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Highlights

- ISG glass was irradiated with 7 MeV gold ions.
- Leaching experiments were performed on irradiated and non-irradiated samples.
- Initial alteration rate of ISG glass increased by a factor of 2 after irradiation with Au-ion.

Abstract

This study addresses the impact of 7 MeV Au irradiation on the initial alteration rate of International Simple Glass (ISG), considered as a reference for nuclear glasses. This irradiation scenario simulates the effect of nuclear collisions of the recoil nuclei of α decays. In order to study the very first moments of glass alteration, non-irradiated and Au-ion irradiated ISG glass monoliths were altered in pure water at 90°C, pH 9 and with a ratio of glass surface area to solution volume of 0.01 cm^{-1}. Glass alteration was monitored by measuring the releases of the glass elements in solution by UV-visible spectrophotometry and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Under these alteration conditions, the releases of the elements in solution are congruent. The initial

alteration rate was found to be (2.0 ± 0.8) times higher for the irradiated glass monoliths than for non-irradiated samples.

Introduction

France has chosen to reprocess spent fuel in order to save part of the uranium resources through the manufacture of MOx fuel. This recycling strategy also reduces the radiotoxicity of final waste as well as its volume [1, 2]. In order to find a management solution suitable to each type of nuclear waste, they are classified according to their level of radioactivity and lifetime [3]. High-level waste (HLW) are packaged into a vitrified form and are intended for long-term disposal in a deep geological repository (Cigeo project)[4, 5]. Once the waste packages are introduced into the disposal site, the glass will initially evolve into a closed (free of water) system and will be subjected to its own self-irradiation due to the fission products and minor actinides incorporated in the glass structure [1]. Fission products produce β decays accompanied by γ transitions that predominate with respect to the total radioactivity of the waste in the short term (after 100 years, beta/gamma and alpha activities are respectively of around $7x10^{9}$Bq/g and 10^{8}Bq/g), while α decays coming from actinide decays are the main contributor to the activity for the long-term (after 1000 years, beta/gamma and alpha activities are respectively of around $3x10^{6}$Bq/g and $4x10^{7}$Bq/g) [6]. α decays are responsible for the production of recoil nuclei (with an energy ranging from 80 to 120 keV) and α particles (with an energy ranging from 4 to 6 MeV). The glass is therefore submitted to dose rate and cumulative dose caused by these radiation sources, which can damage the glass by accumulation of radiation effects into the glass structure.

There are many studies [7-10] on the impact of irradiation on the structure and the macroscopic properties of borosilicate glasses including ISG glass (reference glass chosen by the international scientific community). These studies have shown that nuclear effects are more efficient than electronic ones to damage the glass structure [8]. It was shown that the maximum changes in the glassy state (also called saturation damage state) are induced by nuclear collisions at a dose level of around 30 to 40 MGy, corresponding to around 500 years of radiation ageing of nuclear glass. Electronic effects induced a lower damage level than nuclear effects and require a higher dose level of around 3GGy (corresponding to of around several decades of radiation ageing of nuclear glass) to reach the saturation damage state [8]. Moreover coupled effects between nuclear and electronic collisions have

been observed [8]. Indeed, the α particles induce a partial annealing of the damage generated by the heavy ions. In addition, Angeli et al [11] studied the effect of hyperquenching on ISG glass fibers and reported a disordered structure similar to that of induced by irradiation.

After a few hundred or even a few thousand years, water will access the cells containing the waste packages. Then, the glass will evolve into an open system (presence of water), which represents a risk of dissemination of radionuclides by water. It is thus of primary importance to assess the glass chemical durability. Once the glass package is in contact with the groundwater, exchanges of chemical species take place at the solid/solution interface leading to changes in the properties of the glass [4, 12, 13]. Several successive mechanisms occur at the glass/solution interface with different kinetics. Glass hydration by diffusion of water in its structure precedes the interdiffusion step, which consists of an ion exchange between the protons from the solution and the alkaline elements contained in a layer of a few angstroms at the glass surface. Then, hydrolysis of the vitreous network consists of a nucleophilic attack of a hydroxide ion OH^- on a bridging bond leading to the dissolution of the glass [14]. The maximum alteration rate (called r_0) in a given environment is observed during the hydrolysis stage.

