels.

on the coordination number. The XANES spectra are similar for all the glass and gel samples, although the resonance due to the equatorial oxygen atoms (near 17215 eV) is situated at a lower energy in the gels than in the glasses, indicating that the U–O_{eq} distances are larger in the gels than in the glasses. Furthermore, the white line maximum energy is situated at 17178.6 eV for the glasses and 17177.6 eV for the gels. Although the difference (about 1 eV) corresponds to the order of magnitude of the uncertainty on the XANES spectrum energy, the same trend was observed with all the glasses and all the gels. This slight difference in the white line peaks between the glass and gel could be attributable to a difference in the local environment around the uranium atoms in these compounds.

Comparing the white line maximum energy of the XANES spectra shows that uranium is found predominantly at oxidation state VI in the glasses and gels. This is consistent with a previous study [8] of simplified SON68-type glasses containing only four oxides, which demonstrated that uranium was at oxidation state VI for a 5 wt% UO₂ concentration. However, the presence of tetravalent uranium in the glass and gel cannot be excluded because of the low energy resolution at the uranium L_{III}-edge (typically, the energy shift between U(IV) and UO₂²⁺ XANES spectra is of the order of 1.5–2.0 eV). Furthermore, although the uranium L_{III} absorption edge at oxidation state V is very close to that of U(VI), the glass and gel preparation procedure reasonably precludes any presence of U(V) in these materials (an O₂ fugacity between 10^{−3} and 10^{−7} atm is required to obtain U(V) in borosilicates [9]). Moreover, this is corroborated by UV–VIS spectroscopic studies [10] in which U(V) was not detected, and by the fact that iron was present in the glass as Fe³⁺ rather than Fe²⁺ [11,12]. Earlier XPS studies of uranium speciation in glass [13] showed the presence of uranium at oxidation states IV and VI, but the former was found to have been generated by the X-ray beam used for the analysis.

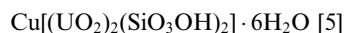
Conversely, a study of the American SLR-131 and ATM-1c glasses [14] revealed a significant difference in the XANES spectra of the glass and gel that was not observed for our SON68 glass. Notwithstanding the differences in the glass chemical composition, the discrepancy is surprising in the case of the gels. The difference could be due to the lower *S/V* ratios used for leaching the SLR-131 and ATM-1c glass samples, which could have produced gels of a different type.

A direct comparison of the XANES spectra of the glasses and gels with those of the reference compounds UO₃, cuprosklo-dowskite and UO₂(OH)₂ is not sufficient to determine the nature of the site occupied by uranium in these materials (UO₃ or uranyl UO₂²⁺). In order to discriminate between these two types of sites, the position of the resonance energies attributed to the axial E_{ax} and equatorial E_{eq} oxygen atoms [15] were used.

The evolution of E_{ax} and E_{eq} versus the U–O_{ax,eq} distance is accounted for by application of the Natoli relation [16] and assuming that all U(VI) compounds described here have similar associated potentials:

$$\Delta E \times R^2 = \text{constant},$$

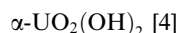
where ΔE is the difference between the resonance energies due to O_{ax} and O_{eq} and the white line peak respectively, and R is the uranium–oxygen interatomic distance. The interatomic distances in the reference compounds are well known, and can be used to plot the calibration between ΔE and R . The following mean distances \bar{R} were calculated for the model compounds from the crystallographic data:



$$\bar{R} \begin{cases} \text{U–O}_{ax} = 1.77 \text{ \AA} \\ \text{U–O}_{eq} = 2.36 \text{ \AA} \end{cases}$$

γ -UO₃ [3] (average (O_{eq} at $\approx 3.05 \text{ \AA}$ not taken into account) of two sites)

$$\bar{R} \begin{cases} \text{U–O}_{ax} = 1.82 \text{ \AA} \\ \text{U–O}_{eq} = 2.26 \text{ \AA} \end{cases}$$



$$\bar{R} \begin{cases} \text{U–O}_{ax} = 1.79 \text{ \AA} \\ \text{U–O}_{eq} = 2.50 \text{ \AA} \end{cases}$$

