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► **To cite this version:**

C. Gillet, S. Szenknect, M. Tribet, H. Arena, S. Peugot. Impact of gold ion irradiation on the initial alteration rate of the International Simple Glass. *Journal of Nuclear Materials*, 2024, 588, pp.154817. 10.1016/j.jnucmat.2023.154817 . hal-04679088

**HAL Id: hal-04679088**

**<https://hal.science/hal-04679088v1>**

Submitted on 27 Aug 2024

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# Impact of gold ion irradiation on the initial alteration rate of the International Simple Glass

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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  $\alpha$  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<sup>-1</sup>. 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

27 alteration rate was found to be  $(2.0 \pm 0.8)$  times higher for the irradiated glass monoliths than for non-  
28 irradiated samples.

## 29 Introduction

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

46 There are many studies [7-10] on the impact of irradiation on the structure and the macroscopic  
47 properties of borosilicate glasses including ISG glass (reference glass chosen by the international  
48 scientific community). These studies have shown that nuclear effects are more efficient than electronic  
49 ones to damage the glass structure [8]. It was shown that the maximum changes in the glassy state  
50 (also called saturation damage state) are induced by nuclear collisions at a dose level of around 30 to  
51 40 MGy, corresponding to around 500 years of radiation ageing of nuclear glass. Electronic effects  
52 induced a lower damage level than nuclear effects and require a higher dose level of around 3GGy  
53 (corresponding to of around several decades of radiation ageing of nuclear glass) to reach the  
54 saturation damage state [8]. Moreover coupled effects between nuclear and electronic collisions have

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

58

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

70 The impact of the recoil nuclei of  $\alpha$  decays on the glass initial alteration rate regime has already been  
71 partially addressed in the literature. Most studies are dedicated to glasses of complex composition and  
72 did not show any effect of radiation on the initial alteration rate [15, 16]. Recent studies, rather focused  
73 on simplified glasses, seem to indicate an impact of this type of irradiation at short alteration times  
74 [17-19]. However, these studies did not fill all the gaps. Indeed, Karakurt et al.[17] studied the  
75 alteration of ISG glass irradiated with 7 MeV Au ion up a fluency of  $6.4 \cdot 10^{13} \text{at.cm}^{-2}$ , but the first  
76 measurements of altered depths were already beyond the irradiated zone (after 2 days reached  $3 \mu\text{m}$ ,  
77 so beyond the irradiated zone) and therefore the measured rates corresponded rather to non  
78 irradiated glass. Zhang et al. [19] studied a simple 3-oxide glass, as well as Lonartz et al. [18]. In  
79 addition, the ions used have a high energy whose representativeness of the effects of self-irradiation  
80 by  $\alpha$  decay is not yet fully demonstrated and the alteration conditions do not quite correspond to an

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

89

## 90 Materials and methods

### 91 Glass samples preparation

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

94 *Table 1: ISG glass composition.*

Oxide	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	CaO	ZrO <sub>2</sub>	
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

95

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

## 102 Irradiation scenario

103 ISG glass monoliths were irradiated on both sides with 7 MeV Au<sup>3+</sup> ions on the 2MV Aramis accelerator  
104 at the SCALP facility (CNRS-CSNSM, Orsay, France) to induce a significant nuclear damage in the glass  
105 structure as demonstrated in numerous studies that have been recently reviewed in [8]. A fluence of  
106  $2 \times 10^{14}$  at.cm<sup>-2</sup> was used, which induces a minimum nuclear dose of around 40 MGy in the whole  
107 irradiated depth [9] and thus to reach the saturation damage, i.e. the maximum damage level that can  
108 be induced in a glass with nuclear collisions [8]. However, the concentration of Au ion in the glass is  
109 very low in the present study (< 0.006 at.%) so that any chemical modification induced by Au on the  
110 structure of the glass can be ruled out. The Au implantation profile was measured by negative ions  
111 analysis by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and was also obtained by  
112 simulation with the Stopping and Range of Ions in Matter (SRIM) software [22]. It was shown that the  
113 7 MeV Au<sup>3+</sup> ions stop after a range of around 2 μm within the glass [9], creating thus a damage depth  
114 of 2 μm thick. It is worth noting that the alteration protocol was chosen to generate an altered depth  
115 less than or equal to the damaged depth so that the non-irradiated glass does not contribute to the  
116 initial alteration rate value. However, in addition to the two main irradiated faces, the edges of the  
117 sample which had not been irradiated and represented 10 % of the geometrical surface area  
118 contributed to the release of elements in solution. Thus, a correction was achieved when calculating  
119 the alteration rate (see equation 3).

