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Alteration kinetics of the glass-ceramic zirconolite and role of the alteration film – Comparison with the SON68 glass

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Abstract

The glass-ceramic zirconolite is being considered for specific conditioning of plutonium or the minor actinides. The actinides are distributed throughout the zirconolite crystals and the residual glass phase. Since zirconolite alteration is extremely limited, actinide release from the glass-ceramic material is mainly attributable to alteration of the residual glass. Specimens corresponding to the residual glass phase alone were therefore altered under different conditions to compare their kinetics with the one of the SON68 glass (inactive R7T7 type glass). Glass-ceramic zirconolite presents a more important rate decrease occuring more rapidly and that induces a quantity of glass altered at least 10 times as small as for SON68 glass. This slowdown of the alteration rate is attributed to the formation of an alteration film that has been the subject of a specific study. We have in particular identified a dense phase enriched in titanium and neodymium that probably influences deeply the kinetics.

1. Introduction

The nuclear glass R7T7 is presently used for the conditioning of the different radionuclides coming from the reprocessing of spent fuel of the French nuclear power plants. However, the conditioning of long-lived radionuclides in new dedicated host phases was one aspect of the enhanced separation strategy in the framework of the 1991 French law [1]. In the case of minor actinides (Am, Cm, Np), studies are conducted on ceramic or glass-ceramic matrix based on zirconolite $CaZrTi_2O_7$, and on ceramics based on britholite, thorium phosphate–diphosphate and monazite. This application is in particular contingent on a demonstration of the long-term aqueous corrosion resistance of the material.

Previous studies on natural analogues and on the Synroc have demonstrated the excellent chemical durability of the zirconolite ceramic: the alteration rate is 100 times as small as for SON68 glass (inactive R7T7 type glass) [2–5]. Since zirconolite alteration is extremely limited, actinide release from

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the glass-ceramic material is mainly attributable to alteration of the residual glass [6,7].

Dissolution kinetics of silicate glasses have been extensively studied [8–13]. For nuclear glasses, and especially for SON68 glass, these studies have allowed to identify several alteration steps characterized by different mechanisms: interdiffusion, alteration at the maximal alteration rate in pure water (r_0 so-called), slowdown of the alteration rate and a residual alteration rate (r_r so-called). The importance of these different phases deeply depends on the composition of the material.

Studies of the alteration kinetics of nuclear glasses have long attributed the observed slowdown in the rate to chemical affinity mechanisms (affinity laws) [14–16]. However, this theory has been called into question [17–19]. The mechanism currently taken into consideration by the CEA is the development of a protective gel forming a diffusion barrier for reactive species [20,21].

The formation of a protective gel implies the presence of silicon together with other elements (Al, Zr, Ca, etc.) at the reaction interface. The incorporation of insoluble elements in the glass does not always result in the formation of protective gels, however. Conversely, the alkaline-earths (calcium in particular) favour the development of protective gels. Synergy phenomena between Al/Ca and Zr/Ca have been observed during studies of simplified glasses with the same elemental ratios as SON68 glass [17,19,22]. Silicon retention within the gel is also considered to be one of the parameters affecting the protective properties of the gel layer [23].

The alteration film does not consist only of a potentially protective amorphous gel: the alteration of most complex glass compositions leads to the precipitation of ‘secondary’ phases from solution. They crystallize and are not considered to have protective properties. Some of these phases are thought to sustain glass alteration, or even to induce renewed alteration [24]. The gels formed by SON68 glass alteration at temperatures below 200 °C are mainly amorphous: the only crystalline phases detected are smectitic phyllosilicates [25].

Leach tests were therefore carried out to verify if the kinetics of glass-ceramic zirconolite was similar to the kinetics of the other nuclear glasses and more precisely: (i) to identify the different alteration steps and to assess their relative importance, (ii) to characterize the alteration film that is formed on the surface of the material, and (iii) to determine the role of the alteration film on the alteration kinetics of the glass-ceramic.

2. Studied materials

Zirconolite glass-ceramic is produced by melting an oxide mixture, the parent glass (Table 1), and submitting it to a heat treatment that directly determines the degree of crystallization, and thus the composition of the residual vitreous phase. Neodymium, is used as an actinide surrogate.

A reference composition of the residual glass has been defined for most of the kinetic tests (Table 2), with a small quantity of B_2O_3 used as an alteration tracer. In parallel, we have demonstrated that the glass-ceramic alteration is mainly attributable to the alteration of the vitreous phase and we have studied the influence of the presence of crystals on the alteration of the material [6,7].