The resulting plots of ΔE_{ax} and ΔE_{eq} versus $1/R^2$ are shown in Fig. 3 (O_{ax}) and Fig. 4 (O_{eq}). The $1/R_{ax}^2$ and $1/R_{eq}^2$ points for the glasses and gels are determined by the intersection of the ΔE_{ax} , ΔE_{eq} values with the calibration line. It should be noted that the position of ΔE_{ax} is determined with less accuracy than the one of ΔE_{eq} because it corresponds to a weak shoulder of the absorption

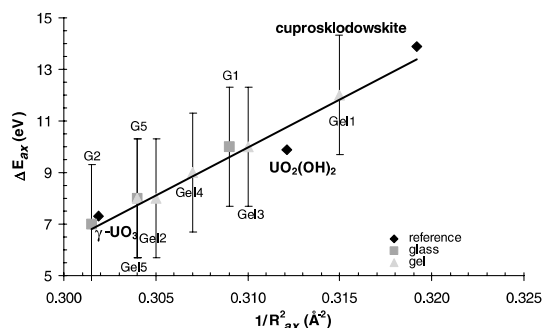


Fig. 3. Deviation between the maximum white line energy and the resonance due to axial oxygen atoms versus $1/R^2$ for the reference compounds.

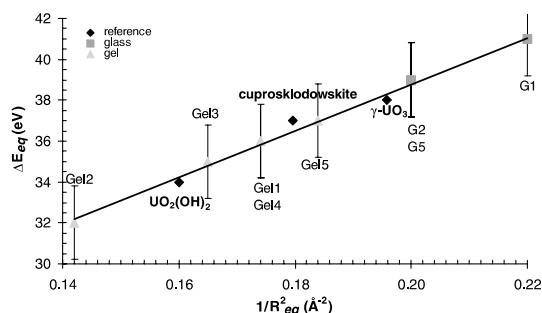


Fig. 4. Deviation between the maximum white line energy and the resonance due to equatorial oxygen atoms versus $1/R^2$ for the reference compounds.

peak. Given the error bars estimated for ΔE_{ax} and ΔE_{eq} , the results relative to glasses and gels should be taken as indicative.

Figs. 3 and 4 show the data points corresponding to glass samples G1, G2, G5 and gel samples from Gel1 to Gel5. All data points fall within the UO₃–UO₂(OH)₂ range, excluding the resemblance of any of the samples with the cuprosklodowskite like local structure.

In conclusion, it appears from the XANES investigation that U(VI) is present in all of the glass and gel samples. Furthermore, a γ -UO₃ or UO₂(OH)₂ like local structure seems to be a good model for the uranium environment in both glasses and gels. In the next section, EXAFS data analysis is used to precise the uranium sites.

4. EXAFS spectra and radial pseudo-distance distribution

4.1. Qualitative approach

The EXAFS spectra of the three reference compounds UO₃, cuprosklodowskite and UO₂(OH)₂ are compared in Fig. 5. They all present different oscillation frequencies accounting for the different uranium environments.

The uranium L_{III}-edge EXAFS spectra of the glass samples (Fig. 5) are identical up to 10 Å⁻¹, beyond which the increasing noise level prevents valid comparisons. The glass spectra clearly differ from that of cuprosklodowskite but resemble that of UO₃, confirming the XANES results. No contribution from silicon was observed on the FT, but the spectral signal to noise ratio prevented us from drawing any conclusions regarding slight incorporation of uranium in the glass silicate network. An earlier study [17] of simplified glass compositions showed that uranium was weakly bonded to the silicate network.