The impact of the recoil nuclei of α decays on the glass initial alteration rate regime has already been partially addressed in the literature. Most studies are dedicated to glasses of complex composition and did not show any effect of radiation on the initial alteration rate [15, 16]. Recent studies, rather focused on simplified glasses, seem to indicate an impact of this type of irradiation at short alteration times [17-19]. However, these studies did not fill all the gaps. Indeed, Karakurt et al.[17] studied the alteration of ISG glass irradiated with 7 MeV Au ion up a fluency of $6.4 .10^{13} at.cm^{-2}$, but the first measurements of altered depths were already beyond the irradiated zone (after 2 days reached 3 µm, so beyond the irradiated zone) and therefore the measured rates corresponded rather to non irradiated glass. Zhang et al. [19] studied a simple 3-oxide glass, as well as Lonartz et al. [18]. In addition, the ions used have a high energy whose representativeness of the effects of self-irradiation by α decay is not yet fully demonstrated and the alteration conditions do not quite correspond to an

initial alteration regime. That's why this study focused on ISG glass (reference glass chosen by the scientific community), irradiated with 7 MeV gold ion irradiation in order to simulate the nuclear damage caused by recoil nuclei of α decays. In addition, the structural evolution of ISG submitted to this type of irradiation has already been described in the literature [8-10]. Leaching tests have been performed using low surface over solution volume ratio to determine the initial leaching rate of irradiated and non-irradiated ISG glass samples. The current article presents the experimental conditions, the results of the leaching tests and discusses the origin of the effect of the external irradiation on the leaching rate.

Materials and methods

Glass samples preparation

In this study, the alteration experiments were carried out on the International Simple Glass (ISG) provided by MoSCI Corporation (Rolla, Missouri, USA). Its composition is given in Table 1 [4].

Table 1: ISG glass composition.

Oxide	**SiO_2**	**B_2O_3**	**Na_2O**	**Al_2O_3**	**CaO**	**ZrO_2**	
wt %	56.2	17.3	12.2	6.1	5.0	3.3	
mol %	60.1	16.0	12.7	3.8	5.7	1.7	
Element	**Si**	**B**	**Na**	**Al**	**Ca**	**Zr**	**O**
wt %	26.3	5.4	9.0	3.2	3.6	2.4	50.1
mol %	18.0	9.6	7.6	2.3	1.7	0.5	60.3

Glass monoliths were obtained from a glass cylinder of 2 cm in diameter that was cut into six monoliths (more or less equivalent in size) which were polished to optical grade (1/4 micron finish) on both sides (up to reach a sample thickness of 700 µm) and on the edge (Prime Verre company, Montpellier, France). Indeed, surface roughness may influence glass alteration [20, 21] therefore, it is necessary that the samples would be completely polished. The geometric surface area of the polished monoliths was considered in calculations of the normalized alteration rate.

Irradiation scenario

ISG glass monoliths were irradiated on both sides with 7 MeV Au^{3+} ions on the 2MV Aramis accelerator at the SCALP facility (CNRS-CSNSM, Orsay, France) to induce a significant nuclear damage in the glass structure as demonstrated in numerous studies that have been recently reviewed in [8]. A fluence of 2×10^{14} at.cm^{-2} was used, which induces a minimum nuclear dose of around 40 MGy in the whole irradiated depth [9] and thus to reach the saturation damage, i.e. the maximum damage level that can be induced in a glass with nuclear collisions [8]. However, the concentration of Au ion in the glass is very low in the present study (< 0.006 at.%) so that any chemical modification induced by Au on the structure of the glass can be ruled out. The Au implantation profile was measured by negative ions analysis by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and was also obtained by simulation with the Stopping and Range of Ions in Matter (SRIM) software [22]. It was shown that the 7 MeV Au^{3+} ions stop after a range of around 2 µm within the glass [9], creating thus a damage depth of 2 µm thick. It is worth noting that the alteration protocol was chosen to generate an altered depth less than or equal to the damaged depth so that the non-irradiated glass does not contribute to the initial alteration rate value. However, in addition to the two main irradiated faces, the edges of the sample which had not been irradiated and represented 10 % of the geometrical surface area contributed to the release of elements in solution. Thus, a correction was achieved when calculating the alteration rate (see equation 3).