In parallel, a specific study has been led on the influence of a variation of the residual glass composition [7,26]. Table 3 summarizes the glass domain studied (VRZ so-called). The experimentation plan methodology was applied to this mixture problem and Table 4 presents the studied glass compositions

Table 1
Composition of the parent glass of the glass-ceramic zirconolite (oxide wt%)

SiO_2	Al_2O_3	CaO	TiO_2	Nd_2O_3	ZrO_2
40.75	12	19.72	12.51	6.52	8.5

Table 2
Composition of the reference residual glass of the glass-ceramic zirconolite (oxide wt%)

SiO_2	Al_2O_3	CaO	TiO_2	ZrO_2	Nd_2O_3	B_2O_3
46.7	13.5	20.8	7.7	4.0	6.3	1

Table 3
Glass domain VRZ

Variables	Constant
$40.8 < SiO_2 < 55.6$	$B_2O_3 = 1$
$19.7 < CaO < 24.6$	
$9 < Al_2O_3 < 13.7$	
$1 < Nd_2O_3 < 6.5$	
$2 < ZrO_2 < 12$	
$6.2 < Ti_2O_2 < 15.5$	
($\Sigma = 99$ wt%)	

Table 4
Studied glass compositions from the domain VRZ (oxide wt%)

Glass	SiO_2	Al_2O_3	CaO	TiO_2	ZrO_2	Nd_2O_3	B_2O_3	Glass	SiO_2	Al_2O_3	CaO	TiO_2	ZrO_2	Nd_2O_3	B_2O_3
1	51.5	13.7	24.6	6.2	2.0	1.0	1	12	55.6	9.0	19.7	10.9	2.9	1.0	1
2	55.6	9.0	19.7	6.2	2.0	6.5	1	13	42.2	13.7	24.6	10.0	2.0	6.5	1
3	50.7	9.0	24.6	6.2	2.0	6.5	1	14	40.8	13.7	24.6	13.5	5.5	1.0	1
4	41.8	9.0	19.7	15.5	12.0	1.0	1	15	40.8	9.0	24.6	13.1	5.1	6.5	1
5	55.6	9.0	24.6	6.2	2.6	1.0	1	16	51.2	13.7	19.7	6.2	7.2	1.0	1
6	40.8	13.7	24.6	6.2	7.2	6.5	1	17	41.4	9.0	24.6	11.0	12.0	1.0	1
7	40.8	9.0	24.6	15.5	8.1	1.0	1	18	40.9	13.7	19.7	8.6	9.6	6.5	1
8	40.8	9.0	19.7	11.0	12.0	6.5	1	19	40.7	9.0	24.6	8.6	9.6	6.5	1
9	40.8	9.0	19.7	15.5	7.5	6.5	1	20	55.6	9.0	19.7	6.4	7.4	1.0	1
10	41.6	13.7	19.7	15.5	7.5	1.0	1	21	46.9	11.1	21.9	10.1	6.4	2.7	1

[26]. In all cases, a small quantity of B_2O_3 was added to materials as an alteration tracer.

3. Experimental protocols

3.1. Standard testing under 'initial' and 'saturation' conditions

The initial alteration rate in pure water at 100 °C (±0.5 °C) was determined using a Soxhlet device in compliance with the applicable French standard [27] on coupons polished to grade 4000 and washed; the shape of the test coupons allowed their surface area to be estimated simply and accurately [28]. Solution samples were taken at regular intervals (3, 7, 14, 28 d), acidified with 1 N HNO_3 and analyzed by ICP-AES (Si, B, Na, Al, Ca). The uncertainty ranged from 3% to 5% depending on the elements considered.

The glass alteration kinetics at high reaction progress were studied by static leaching experiments at 90 °C with the 63–100 μm powder size fraction and a monolith; the specimen-surface-area-to-solution-volume (S/V) ratio was between 6000 and $7000\,m^{-1}$. Each 500 mL PTFE reactor was placed in a 1-liter container with a few milliliters of water to limit evaporation. Solution samples were taken at regular intervals (7, 14, 28, 56, 91, 182, 364, 508, 600 and up to 1000 d) from each reactor, ultrafiltered to 10000 Da, acidified with 1 N HNO_3, and analyzed by ICP-AES (Si, B, Na, Al, Ca). The uncertainty ranged from 3% to 5% depending on the elements considered. The pH and temperature were measured for each sample with an ORION electrode.

The kinetic results of these tests have been already presented in a previous article [26]. We will remind the main results and focus on the characterization of the alteration film.

3.2. Static testing at different S/V

Other static leaching experiments at 90 °C corresponding to different S/V ratios have been carried out:

- $S/V = 10\,m^{-1}$: a low S/V corresponds to the alteration under initial conditions. As the volume of the solution is important, the concentrations in solution stay low during several days or months: that is why the alteration rate is closed to the initial rate r_0.
- $S/V = 3500\,m^{-1}$: a high S/V allows to access quickly to high aqueous concentrations. These experimental conditions allow to study the alteration of the material at high reaction progress.

All tests have been led with monoliths and, for high S/V, with 63–100 μm powder size fraction.

3.3. Perturbation tests (90 °C, $3500\,m^{-1}$)

These tests have been carried out in pure water at $S/V = 3500\,m^{-1}$ on two residual glasses from the VRZ domain prealtered 470 d at $7000\,m^{-1}$. The objective is to assess the possible protective effect of the alteration film by changing experimental conditions.

3.4. Expression of results

The results are expressed in terms of normalized mass loss for element (i) NL(i) or in terms of the equivalent alteration thickness e(i). NL(i) is calculated from the mass losses for element (i) normalized in terms of its mass fraction $x(\mathrm{i})$ in the glass and the surface area S in contact with the solution; it corresponds to the glass thickness of density ρ altered to obtain the concentration $C(\mathrm{i})$ in the solution volume V. The retention factor of an element in the alteration film is defined with respect to the alteration tracer elements (boron, for the tests described here).

$$\text{Thus}: \quad \mathrm{NL}_{(\mathrm{i})} = \frac{C_{(\mathrm{i})}.V}{S.x_{(\mathrm{i})}}\ (\mathrm{g}\cdot\mathrm{m}^{-2}) \quad e_{(\mathrm{i})} = \frac{\mathrm{NL}_{(\mathrm{i})}}{\rho}\ (\mathrm{m}).$$

The initial alteration rate r_0 is calculated by linear regression from the normalized mass loss for boron NL(B) obtained during the Soxhlet tests.