The EXAFS spectra of the gels (Fig. 5) have a better signal to noise ratio than the glass samples do (the U

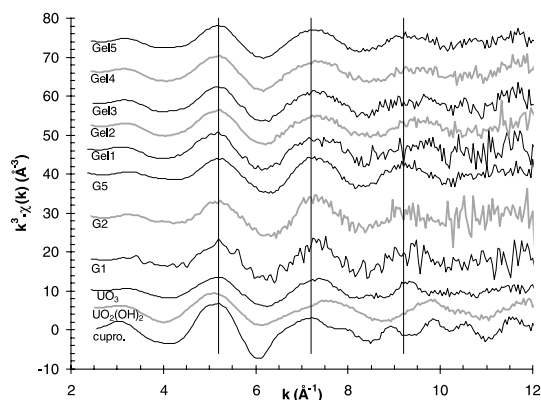


Fig. 5. Uranium L_{III} -edge EXAFS spectra of reference compounds, glasses and gels.

concentrations were higher in the gels than in the corresponding glasses), and no significant differences were observed among all the gels. The gel formation process thus did not affect the uranium structure in the gels, at least within the range of solution renewal rates studied here. Although the noise level is lower for the Gel4 and Gel5 gels than for the glasses, here is no evidence of silicium or uranium contribution. A comparison of the gel EXAFS spectra with those of cuprosklodowskite or of an uranyl orthosilicate $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ [18] shows significant differences, indicating that uranium is not present as a silicate in the gels as assumed from the XANES investigation. However, the EXAFS spectra and FT moduli of uranyl hydroxide are very similar to those of our gels, thus confirming the XANES results. Moreover, uranyl hydroxides EXAFS spectra obtained by precipitating $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at pH 9 are very similar too to those of our gels [19].

In order to qualitatively describe the glass and gel structures in comparison with the UO_3 and $\text{UO}_2(\text{OH})_2$ ones, we have performed a simulation of the evolution of the EXAFS spectra when going from $\text{UO}_2(\text{OH})_2$ to octahedral site in UO_3 like structure. The EXAFS spectra of uranyl hydroxide with different simulated uranium–oxygen distances were calculated using the FEFF7.02 code. The initial molecular structure was that of $\alpha\text{-UO}_2(\text{OH})_2$; the U-O_{ax} and U-O_{eq} distances were varied to visualize the evolution of the FT moduli for these simulated compounds. With U-O_{ax} distances equal to 1.82 Å, we have decreased the U-O_{eq} distances from 2.50 (uranyl hydroxide like structure) to 2.26 Å (U(1) site in $\gamma\text{-UO}_3$ considered as octahedron instead of dodecahedron to be consistent with EXAFS data). The calculations were simplified by taking into account only the oxygen atoms that are contained in the first uranium coordination sphere. The calculated results for the large U–O distances show two peaks on the FT (Fig. 6); the spectra obtained for equatorial distances of 2.50 and 2.44 Å were

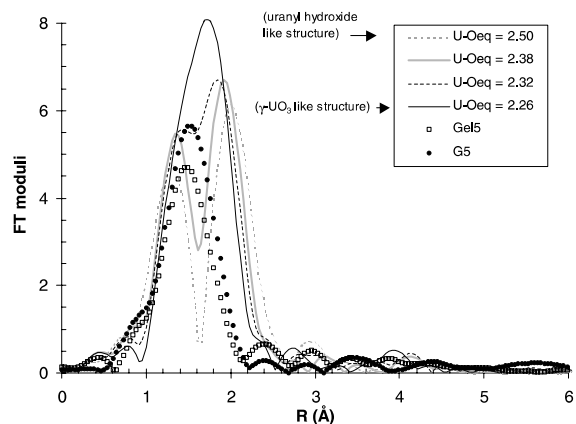


Fig. 6. FTs of uranyl hydroxides versus uranium–oxygen distance (R , in angstroms) simulated using the FEFF7.02 code and of experimental Gel5 spectrum.

identical. Conversely, the FTs evolved as the distances diminished, notably with a convolution of the two oxygen peaks at $\text{U-O}_{\text{eq}} = 2.32$ Å. This clearly shows the ambiguity between the two structures from the EXAFS point of view. In the next section, adjustments of the glass and gel EXAFS spectra are performed in order to quantify the uranium polyhedron. According to this simulation, the simplified EXAFS $\gamma\text{-UO}_3$ like structure (two octahedral sites instead of one octahedral and one dodecahedral site) seems to be a good model for glass and gel fitting. This is in agreement with the previous XANES results that suggested that either the uranyl hydroxide or the $\gamma\text{-UO}_3$ like structures would be suitable.