Alteration protocol

The leaching experiments were carried out in PFA (Perfluoroalkoxy) reactors, Savillex® brand. These experiments were conducted on the non-irradiated ISG glass (named NI_glass later) and on the ISG glass irradiated with Au-ion (named Au_glass later). The alteration experiments were performed in an oven at 90°C and at a $pH_{90°C}$ of 9.0 ± 0.2. Several reasons explain the choice of this pH. Hydrolysis is a mechanism closely linked to protonation and hydroxylation of the glass surface, in particular the

adsorption of OH^- on Si sites in basic media. This mechanism is clearly favored in basic media. In order to be at a basic pH in a buffered solution (in order to remain the pH stable during the whole experiment duration), to be close to the pH measured on long term leaching experiments implemented in initial pure water and to have the possibility to compare our study to results in the literature, $pH_{90°C}$ 9 was a good compromise.

The solution was continuously stirred thanks to a magnetic stirrer. The volume of solution (approximately 670 mL) was adapted to the surface area of the coupon to reach the chosen surface over solution volume ratio (SA/V) of 0.01 cm^{-1}. The pH 9 solution was prepared by adding 9.53 mg of lithium hydroxide (99.995% purity, Alfa Aesar) into 1 L of deionized water. The pH was measured once the solution was prepared, at 90°C, under strong stirring and reached 9.0 ± 0.2. Then, the lithium hydroxide solution was introduced into the Savillex® reactor that was placed for the night in an oven at 90°C the day before the start of the experiment. At the beginning of the experiment, a PFA sample holder was held in the middle of the leachate, using a Teflon ribbon. The glass monolith was finally placed on this sample holder so it would be completely immersed in the solution. The complete set-up is shown in Figure 1.

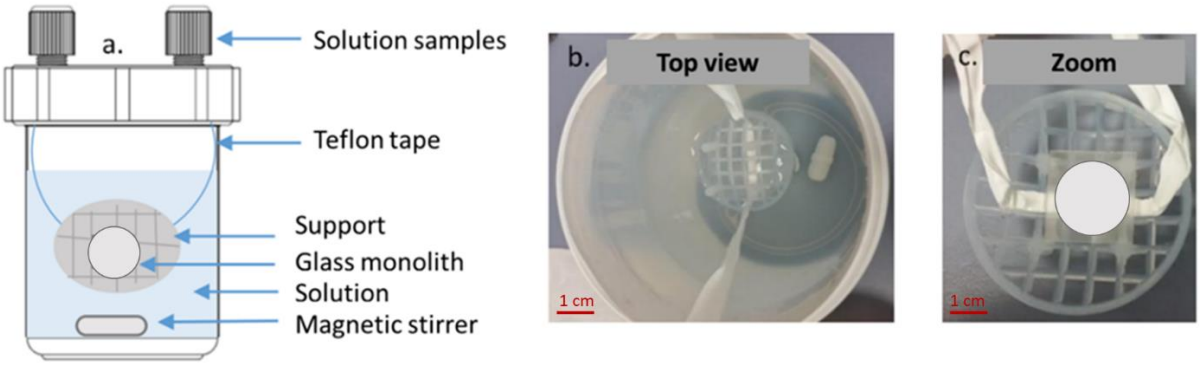

Figure 1 : Schematic representation of a Savillex® reactor (a), top view of the reactor (b) and zoom on the glass monolith on its holder (c).

The alteration experiment lasted 24 hours but the initial alteration rate was calculated over the first 8 hours to guarantee a concentration in silicon less than 1 $mg.L^{-1}$. This choice was made to avoid the

influence of saturation phenomenon of the solution with respect to silica on the alteration rate [20]. In addition, for Au_samples, beyond 8 hours of alteration, the altered thickness became greater than the irradiated depth (2 µm). This statement is done by calculating the altered depth from elemental releases in solution, by applying equation (4). Moreover, to limit disruptions of the system, the number of samples taken (one per hour) and each leachate sample volume (10 mL) were adapted to limit the total sampled volume (less than 20 % of the total volume). Experiments on NI_glass and Au_glass were repeated 3 times each.