The alteration rate at advanced stages of reaction progress r_r is determined from the static leaching experiments under 'saturation' conditions (high S/V) by linear regression from the NL(B) values obtained for the last three samples. However, during alteration of residual glass samples at high S/V ratios, r_r could not be determined in this way because the normalized boron mass loss appear to be constant over time. We therefore considered the one-year mean value $\mathrm{NL(B)}_\mathrm{mean}$ as well as the mean alteration rate estimated from $\mathrm{NL(B)}_\mathrm{mean}$:

$$r_\mathrm{mean}(1\ \text{year}) = \mathrm{NL(B)}_\mathrm{mean}/360\ (\mathrm{g}\cdot\mathrm{m}^{-2}\ \mathrm{d}^{-1}).$$

This is the only statistically possible calculation mode, but it considerably overestimates the one-year alteration kinetics.

3.5. SEM and STEM observations

The altered glass samples were observed with a scanning electron microscope. The altered glass coupons were cut at right angles to their largest surface, then embedded in resin. Polishing to within one micrometer revealed their alteration profile. The surface of the polished cross sections was covered with carbon or platinum prior to field-effect scanning electron microscope observation (JEOL 6330 with PGT analysis system). Coupling with an energy-dispersive (EDS) analyzer allowed element distribution maps to be plotted, making qualitative or semi-qualitative chemical analysis possible on the carbon-metallized specimens. Platinum metallization was used to enhance the image quality at high magnification, and thus to measure very thin alteration depths.

Some other altered glass samples were cut by ultramicrotomy and observed with a scanning transmission electron microscope MET JEOL 2000FX with a SiLi detector and coupled with a system of chemical microanalysis EDS TRACOR 5500 Série 2.

4. Results

4.1. Initial alteration rate

The Soxhlet tests have allowed to determine the initial alteration rate r_0 of the reference residual glass: $1.2 \pm 0.1\ \mathrm{g\,m^{-2}\,d^{-1}}$. Table 5 presents the initial alteration rates r_0 measured on the VRZ composition domain: they vary between 0.5 and $2.6\ \mathrm{g\,m^{-2}\,d^{-1}}$ [7,26]. The initial alteration rates of SON68-glass, reference residual glass and VRZ glasses are relatively similar.

4.2. Slowdown of the alteration rate and residual alteration rate

Studies on SON68-glass have shown that the initial phase of the alteration is followed by a slowdown of the alteration rate. The analysis of results obtained for residual glasses altered at low S/V ($10\ \mathrm{m^{-1}}$, 90 °C) reveals an almost immediate and very important decrease of the alteration rate (Fig. 1). We point out that for the last two samples, we observed a significant water loss due to evaporation (about 4%). Then, we did not consider these points as representative and did not try to analyse the apparent decrease of NL(i).

The fall of alteration rate at 90 °C has been determined by considering kinetic tests at $10\ \mathrm{m^{-1}}$ and $7000\ \mathrm{m^{-1}}$ (Fig. 2). The leaching test at low S/V

Table 5
Initial alteration rate r_0 ($\mathrm{g\,m^{-2}\,d^{-1}}$) of residual glasses VRZ (90 °C, $10\ \mathrm{m^{-1}}$)

Glass°	1	2	3	4	5	6	7	8	9	10	11
r_0 exp.	0.49	0.78	1.25	0.79	0.55	1.74	1.43	1.03	1.08	0.98	1.06
Glass°	12	13	14	15	16	17	18	19	20	21	
r_0 exp.	0.97	2.60	1.54	2.07	0.55	1.64	1.26	1.36	0.57	1.06	

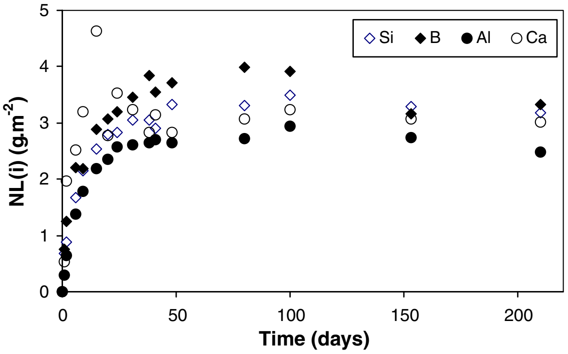

Fig. 1. Variability of normalized mass losses of Si, B, Al and Ca (g m^{-2}) during the alteration test (10 m^{-1}, 90 °C) of the reference residual glass.

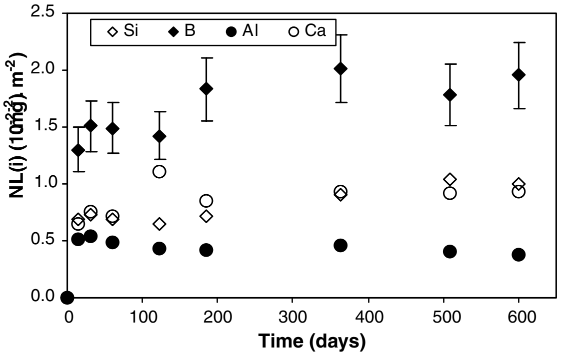

Fig. 2. Variability of normalized mass losses of Si, B, Al and Ca (g m^{-2}) during the alteration test (90 °C, 7000 m^{-1}) of the reference residual glass.