4.2. Quantitative approach

All EXAFS spectra from the glasses and gels were fitted using the $\gamma\text{-UO}_3$ electronic parameters calculated from FEFF7.02 code as described in Section 2.5. A 3-shell fit was necessary to obtain good fit for both glasses and gels as in the case of $\gamma\text{-UO}_3$.

4.2.1. Glasses

Fitting the EXAFS spectra with the electronic parameters of $\gamma\text{-UO}_3$ allowed us to determine the uranium–oxygen distances and the number of neighbors surrounding the uranium atoms in the glass (Table 6).

The 3-shell fit is in good agreement with the experimental glass spectra, as shown for G1 as an example in Fig. 7. The spectra fitted with only two oxygen shells did not account for the experimental spectra, as they are affected by a phase shift on the order of π near 10 \AA^{-1} compared with the experimental spectra, even if larger Debye–Waller values than 0.1 Å are used. We assume here, as suggested by all previous results, that the 3-shell fit does not account for two different U–O distances on

Table 6
Best fit parameters of the uranium L_{III}-edge glass EXAFS spectra

Material	N_i	R_i (Å)	σ_i (Å)	r factor
G1	2.0 ± 0.1	1.80 ± 0.01	0.0669 ± 0.0007	4.89×10^{-3}
	2.0 ± 0.1	2.20 ± 0.01	0.0060 ± 0.0013	
	2.0 ± 0.1	2.32 ± 0.01	0.0508 ± 0.0007	
G2	2.1 ± 0.1	1.79 ± 0.01	0.0570 ± 0.0167	1.12×10^{-3}
	2.0 ± 0.1	2.20 ± 0.013	0.0018 ± 0.0003	
	2.0 ± 0.1	2.31 ± 0.01	0.0645 ± 0.0088	
G5	2.0 ± 0.1	1.81 ± 0.01	0.0589 ± 0.0005	1.95×10^{-3}
	2.1 ± 0.1	2.20 ± 0.01	0.0045 ± 0.0012	
	2.1 ± 0.1	2.32 ± 0.01	0.0555 ± 0.0005	
	Site 1		Site 2	
G1	$N_{ax} = 2.0$	$R_{ax} = 1.80$	$N_{ax} = 2.0$	$R_{ax} = 1.80$
	$N_{eq} = 4.0$	$R_{eq} = 2.20$	$N_{eq} = 4.0$	$R_{eq} = 2.32$
G2	$N_{ax} = 2.14$	$R_{ax} = 1.79$	$N_{ax} = 2.1$	$R_{ax} = 1.79$
	$N_{eq} = 4.0$	$R_{eq} = 2.20$	$N_{eq} = 4.0$	$R_{eq} = 2.31$
G5	$N_{ax} = 2.0$	$R_{ax} = 1.81$	$N_{ax} = 2.0$	$R_{ax} = 1.81$
	$N_{eq} = 4.2$	$R_{eq} = 2.20$	$N_{eq} = 4.2$	$R_{eq} = 2.32$

Coordination numbers and distances in the two sites occupied by uranium in the glasses.