Solution analyses

Under these conditions, all the elements coming from the glass are expected to be released in solution (except zirconium which is very poorly soluble at a pH of 9.0) [23] and can be used to determine the alteration rate. Measurements of the elemental concentrations were conducted using both UV-visible spectrophotometry (Cary Varian 50 Scan) for Si and ICP-AES (Spectro Arcos EOP) for other elements. For UV-visible spectroscopy measurements, commercial Spectroquant® kits were used to prepare the standard solutions and unknown samples. The absorbance was measured at a wavelength of 665 nm for silicon and 405 nm for boron using a UV-visible spectrophotometer. The absorbance measurement was repeated 5 times to check the stability of the signal and an average of the 5 measurements was retained. Calibration was done using several standard solutions prepared by dilution in deionized water of commercial standard solutions at 1 $g.L^{-1}$ (ARISTAR® single element calibration standard for ICP-AES 1000 mg L^{-1}, VWR). The concentrations of the standard solutions were in the range from 0.1 to 2 $mg.L^{-1}$ for B and from 0.5 to 5 $mg.L^{-1}$ for Si. 9 mL of each sample was used for UV-visible measurements and the remaining leachate sample (1 mL) was then acidified by adding a small amount (about 70 µL) of 14 N nitric acid (Suprapur®,14 N, 65%) to reach $[HNO_3]$ = 1 $mol.L^{-1}$ and analyzed by ICP-AES. All analyses were carried out the day after the end of the experiment. Two to four wavelengths per element were selected to measure the elemental concentration with ICP-AES. For each wavelength, calibration curves were determined from the analysis of several standard solutions

prepared by dilution in 1 mol.L^{-1} HNO_3 solution of certified standard solutions at 1 g.L^{-1} (PlasmaCAL single element calibration standard for ICP-AES 1000 mg L^{-1}, SCP-Science). Three measurements were done for each selected wavelength. Then, the elemental concentrations were calculated as the average of the results obtained for all wavelengths.

The relative experimental uncertainty on the concentration obtained by using UV-visible spectrophotometry was estimated to 10 %. For ICP-AES analyses, it corresponded to twice the relative standard deviation of the concentrations obtained for the different selected wavelengths (i.e. 5 % for B, Na and 10 % for Ca and Al).

The normalized mass losses (NL_i(t)) for element *i* at time *t* were calculated from the concentrations measured by UV-visible spectrophotometry or by ICP-AES, according to equation 1.

$$NL_{\mathrm{i}}(t) = \frac{C_{\mathrm{i}}(t)\times V(t) + \sum_1^{\mathrm{t}-1}[C_{\mathrm{i}}(t)\times V_{\mathrm{j}}]}{x_{\mathrm{i}}\times S} \text{ with } V(t) = V_0 - \sum_1^{\mathrm{t}-1} V_{\mathrm{j}} \quad (1)$$

where: $C_i(t)$ is the concentration of element *i* measured in solution at time *t* (in g.L^{-1}); $V(t)$ is the volume of solution remaining in the Savillex® reactor at time *t* (in L); V_j is the solution volume removed from the reactor at each sampling time (in L); V_0 is the initial volume of solution in the reactor (in L); x_i is the mass fraction of element *i* in the glass and *S* is the geometric surface area of the glass (in m^2).

The alteration rate (r_i) for a given element *i* corresponds to the time derivative of the normalized mass loss (equation 2). It is usually expressed in g.m^{-2}.d^{-1}.

$$r_{\mathrm{i}} = \frac{d\,(NL_{\mathrm{i}}(t))}{dt} \quad (2)$$

The releases of the different elements of the glass were found to be congruent. Therefore, the effective rate, $r_{\text{effective}}$ was calculated by averaging the results obtained for the various replicated leaching experiments and all the elements (Si, B, Na, Ca, Al).

Moreover, a correction was performed to calculate the initial alteration rate in order to take into account that 10 % of the geometric surface area (i.e. the edges) of the monolith was not irradiated.

The corresponding initial alteration rate of a monolith entirely irradiated with Au-ion, *r*(Au_glass), was calculated using equation (3):

$$r(\text{Au\_glass}) = \frac{r_{\text{effective}} - 0.1 \times r(\text{NI-glass})}{0.9} \quad (3)$$

where *r(NI_glass)* is the alteration rate of the non-irradiated glass and $r_{\text{effective}}$ is the alteration rate calculated from the experimental normalized mass losses of the monolith irradiated on the two main faces.