(10 m^{-1}) leads to an initial rate (calculated from NL(B) 1 d) of 0.8 g m^{-2} d^{-1}. The alteration rate at advanced stages of reaction progress r_r is determined by linear regression from the NL(B) values obtained for the last four samples during the test at 7000 m^{-1}: $r_r = 2 \times 10^{-5}$ g m^{-2} d^{-1}. This leads to a rate fall of the order of 40000.

We have already shown that the composition does not appear to have a significant effect on the normalized boron mass loss and thus on the alteration rate within the VRZ domain. All the glasses studied exhibited a kinetic profile characteristic of an extremely low long-term alteration rate between 4 and 8×10^{-5} g m^{-2} d^{-1} with steady-state boron mass losses over time [7,26].

4.3. Chemical variability of the alteration film

During the different leaching tests (Soxhlet tests, static tests at 10 m^{-1} and 7000 m^{-1}), the chemical composition of the alteration film of the reference residual glass has been determined from analysis of the aqueous solutions (Table 6). The boron concentration, as alteration tracer, allows to calculate the quantity of altered glass. From the composition of the reference glass, we deduce the total quantity of each other element (Si, Al, Ca, Zr, Ti, Nd) which is either in solution, or retained in the alteration film. Then, the aqueous concentrations of Si, Al and Ca allow to deduce the quantity really retained in the alteration film for each of them. The elements Ti, Zr and Nd have been considered as fully retained in the alteration film because their concentrations in solution are inferior to the detection limits (0.01 ppm for Zr and Nd, 0.1 ppm for Ti).

The obtained composition corresponds to a mean composition of the alteration film: it does not take into account the presence of possible secondary phases.

During the first 8 d of the Soxhlet tests, the composition of the alteration film and the reference residual glass are close, except for silicon. From 15 d, the composition deeply changes with a decrease of silicon and calcium. We observe a similar evolution during the kinetic test (90 °C, 10 m^{-1}) before a stabilisation of the composition of the alteration film from 30 d: the contents of heavy elements are identical to those obtained for the Soxhlet tests, only the distribution $SiO_2/Al_2O_3/CaO$ has clearly changed. For the kinetic test at high S/V (7000 m^{-1}), the composition of the alteration film is constant from the first sample with higher contents in SiO_2, CaO and Al_2O_3.

These results seem to show that the alteration consists first in the release of silicon and calcium after the hydrolysis of the silica network, and then in an evolution with time probably induced by hydrolysis/recondensation of silicon.

4.4. Protective effect

The alteration film that forms at the surface of nuclear glasses is essentially composed of an amorphous gel; some secondary crystalline phases can form through precipitation too. This alteration film is assumed to act as a protective barrier against alteration and to be responsible for the slowdown of the alteration rate.

Perturbation tests allow us to verify if such a protective effect is observed for the residual glasses. The residual glasses from VRZ domain selected for these tests are glasses 15 and 19. They have been chosen

Table 6
Chemical composition of the alteration film (wt%) during kinetic tests led on the reference residual glass (relative uncertainty: 10%): Soxhlet test and kinetic tests at 90 °C for two *S*/*V*: 10 m^{-1} (mean composition 30–300 d) and 7000 m^{-1} (mean composition 14–600 d); the composition of the reference residual glass is reminded on the first line

Test	SiO_2	Al_2O_3	CaO	TiO_2	ZrO_2	Nd_2O_3	B_2O_3
Residual glass	46.7	13.5	20.8	7.7	4.0	6.3	1
Soxhlet (15–28 d)							–
7 d	38	18	20	10	5	9	–
15 d	0	26	1	31	16	26	–
22 d	0	27	0	31	16	26	–
29 d	9	24	5	27	14	22	–
90 °C, 10 m^{-1} (30–300 d)	20	12	10	25	13	20	–
90 °C, 7000 m^{-1} (14–600 d)	40	17	17	11	6	9	–