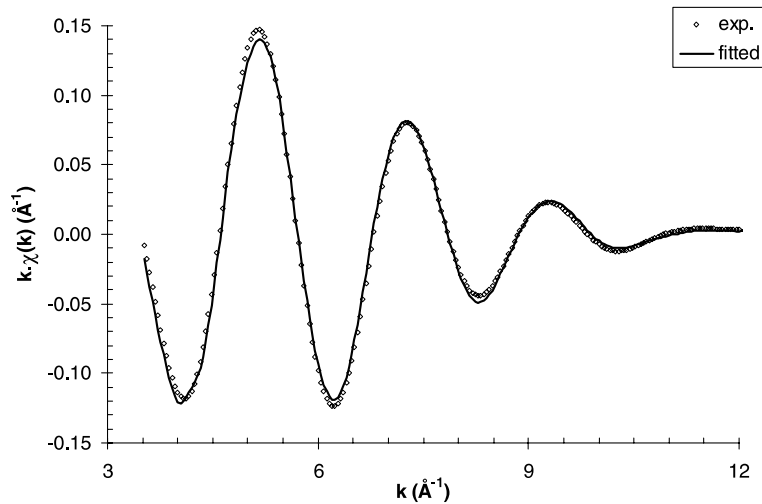


Fig. 7. Comparison between experimental EXAFS spectra and spectra fitted to three oxygen shells for glass G1.

the equatorial plane, but for two distinct sites as in γ - UO_3 for which the structural parameters are indicated in Table 6 ($N_{ax} = N_1$ and $N_{eq} = 2N_2$ or $2N_3$ for sites 1 and 2, respectively). The total uranium coordination numbers found in the glass are 6.0 (V1), 6.1 (V2) and 6.2 (V5), while the distances agree within 0.01 Å with those obtained in γ - UO_3 .

The distance of 1.80 Å obtained for the two axial oxygen atoms and 2.26 Å for the equatorial oxygen atoms (four oxygen atoms at $R_{eq} = 2.20$ Å for one site, and

$R_{eq} = 2.32$ Å for the other) are very close to the values reported for a 10-element American radionuclide containment glass with 3 wt% U_3O_8 ($R_{eq} = 2.22$ Å) [20], and for 5-element simplified R7T7-type glasses with up to 5 wt% UO_2 ($R_{eq} = 2.27$ Å) [8]. The identical N_2 and N_3 numbers suggests the presence of two uranium sites in equal proportions in the glass. The σ values show that the distances were much more scattered for the oxygen atoms situated at 2.32 Å than for those at 2.20 Å. The uranium content of the glass had no effect on the local environment

of uranium, as the uranium–oxygen distances and coordination numbers were identical for all three glass samples. Moreover, no difference was observed between G1 on the one hand and G2 and G5 on the other, indicating that Zr has no effect on the uranium local environment.

4.2.2. Alteration gels

According to the simulation of Fig. 6 and to the XANES results, the uranium environment in the gels appears comparable to that in the glasses. However, the EXAFS spectra of Fig. 5 shows a phase shift in the gel spectra at about 9.2 \AA^{-1} compared to the glass ones. This suggests a modification of the uranium environment. We have extracted the experimental phases and amplitudes from $\alpha\text{-UO}_2(\text{OH})_2$ and then used them to fit the EXAFS spectra of the gels. Very bad fits (r factors equal to about 0.1) were obtained. Phases and amplitudes of $\gamma\text{-UO}_3$ were thus used and gave satisfactory

fitting results (cf. Table 7) despite the slightly underestimated amplitude of the first oscillation on the simulated spectra, as shown for example in Fig. 8 for gel sample Gel2. The fits obtained with two oxygen shells for the gel were unsatisfactory; the 3-shell fits probably reflect the presence of two types of sites in the gels, as in the glasses. Glass alteration very likely results in an evolution of the two UO_3 sites without complete reorganization of the silicate network in the gel, which would lead to a single type of site. The R_2 and R_3 distances thus certainly correspond to the $\text{U}\text{--}\text{O}_{\text{eq}}$ distances for the two uranium sites, rather than a single site with two different equatorial lengths. The mean axial distances were slightly lower than for the glass ($R_{\text{ax}} = 1.79 \text{ \AA}$ rather than 1.80 \AA), while the mean equatorial distances increased from 2.20 to 2.22 \AA and from 2.32 to 2.39 \AA . The second major structural modification, in addition to the greater equatorial distances, is the higher