The rate expressed in µm.d^{-1} is calculated from the rate expressed in g.m^{-2}.d^{-1} by multiplying this latter by the value of the ISG glass density, ρ, (expressed in g.cm^{-3}):

$$r(\text{in } \mu\text{m}.d^{-1}) = r(\text{in g}.m^{-2}.d^{-1}) \times \rho(in\ \text{g}.cm^{-3}) \quad (4)$$

Results

The study of the initial alteration rate regime allows to focus on the first moments of the glass alteration. This regime is controlled by hydrolysis of the vitreous network [14] and corresponds to a maximum rate of alteration of a glass in a given medium.

From the releases in solution, the normalized mass losses were calculated for all the elements of the glass and plotted as a function of the alteration time for the 6 samples in Figure 2. It is worth noting that over a period of 8 hours, the evolution of normalized mass losses was linear, regardless of the element considered and the type of sample considered (NI_glass or Au_glass). Congruency was systematically observed for B, Al and Ca, while normalized mass losses in Na were systematically higher. For Ca, outliers were attributed to potential contaminations (points drawn in red and framed) and these data were not considered in the determination of the r_{Ca}. For NI_1 (NI_1 means Non-Irradiated glass, test number 1) and Au_1 tests (Au_1 means Au irradiated glass, test number 1), the releases of Ca were too scattered, therefore they were not considered in the subsequent calculations

of r_{Ca}. For Si and Na, the initial concentrations are variable. It was thus assumed that an initial contamination in the Savillex® reactor could have induced an initial offset of the concentrations. This initial offset had virtually no impact on the slope of the $NL_{Si}(t)$ and $NL_{Na}(t)$ curves. Thus, these data were used to determine r_{Si} and r_{Na}.