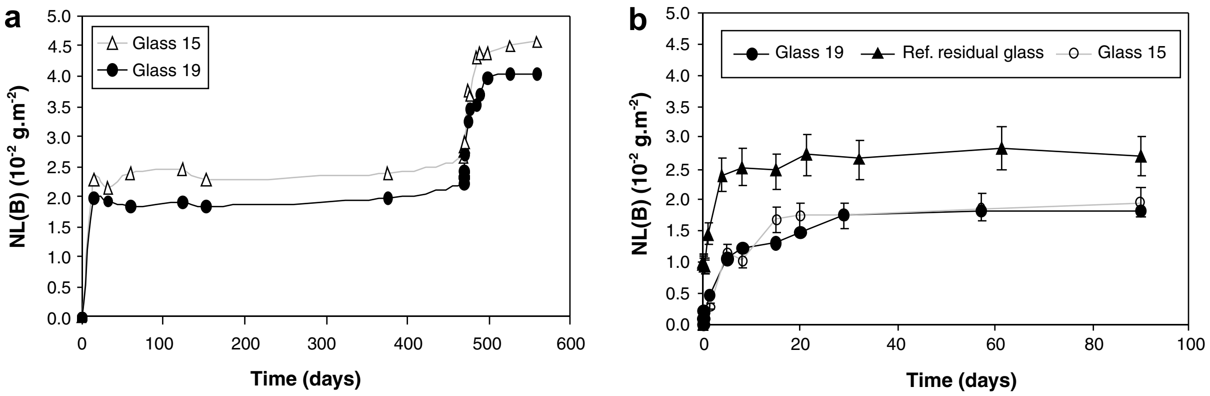

Fig. 3. Evolution of normalized mass loss of boron (10^{-2} g m^{-2}): (a) glasses 15 and 19 prealteration of 470 d (90 °C, 7000 m^{-1}) before alteration in pure water (90 °C, 3500 m^{-1}); (b) comparison between the realteration of prealtered residual glasses 15 and 19 with the alteration of the (non-prealtered) reference residual glass (90 °C, 3500 m^{-1}).

because their compositions only differ by ZrO_2 and TiO_2 contents (Tables 2 and 4). Moreover, according to Table 5, their initial alteration rates are close or superior to the one of the reference residual glass.

Fig. 3 presents the evolution with time of normalized mass loss of boron.

Fig. 3(a) shows that the alteration of prealtered glasses starts again in pure water before a new slowdown of the alteration rate. However, the comparison of this realteration with the non-prealtered glass altered in the same conditions points out that the alteration is less important of 30% (Fig. 3(b)). The initial alteration rate of the residual glasses 15 and 19 does not explain this difference.

Moreover, this difference between normalized mass losses is significative only for boron (Table 7). The normalized mass losses of the other elements (aluminium, calcium and silicon) are very close: this corresponds to a dissolution of the preexisting alteration film.

5. Discussion

We have seen that the kinetic profile (i.e. the evolution of the altered thickness versus time) of the VRZ residual glasses is characterised by an initial alteration rate, and especially an almost immediate and very important decrease of the alteration rate. This leads to an extremely low long-term alteration thickness, lower than for the SON68 glass, as shown in more details in Frugier et al. [26]. The study of residual zirconolite glasses has not pointed out any preponderant effect of any component on the residual alteration rate: the composition of these glasses does not influence long term kinetics. However, the presence of zirconium or titanium and the absence of alkalis and boron could explain the kinetic profile of these glasses and their high durability [7,26].

We will now focus on the role of the alteration film in the case of glass-ceramic zirconolite and on

Table 7
Normalized mass losses of Si, B, Al and Ca (10^{-2} g m^{-2}) measured during the alteration of the reference residual glass (90 °C, 3500 m^{-1}) and realteration in pure water of prealtered residual glasses 15 and 19 (90 °C, 3500 m^{-1})

Time	Reference residual glass				Glass 15				Glass 19			
	Si	B	Al	Ca	Si	B	Al	Ca	Si	B	Al	Ca
5 min	0.020	<1.0	0.022	0.081	0.056	<0.2	0.032	0.13	0.057	<0.2	0.013	0.37
10 min	0.014	<1.0	0.022	0.069	0.042	<0.1	0.026	0.19	0.075	<0.1	0.013	0.42
30 min	0.053	<1.0	0.034	0.11	0.043	<0.1	0.038	0.11	0.011	<0.1	0.064	0.28
1 h	0.10	<1.0	0.076	0.13	0.048	<0.1	0.036	0.084	0.022	<0.1	0.019	0.42
5 h	0.38	<1.0	0.33	0.40	0.16	0.097	0.11	0.21	0.11	<0.1	0.032	0.14
1 d	1.0	1.5	0.92	1.0	0.62	0.29	0.51	0.59	0.50	0.48	0.44	0.49
4 d	1.5	2.4	1.2	1.5	1.1	1.1	0.87	1.3	0.86	1.1	0.75	0.93
8 d	1.6	2.6	1.2	1.6	1.1	1.0	0.80	1.2	0.93	1.2	0.68	1.1
15 d	1.5	2.5	1.2	1.7	1.2	1.7	0.91	1.3	1.0	1.3	0.85	1.4
32 d	1.5	2.6	1.0	1.5	1.2	1.7	0.95	1.2	1.0	1.8	0.82	1.0
61 d	1.5	2.8	1.0	1.5	1.2	1.9	0.99	1.3	1.0	1.8	0.83	1.5
90 d	1.4	2.7	1.0	1.5	1.2	1.9	0.98	1.3	1.0	1.8	0.77	1.5

the alteration mechanisms in order to explain this different comportment. Parallel studies led on SON68 glasses have shown the link between the slowdown of the alteration rate and the alteration film that is considered as a diffusion barrier [29]. We have tried to deduce from the obtained results whether the alteration film could explain the slowdown of rate in the case of residual glasses too. Indeed, as for the SON68 glass, the alteration of the reference residual glass is characterised by an initial alteration before a decrease of the alteration rate, and residual alteration. That’s why a control of the kinetics due to the development of a protective gel as for SON68 seems possible.

This protective effect appears during perturbation tests. However, it is very different from the one observed for SON68. Indeed, the same test done with SON68 leads to a realteration with a rate deeply smaller than for a non-prealtered sample, of the order of $r_0/300$ (Fig. 4) [23].