Table 7
Best fit parameters of the uranium L_{III} -edge gel EXAFS spectra

Material	N_i	R_i (Å)	σ_i (Å)	r factor
Gel1	2.1 ± 0.1	1.79 ± 0.01	0.0541 ± 0.0011	4.00×10^{-3}
	2.7 ± 0.1	2.23 ± 0.01	0.0527 ± 0.0087	
	3.3 ± 0.3	2.41 ± 0.02	0.0746 ± 0.0023	
Gel2	1.8 ± 0.1	1.79 ± 0.01	0.0622 ± 0.0013	1.27×10^{-2}
	2.8 ± 0.1	2.23 ± 0.01	0.0658 ± 0.0006	
	3.2 ± 0.1	2.39 ± 0.01	0.0928 ± 0.0006	
Gel3	1.9 ± 0.1	1.80 ± 0.01	0.0620 ± 0.0013	1.22×10^{-2}
	3.0 ± 0.1	2.22 ± 0.01	0.0765 ± 0.0031	
	3.3 ± 0.1	2.38 ± 0.01	0.0898 ± 0.0011	
Gel4	1.9 ± 0.1	1.79 ± 0.01	0.0578 ± 0.0009	3.74×10^{-3}
	2.6 ± 0.1	2.22 ± 0.01	0.0616 ± 0.0013	
	2.9 ± 0.1	2.39 ± 0.01	0.0796 ± 0.0049	
Gel5	1.8 ± 0.1	1.80 ± 0.01	0.0586 ± 0.0008	7.25×10^{-3}
	2.5 ± 0.1	2.22 ± 0.01	0.0401 ± 0.0007	
	2.8 ± 0.1	2.38 ± 0.01	0.0733 ± 0.0007	
	Site 1		Site 2	
Gel1	$N_{\text{ax}} = 2.1$	$R_{\text{ax}} = 1.79$	$N_{\text{ax}} = 2.1$	$R_{\text{ax}} = 1.79$
	$N_{\text{eq}} = 5.4$	$R_{\text{eq}} = 2.23$	$N_{\text{eq}} = 6.6$	$R_{\text{eq}} = 2.41$
Gel2	$N_{\text{ax}} = 1.8$	$R_{\text{ax}} = 1.79$	$N_{\text{ax}} = 1.8$	$R_{\text{ax}} = 1.79$
	$N_{\text{eq}} = 5.6$	$R_{\text{eq}} = 2.23$	$N_{\text{eq}} = 6.4$	$R_{\text{eq}} = 2.39$
Gel3	$N_{\text{ax}} = 1.9$	$R_{\text{ax}} = 1.80$	$N_{\text{ax}} = 1.9$	$R_{\text{ax}} = 1.80$
	$N_{\text{eq}} = 6.0$	$R_{\text{eq}} = 2.22$	$N_{\text{eq}} = 6.6$	$R_{\text{eq}} = 2.38$
Gel4	$N_{\text{ax}} = 1.9$	$R_{\text{ax}} = 1.79$	$N_{\text{ax}} = 1.9$	$R_{\text{ax}} = 1.79$
	$N_{\text{eq}} = 5.2$	$R_{\text{eq}} = 2.22$	$N_{\text{eq}} = 5.8$	$R_{\text{eq}} = 2.39$
Gel5	$N_{\text{ax}} = 1.8$	$R_{\text{ax}} = 1.80$	$N_{\text{ax}} = 1.8$	$R_{\text{ax}} = 1.80$
	$N_{\text{eq}} = 5.0$	$R_{\text{eq}} = 2.22$	$N_{\text{eq}} = 5.6$	$R_{\text{eq}} = 2.38$

Coordination numbers and distances in the two sites occupied by uranium in the gels.