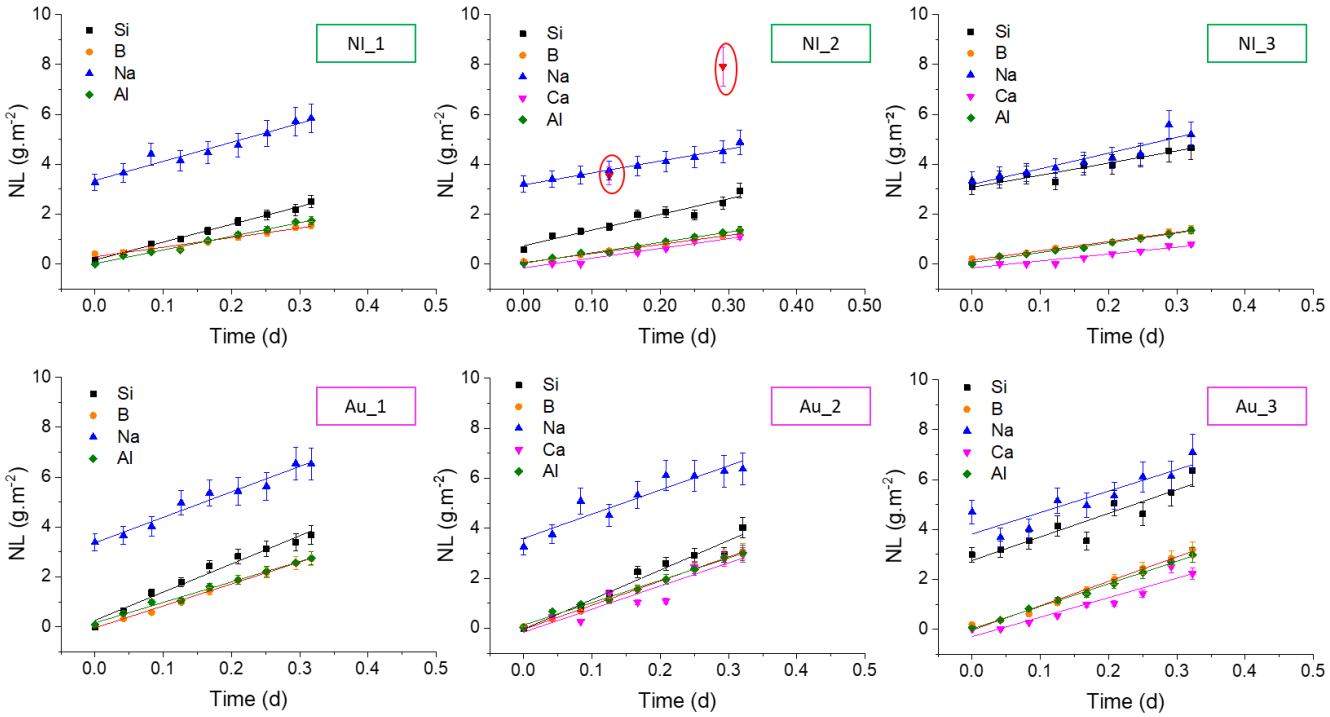

Figure 2 : Normalized mass losses (NL) of the different glass elements as a function of the leaching time for the 3 experiments with NI_samples (NI_1,2,3) and with Au_samples (Au_1,2,3). The data circled in red were not used in the calculation of r_{Ca}.

Linear regression was performed on the NL obtained for each element and the slopes corresponding to the initial rates are reported in

Table 2. We observed that, regardless of the element considered and the series, the results of the various experiments were not significantly different. The initial alteration rates calculated were systematically lower for NI_glasses than for irradiated Au_glasses. For NI_glasses, an average initial rate of (4.9 ± 3.0) $g.m^{-2}.d^{-1}$ was obtained compared to (10.0 ± 2.5) $g.m^{-2}.d^{-1}$ for the glasses irradiated with Au-ion. Therefore, there is a significant impact of Au-ion irradiation on the value of the initial

alteration rate. This impact led to an increase in the average initial alteration rate by a factor F = 2.0 ± 0.8. This higher initial alteration rate in the case of ISG glass samples irradiated with Au-ion indicated a difference in chemical reactivity at the very first moments of alteration.

Table 2: Initial alteration rate (r_i) in $g.m^{-2}.d^{-1}$ for each element of the glass and for each test. The ratio of the average initial alteration rates of irradiated samples to non-irradiated samples (F = r(Au_glass)/r(NI_glass)) is given in the last column of the table. The final rate (given in $g.m^{-2}.d^{-1}$ and $\mu m.d^{-1}$) is the average of all the elements and all the tests. The $r_{effective}$ value is the calculated leaching rate without considering the non-irradiated edges. All uncertainties correspond to twice the standard deviation except for r(Au) where $\Delta r(Au) = \Delta r_{effective} + 0.1 \times \Delta r_{NI}$.

r_i ($g.m^{-2}.d^{-1}$)	NI_1	NI_2	NI_3	Au_1	Au_2	Au_3	*F*
Si	7.1	6.3	4.9	11.3	11.8	9.5	1.8
B	3.8	3.6	3.7	8.8	9.7	9.8	2.5
Na	7.6	4.8	6.3	10.2	9.7	8.6	1.5
Ca		3.9	2.8		9.2	7.8	2.2
Al	5.5	4.1	3.9	8.2	8.9	9.0	1.9
$r_{effective}$ ($g.m^{-2}.d^{-1}$)				9.5 ± 2.2			
r ($g.m^{-2}.d^{-1}$)	**4.9 ± 3.0**			**10.0 ± 2.5**			
r ($\mu m.d^{-1}$)	2.0 ± 1.2			4.0 ± 1.0			

Discussion

Initial alteration rate values of ISG glass

This study allows to determine the initial alteration rate of ISG at 90°C and at pH=9. It is important to note that only few data regarding the value of the initial alteration rate of ISG glass exist in the literature and that the published data are variable (see Table 3). Most of these data concern non-irradiated ISG specimens. Some studies were conducted on ISG glass powder (the surface area was measured by the BET method or using the geometric surface of the powder) and others on monoliths. In order to be able to compare the initial alteration rate values obtained for powders and for monoliths, it is necessary to use corrective factors as assessed by Fournier et al. [20]. Indeed, the initial alteration

rate obtained from the powder should be multiplied by a factor of 0.8 when the surface area considered is the geometric one and by 1.9 when the surface area is measured by the BET method.

Jegou [24] studied the initial alteration rate of non-irradiated ISG glass powder altered in pure water at 90°C, with SA/V = 0.1 cm^{-1} and pH = 9, over 2 days. Jegou reported an initial alteration rate of r_0 =1.7 $g.m^{-2}.d^{-1}$, which becomes r_0(monolith) = 3.2 $g.m^{-2}.d^{-1}$, using the corrective factor recommended by Fournier et al. [20].