It reveals that the gel of the residual glass, even if it is more protective than the gel of SON68 (because it slowdowns quickly and deeply the alteration rate of the glass) is however more fragile. Indeed, when the prealtered sample is put back in pure water, the gel loses a great part of its protective effect: the alteration rate is inferior of only 30% to the alteration rate of the non-prealtered glass. The gel of the SON68 glass preserves its protective properties, hence a very small alteration ($r_0/300$).

This result conducts us to assume that the two gels are deeply different and that the difference of kinetic comportment is probably linked with the structure of the gel, in terms of composition and/or porosity.

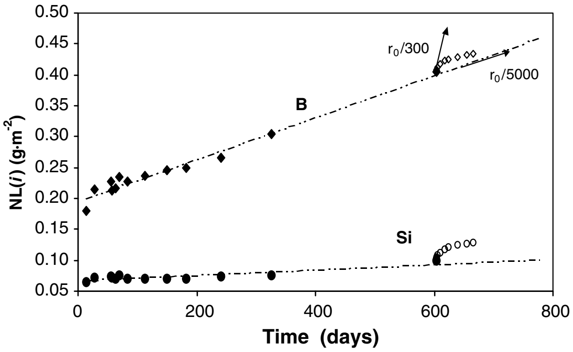

Fig. 4. Normalized mass losses in boron and silicon (g m^{-2}) measured during the prealteration of SON68 glass (dark) and after putting back in pure water (white) (90 °C, 5000 m^{-1}).

The comparison of concentrations in solution measured for the different kinetic tests (90 °C, different S/V) carried out on residual glasses does not show any significative influence of the S/V ratio on long-term concentrations (Fig. 5(a)). This is completely different in the case of SON68 (Fig. 5(b)).

The results of kinetic tests (90 °C, 7000 m^{-1}) during 1000 d on 7 residual glasses give us new informations. Whereas all the glasses present a very low alteration rate (between 4 and 5×10^{-5} g m^{-2} d^{-1}), the silicon concentration is constant for three glasses (glasses 14-18-20, Fig. 6(b)) and increases significantly for the four others (glasses 1-4-5-7, Fig. 6(a)). This observation calls the hypothesis of a control of the kinetics by silicon into question.

This calls the supposed link between protective effect and the silicon retention factor into question

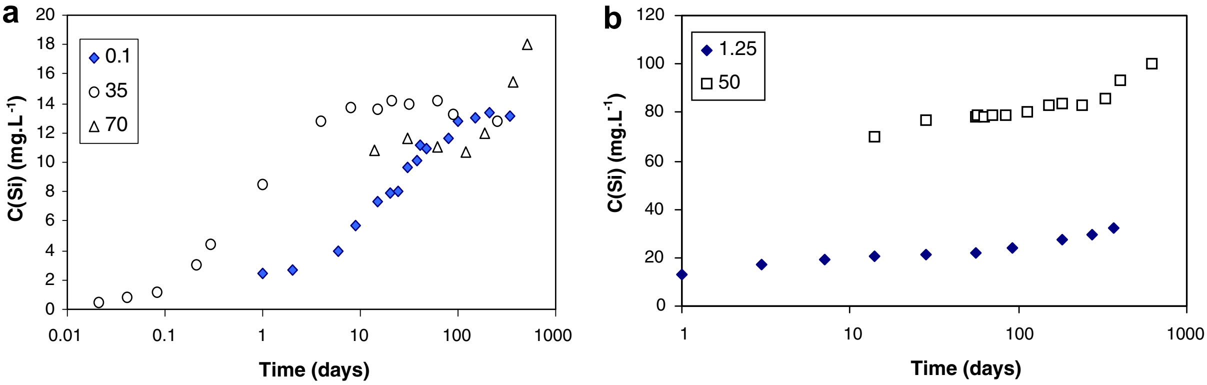

Fig. 5. Evolution of Si concentrations (mg L^{-1}) during the alteration: (a) of the reference residual glass (90 °C, 10 m^{-1}, 3500 m^{-1}, 7000 m^{-1}); (b) of the R7T7 glass (90 °C, 125 m^{-1}, 5000 m^{-1}).

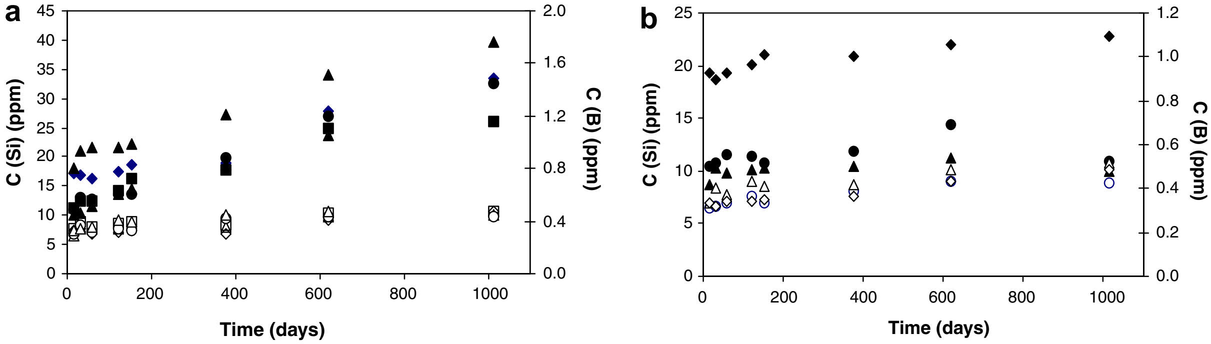

Fig. 6. Evolution of concentrations (ppm) of boron (white) and of silicon (dark) of the seven glasses from the VRZ domain altered in pure water (90 °C, 7000 m^{-1}): (a) VRZ glasses 1-4-5-7, (b) VRZ glasses 14-18-20.