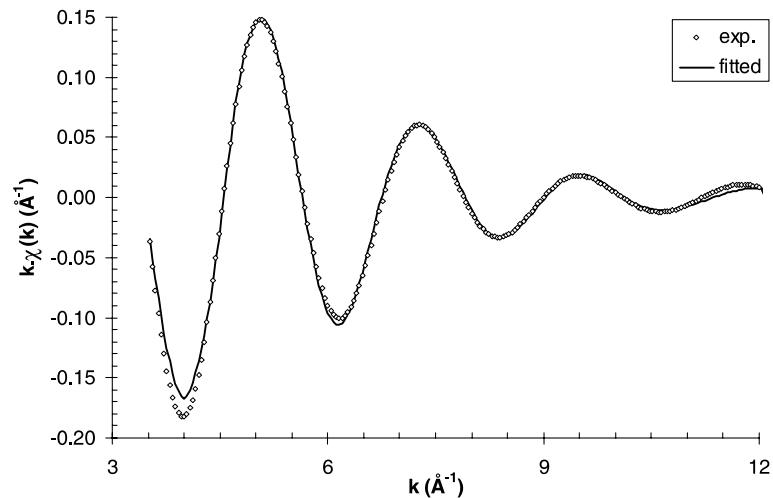


Fig. 8. Comparison between experimental EXAFS spectra and spectra fitted to three oxygen shells for gel Gel2.

uranium coordination number in the gel than in the glass.

The structural parameters of the two sites are shown in Table 7. During alteration, the coordination number of site 1 increased from 6 to about 7, with a slight (0.02 Å) increase in the equatorial distance. Site 2 changed to coordination number 8 with a greater increase in the equatorial distance (0.07 Å). This is a predictable evolution, since the largest increase in the coordination number occurred about the uranium site with the greatest equatorial distance.

It appears from these results that the uranium environment in the gels can be best described as simplified EXAFS γ - UO_3 like structure. However, the shortening of the two axial oxygen distances to 1.79 Å suggests the formation of an uranyl type of bond. So does the increase of coordination number and distances in the equatorial plane, we shall conclude at this point of our investigation that the uranium environment in the gels might be best described as locally distorted simplified EXAFS γ - UO_3 like structure rather than uranyl like structure due to the lack of obtaining satisfactory fit results with the uranyl hydroxide electronic parameters. Neither the uranium concentration in the gel nor the alteration conditions (renewal rate) affected the uranium–oxygen distances, which were identical in all the gels.

5. Conclusion

The uranium local environment in three SON68 glass samples doped with 0.75–3.5 wt% uranium and in the gels formed by pseudo-dynamic alteration of the glasses was investigated by XAS (XANES and EXAFS).

Uranium was found in the glass at oxidation state VI and at coordination number 6 with the same average distances than in UO_3 . The uranium was present at two sites, with axial uranium–oxygen distances of 1.80 Å and equatorial uranium–oxygen distances of 2.20 and 2.32 Å, respectively. Although the FT moduli accounting for the interatomic distance distribution showed no signs of a contribution from silicon, it is not possible to conclude that uranium was weakly bonded to the glass silicate network because of the noise level of the EXAFS spectra. The absence of any U–U signal suggests that uranium was uniformly distributed throughout the glass matrix, with no major U–U aggregates, although this interpretation is also subject to caution in view of the spectral noise. The uranium content of the glass had no effect on its structure, since the uranium–oxygen distances were identical in all three glass samples. Zirconium, a cross-linking element in the silicate network, had no effect on the local environment of uranium in the glass.

During glass alteration at various solution renewal rates, modifications were observed in the nature of the sites occupied by uranium in the gels. In the gels, uranium was found in a distorted simplified EXAFS UO_3 form that might better be viewed as an intermediate local environment between γ - UO_3 and uranyl hydroxide. The axial U–O distances were observed to diminish very slightly (–0.01 Å) while the equatorial distances and the coordination number increased by different amounts depending on the site concerned. At the site for which the U– O_{eq} distance was 2.20 Å in the glass, the distance increased to 2.22 Å and the coordination number increased to about 7, while for the other site the distance increased from 2.32 to 2.39 Å and the coordination number to about 8. The site with the shortest