Gin et al. [25] also altered ISG glass powder in initial rate regime in pure water at pH 9, 90°C, with a SA/V ratio of 0.076 cm^{-1} and for 5.7 h. They obtained a r_0 value of 8.2 ± 2.5 $g.m^{-2}.d^{-1}$. After applying the appropriate corrective factor of 0.8, the corresponding average rate for a monolith is 6.6 $g.m^{-2}.d^{-1}$.

Inagaki et al. [26] carried out leaching experiments at different pH and temperatures on ISG glass monoliths and determined a relation between the alteration rate at 90°C and the pH (log r_{Si}= -1.56 + 0.236 × pH). The use of this relation for pH = 9 gave r_{Si}= 3.7 $g.m^{-2}.d^{-1}$.

Fournier et al. [17] carried out leaching experiments at pH=10 and 90°C on ISG glass monoliths. Using the relation between the alteration rate at 90°C and the pH (log r_{Si}= -1.56 + 0.236 × pH) [21], r_{Si}= 3.9 $g.m^{-2}.d^{-1}$.

Thus, considering data from the literature, the initial alteration rate of a non-irradiated ISG glass in pure water at pH 9 and 90°C ranges from 3.2 to 6.6 $g.m^{-2}.d^{-1}$. The value obtained in this work for non-irradiated ISG monoliths (i.e. 4.9 ± 3.0 $g.m^{-2}.d^{-1}$) is well included in this range. This observation led to the conclusion that the experimental protocol and the data treatment were reliable.

Table 3 : r_0 values of ISG glass reported in the literature and from the current study. SPFT means Single-pass flow-through. Results from Neeway et al. were acquired at pH22°C 10 and 11, a mean value corresponding to pH90°C 9 (i.e. pH22°C 10.7) was extrapolated to be compared to our study.

References	$pH_{90°C}$	Temperature (°C)	S/V (cm^{-1})	Powder or monolith?	Corrective factor	Leaching protocol	Time (d)	Corrected r_0 ($g.m^{-2}.d^{-1}$)
Jegou 1998	9	90	0.1	Powder	×1.9	Static	2	3.2
Gin 2020	9	90	0.076	Powder	×0.8	Static	0.24	6.6 ± 2.5
Inagaki 2013	9	90		Monolith		Flow cell		3.7
Neeway 2018	~ 9	90		Powder		SPFT	21	2.9
This study	9	90	0.01	Monolith		Static	0.33	4.9 ± 3.0

To the best of our knowledge, there are only two studies reporting results on the initial alteration rate of ISG glass whose structure was damaged before alteration. Angeli et al. [11] studied ISG glass fibers hyperquenched (simulating structural disorder close to the one induced by irradiation) and therefore structurally more disordered. They showed that the silicate network, was hydrolyzed 1.4 to 1.8 times faster than for annealed fibers. This result is close to the increase factor obtained in this study, which is 2.0 ± 0.8. However, the second study of Karakurt et al. [17] on the initial rate of ISG glass irradiated with gold ions cannot be considered since the glass was altered deeper than the irradiated zone.

Thus, the results obtained in our study brings new information and showed an effect of the glass disorder on its initial alteration rate and is consistent with the literature: the r_0 of an irradiated or hyperquenched ISG glass is increased compared to the one of a non-irradiated ISG glass.

Origin of the rate difference between NI_glass and Au_glass

The initial alteration rate of Au_glass samples was found to be higher than that of NI_glass by a factor of 2.0 ± 0.8. This observation means that the chemical reactivity of the Au_glass with respect to the