too. In the case of the SON68 glass, it has been demonstrated that the higher the silicon retention factor is, the more protective the gel is [30]. But the silicon retention factor measured for SON68 glass reaches 80–90% whereas the retention factors measured for residual glasses in the same conditions vary between only 40% and 60%.

Moreover, whereas an increase of the silicon concentration in solution corresponds to a decrease of the silicon retention factor of residual glasses (Fig. 6(a)), the protective effect of the gel is not modified since the alteration rate stays weak (between 4 and 4.9 g m^{-2} d^{-1}).

These results lead us to suppose that the alteration of the residual glass is linked with a diffusive phenomenon through the gel that forms by hydrolysis/recondensation of silicon. However, it is probably not the preponderant mechanism that can explain the slowdown of the alteration rate and the protective effect of the gel: an other chemical element could control the alteration.

We have observed by STEM microscopy samples of the reference residual glass altered at 90 °C or 150 °C and at 10 m^{-1}. At 90 °C, we remind that the alteration rate slows after one month. Then, the alteration continues with a weak residual alteration rate: the gel is then considered as protective. The alteration film after 300 d of alteration at 90 °C is of the order of 1 μm and we can observe (Fig. 7): (i) an outer crystalline 300 nm-thick phase which is rich in titanium, (ii) the inner gel whose total thickness is close to 700 nm with an intermediate dark part of 170 nm.

An EDS-analysis has allowed to characterize more precisely secondary phases and the superior part of the amorphous gel (called dark zone) on sample altered at 150 °C. Table 8 and Fig. 8 present the obtained results. We consider the elementary ratio with zirconium as reference: this choice allows a fairer description of the observed variations.

The crystalline phase is mainly composed of TiO_2 and Nd_2O_3.

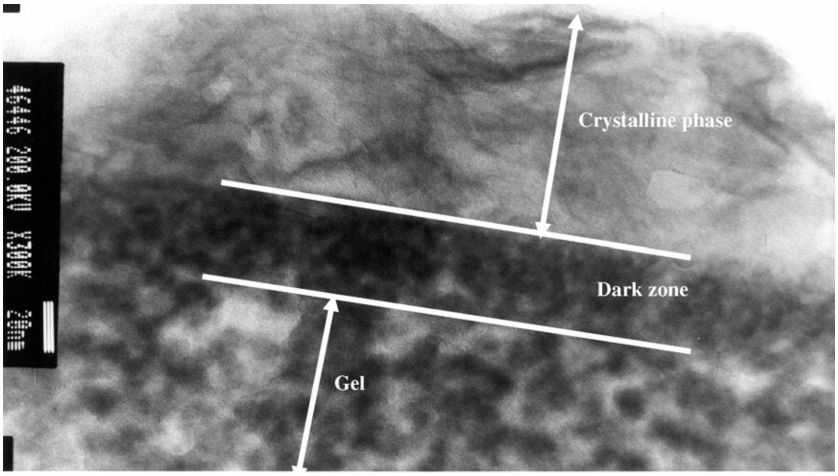

Fig. 7. STEM image of the alteration film of the reference residual glass after 300 d of alteration (90 °C, 10 m^{-1}). (The non-altered glass is below the gel, the solution above the crystalline phase.)

Table 8
Elementary ratios (with zirconium as reference) in the different analyzed zones

	Si/Zr	Al/Zr	Ca/Zr	Ti/Zr	Nd/Zr
Residual glass	**16.8**	**4.6**	**8.1**	2.0	1.1
abs. uncertainty	0.5	0.5	0.8	0.2	0.1
Gel	**3.0**	**1.0**	**0.57**	**1.0**	**0.8**
abs. uncertainty	0.3	0.1	0.06	0.2	0.1
Dark zone	2.1	0.8	0.5	**2.5**	**1.6**
abs. uncertainty	0.3	0.2	0.1	0.5	0.2
Crystalline phase	3.0	2.0	0.8	**21**	3.0
abs. uncertainty	1.4	0.6	0.4	7	1.1

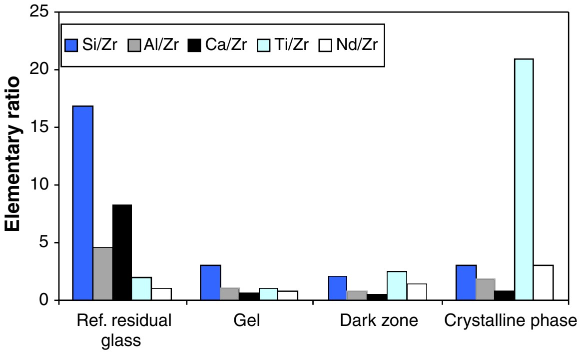

Fig. 8. Variation of elementary ratios (with zirconium as reference) in the different zones observed on sample of the reference residual glass (150 °C 10 m^{-1}).