bonds in the glass thus sustained relatively minor environmental changes, while significantly greater changes were observed for the site with the longest bonds. Moreover, as in the glasses, the distance distributions revealed no contribution by silicon or uranium and the noise level was lower in the EXAFS spectra for the gels than for the glasses. Apparently, no uranium aggregates were formed in the gels, even at very high renewal rates. The structural modifications around the uranium atoms thus occur practically in situ; uranium, when it is trapped in the gel, thus exhibits very low mobility, even if a significant change was observed in the nature of the site with the longest uranium–oxygen bonds. The solution renewal rate has no effect on the nature and structure of the uranium sites in the gel. The behavior of uranium during glass leaching thus more closely resembles that of iron than of zirconium [12].

Further coming investigation will involve glass leaching tests in reducing media (for a more realistic simulation of the conditions prevailing in a geological repository) to determine whether the uranium(VI) in the glass is reduced to oxidation state IV in the gel. Another related area of further investigation is the use of SON68 glass samples doped with Np, Pu and Am.

Acknowledgements

The authors are grateful to the personnel of the LURE facility at Orsay where the XAS spectra were acquired, to Dr L. Touret of the *École des Mines* in Paris for supplying the cuprosklodowskite, and to Dr F. Garrido of the Orsay CSNSM for supplying the γ - UO_3 .

References

- [1] D. Vollath, H. Wedemeyer, in: *Gmelin Handbook*, U suppl., vol. C4, 1984, p. 103.
- [2] B. Loopstra, *J. Inorg. Nucl. Chem.* 39 (1977) 75.
- [3] B. Loopstra, J. Taylor, A. Waugh, *J. Solid State Chem.* 20 (1977) 9.
- [4] J. Taylor, H. Hurst, *Acta Crystallogr. B* 27 (1971) 2018.
- [5] A. Rozenzweig, R. Ryan, *Am. Mineral.* USA 60 (1975) 448.
- [6] A. Michalowicz, *J. Phys. IV (Paris)* C2 (1997) 235.
- [7] A.L. Ankudinov, J.J. Rehr, *Phys. Rev. B* 56 (1997) 1712.
- [8] D. Petit-Maire, PhD thesis, University of Paris VI—P. and M. Curie, 1988.
- [9] F. Farges, C. Ponader, G. Calas, G. Brown, *Geochim. Cosmochim. Acta* 56 (1992) 4205.
- [10] P.G. Eller, G.D. Jarvinen, J.D. Purson, et al., *Radiochim. Acta* 39 (1985) 17.
- [11] S. Ricol, PhD thesis, University of Paris VI—P. and M. Curie, 1995.
- [12] E. Pelegrin, PhD thesis, University of Paris VII—D. Diderot, 2000.
- [13] D.J. Lam, B.W. Veal, A.P. Paulikas, *ACS Symposium Series* 216 (1983) 145.
- [14] B.M. Biwer, L. Soderholm, R.B. Gregor, F.W. Lytle, *Mater. Res. Soc. Symp. Proc.* 465 (1997) 229.
- [15] C. Den Auwer, E. Simoni, S. Conradson, J. Mustre de Leon, et al., *C. R. Acad. Sci. Série II Fascicule C-Chimie*, Paris 3 (2000) 327.
- [16] J. Petiau, G. Calas, D. Petit-Maire, *Phys. Rev. B* 34 (10) (1986) 7350.
- [17] G.N. Greaves, N.T. Barrett, G.M. Antonini, et al., *J. Am. Chem. Soc.* 111 (1989) 4313.
- [18] T. Reich, H. Moll, M.A. Denecke, et al., *Radiochim. Acta* 74 (1996) 219.
- [19] P.G. Allen, D.K. Shuh, J.J. Bucher, et al., *Radiochim. Acta* 75 (1996) 47.
- [20] N.J. Hess, W.J. Weber, S.D. Conradson, *J. Nucl. Mater.* 254 (1998) 175.