301 solution (pure water) is greater than that of the NI_glass during the hydrolysis step. Several authors
302 [10, 11, 27, 28] showed that there is a link between the structural disorder of glass, whether thermally
303 induced [11] or by irradiation [10, 27, 28], and its chemical durability in the long term alteration rate
304 regime. The current study demonstrated that this is also true for the initial alteration rate of ISG glass.
305 Several explanations could be proposed to explain the increase of r_0 due to the glass disorder induced
306 by Au-ion irradiation.
307 Firstly, radiation damage as well as high quenching rate induce a modification of the glass short range
308 order (SRO) with the creation of point defects (electronic defects on atoms or bonds in the glassy
309 network, often called color centers) and non-bridging oxygen atoms that induce a decrease of the
310 polymerization of the glass network. Moreover a partial conversion of BO_4 (B(+IV)) to BO_3 (B(+III))
311 species [7, 9-11, 18, 29, 30] is observed that also participates to the decrease of the glass
312 polymerization degree which could induce a higher hydrolysis of the silicate network and result in an
313 increase in glass alteration rate. Overall, the general depolymerisation of the glass network results in
314 a lower number of bridging bonds between network former atoms. The initial rate regime is controlled
315 by the hydrolysis of the vitreous network through the breaking of its bridging bonds (Si-O-Si, Si–O–Al
316 or Si-O-Zr for example) by protonation or hydroxylation of reactive surface sites [14]. Thus, the
317 hydrolysis of the glass can be favoured by a low degree of polymerization of the vitreous network. This
318 was recently confirmed by Monte Carlo simulations which showed that the primary cause for the
319 increase of glass alteration rate was the extent of the depolymerization of the glass network
320 introduced by these local structural changes (boron coordination, number and nature of Q^n species,
321 and angular distribution of Si-O-Si linkages) [31]. Moreover the reactivity of B(III) was shown to be
322 higher than that of B(IV). Kapoor et al. [32] showed that the boron (+III) could be seen as a Lewis acid,
323 with water acting as a Lewis base. Moreover, by considering the Lewis acido-basicity of borate species,
324 an increased reactivity of the B(+III) compared to B(+IV) can be assumed to increase the glass network
325 hydrolysis.

Secondly, the radiation damage generated by nuclear collisions also induces a modification of the glass medium range order (MRO) with mainly a broadening of the ring size and angle distribution [10, 33], as indicated by the increase of three membered silicate rings and the shift of R band (which corresponds to bending and rotation modes of Si-O-Si bands). The MRO modification was also observed by molecular dynamic simulation of radiation damage and high quenching rate in simple borosilicate glasses [34]. This modification of the ring size distribution directly affects the glass free volume and thereby the accessibility of the water into the glass network [34], that may also favour its hydrolysis.

Finally, the modification of short and medium range orders can occur either upstream of the hydrolysis step, the water penetrates faster into the glass and therefore leads to a deeper hydrolysis [35] or are directly related to the increase of B(III), more reactive towards water [29, 32]. These two processes can effectively act concomitantly and synergistically.

Comparison between ISG and SON68 complex nuclear glass

In the literature, it was shown for SON68 glass that irradiation with Au-ion had no significant impact on the initial alteration rate [15]. Indeed, the initial rate of SON68 glass was about 2 $g.m^{-2}.d^{-1}$, whether the glass was irradiated with Au-ion or not [15], which was also the case for SON68 glasses doped with actinides [15, 16, 36]. The more complex chemical composition of SON68 glass compared to ISG glass may have a role in the weaker impact of Au-ion on the glass structure and thus on the initial alteration rate [8], because it could favour a higher degree of chemical mixing and random organisation of the glassy network that could reduce the glass sensitivity to nuclear damage, that induce a ballistic mixing of the material due to the displacements cascades. More experiments on complex SON68 glass are needed to quantify its structural evolution versus irradiation and compare it to the one of ISG glass so as to try to explain the lower sensitivity of SON68 glass initial alteration rate under irradiation.

Conclusion

This study was dedicated to the impact of nuclear collisions (simulating the effects of the recoil nuclei of α decays) on the initial alteration rate of the ISG glass. It was shown that the initial alteration rate of the ISG glass irradiated with 7 MeV Au-ion was 2.0 ± 0.8 times higher than that of a non-irradiated ISG glass. This work demonstrated that there is a link between the structural changes of ISG glass caused by nuclear collisions and its initial alteration rate. The origin of the increase of the alteration rate seems to be associated to the short and medium range order changes induced by the nuclear collisions, and certainly by the amplitude of the boron coordination change (B(IV) to B(III)). Similar irradiation conditions on SON68 glass did not induce any changes of its alteration rate which suggests that the more the structure of the glass is modified by irradiation (change in boron coordination, change in NBO), the higher the alteration rate of the glass is.

Subsequently, it would be interesting to continue the investigation of the structural changes induced by irradiation on more complex glasses, up to SON68 one, in order to identify the glass composition domain that did not show any dependence of its initial alteration rate with irradiation.

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