The gel distinguishes from residual glass by a sharp decrease of the contents of Si, Al and Ca. Any significative gradient has been pointed in the gel because of an important experimental incertitude.

The amorphous part of the alteration film is composed of two distinct parts: the superior 20 nm-thick layer (dark zone) appears particularly dense and is characterized by an impoverishment in Si and by an important enrichment in Ti and Nd.

The observation of this dark dense zone at the interface gel/crystalline phase seems an important step for the comprehension of the alteration mechanisms of the residual glass. It appears dense enough to explain a sharp decrease of the alteration rate. Although this hypothesis seems the more likely, we need some elements to validate it definitely. Complementary observations before and during the rate decrease should have been done to confirm the role of the dark zone. However, parallel studies of Rebiscoul et al. [29,31,32] have confirmed our observations for residual glasses which present characteristic kinetic profile.

As the influence of components is concerned, a more systematic study based on the main components of nuclear glasses (Si, Al, Ca, Na, Zr, Ti, Mg) has begun. These experiments focus on the interactions between two components, in particular Ca/Zr that seem to have a benefic role according different recent obtained results.

First, we have seen in the case of residual glasses that the sharp decrease of the alteration rate is associated with a zirconium-rich gel. Other studies have already pointed out that calcium, in synergy with aluminium or zirconium could favour the decrease

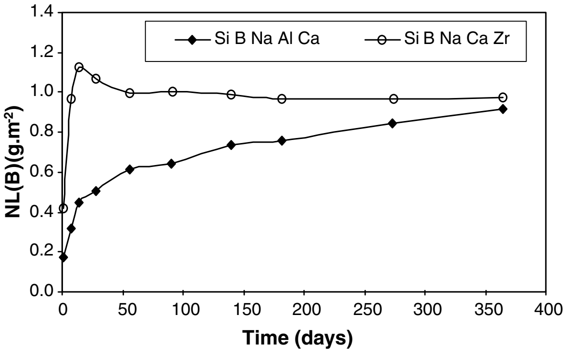

Fig. 9. Evolution of the alteration of glasses CJ3 (Si, B, Na, Ca, Al) and CJ9 (Si, B, Na, Ca, Zr) (Gin, unpublished).

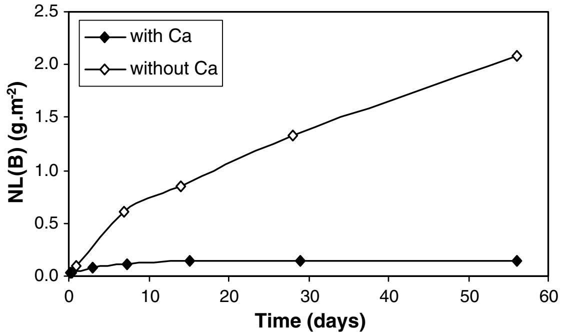

Fig. 10. Evolution of normalized mass loss of boron during the alteration of the glass (Si, B, Na, Al, Zr) at 90 °C in a solution containing calcium (200 ppm) (Frugier, unpublished).

of the alteration rate. Then, the kinetic profile of a glass composed of Si, B, Na, Ca, Zr (CJ9 glass whose composition is defined from the SON68 glass) is similar to the profile of residual glasses with a sharp decrease of the alteration rate (Fig. 9). Another alteration test in a calcium-rich solution carried out on a glass composed of Si, B, Na, Al, Zr shows that calcium in solution modifies the kinetic profile and leads to a slowdown of the alteration rate as for CJ9 glass and residual glasses (Fig. 10). All these results could bear out a predominant effect of zirconium, probably in association with Ca, on alteration kinetics [22,30,32].

6. Conclusions

This study points out that the reference residual glass, and then the zirconolite glass-ceramic, presents a better chemical durability than the glass SON68. The two materials present a similar initial alteration rate but their kinetic profiles (the evolution of the altered thickness versus time) are different.

Indeed, the reference residual glass is characterized by a more important slowdown of the rate and a smaller residual alteration rate than for the SON68 glass ($<10^{-5}$ g m^{-2} d^{-1}). It's reminded that an alteration rate of 10^{-5} g m^{-2} d^{-1} corresponds (taking into account the density of materials) to an alteration of roughly 10^{-3} nm d^{-1}, 0.36 nm year^{-1} and 3.6 μm in 10000 years, that stays extremely weak. Moreover, this residual alteration rate is independent of the glass composition in the studied glass domain VRZ. This enables to consider a certain flexibility in the zirconolite glass-ceramic elaboration: a modification of the parent glass in order to increase the crystallization ratio will not call the chemical durability of the glass-ceramic into question.

The high slowdown of the alteration rate is attributed, as for the SON68 glass, to the formation of an alteration film that is considered as a diffusive barrier. The characterization of this film has pointed out that the amorphous gel is composed of two distinct parts: the superior layer containing Ti and Nd is likely to slow down sharply, or even to stop the alteration. Moreover, silicium does not appear as the 'key element' controlling the alteration of the reference residual glass. This points out that parameters used to characterize the protective effect of the alteration film have to be chosen with attention. The obtained results for the reference residual glass lead us to study more in details the interaction Ca/Zr and the superior layer of the gel that could contribute to the high slowdown of the alteration rate.

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