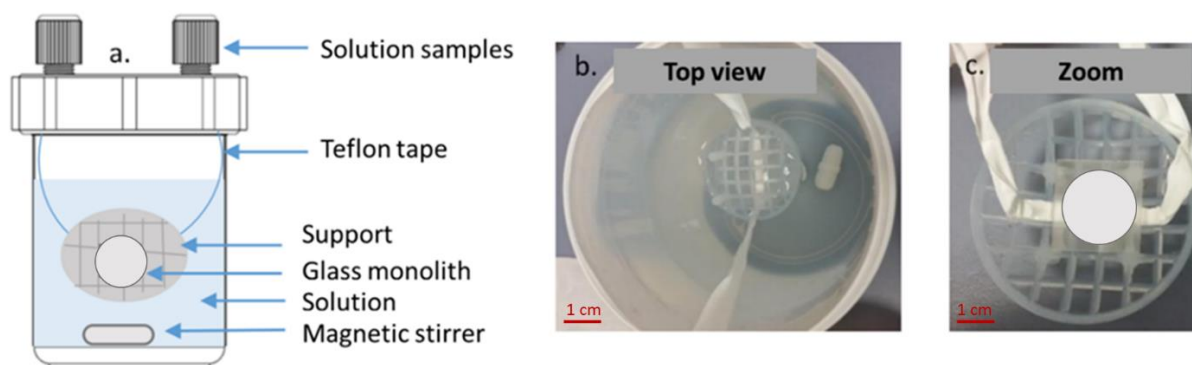
120

## 121 Alteration protocol

122 The leaching experiments were carried out in PFA (Perfluoroalkoxy) reactors, Savillex® brand. These  
123 experiments were conducted on the non-irradiated ISG glass (named NI\_glass later) and on the ISG  
124 glass irradiated with Au-ion (named Au\_glass later). The alteration experiments were performed in an  
125 oven at 90°C and at a pH<sub>90°C</sub> of  $9.0 \pm 0.2$ . Several reasons explain the choice of this pH. Hydrolysis is a  
126 mechanism closely linked to protonation and hydroxylation of the glass surface, in particular the

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

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



142

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

145

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



148 influence of saturation phenomenon of the solution with respect to silica on the alteration rate [20].  
149 In addition, for Au\_samples, beyond 8 hours of alteration, the altered thickness became greater than  
150 the irradiated depth (2  $\mu\text{m}$ ). This statement is done by calculating the altered depth from elemental  
151 releases in solution, by applying equation (4). Moreover, to limit disruptions of the system, the number  
152 of samples taken (one per hour) and each leachate sample volume (10 mL) were adapted to limit the  
153 total sampled volume (less than 20 % of the total volume). Experiments on NI\_glass and Au\_glass were  
154 repeated 3 times each.

### 155 Solution analyses

156 Under these conditions, all the elements coming from the glass are expected to be released in solution  
157 (except zirconium which is very poorly soluble at a pH of 9.0) [23] and can be used to determine the  
158 alteration rate. Measurements of the elemental concentrations were conducted using both UV-visible  
159 spectrophotometry (Cary Varian 50 Scan) for Si and ICP-AES (Spectro Arcos EOP) for other elements.  
160 For UV-visible spectroscopy measurements, commercial Spectroquant® kits were used to prepare the  
161 standard solutions and unknown samples. The absorbance was measured at a wavelength of 665 nm  
162 for silicon and 405 nm for boron using a UV-visible spectrophotometer. The absorbance measurement  
163 was repeated 5 times to check the stability of the signal and an average of the 5 measurements was  
164 retained. Calibration was done using several standard solutions prepared by dilution in deionized  
165 water of commercial standard solutions at 1  $\text{g.L}^{-1}$  (ARISTAR® single element calibration standard for  
166 ICP-AES 1000  $\text{mg L}^{-1}$ , VWR). The concentrations of the standard solutions were in the range from 0.1  
167 to 2  $\text{mg.L}^{-1}$  for B and from 0.5 to 5  $\text{mg.L}^{-1}$  for Si. 9 mL of each sample was used for UV-visible  
168 measurements and the remaining leachate sample (1 mL) was then acidified by adding a small amount  
169 (about 70  $\mu\text{L}$ ) of 14 N nitric acid (Suprapur®, 14 N, 65%) to reach  $[\text{HNO}_3] = 1 \text{ mol.L}^{-1}$  and analyzed by  
170 ICP-AES. All analyses were carried out the day after the end of the experiment. Two to four  
171 wavelengths per element were selected to measure the elemental concentration with ICP-AES. For  
172 each wavelength, calibration curves were determined from the analysis of several standard solutions

173 prepared by dilution in 1 mol.L<sup>-1</sup> HNO<sub>3</sub> solution of certified standard solutions at 1 g.L<sup>-1</sup> (PlasmaCAL  
174 single element calibration standard for ICP-AES 1000 mg L<sup>-1</sup>, SCP-Science). Three measurements were  
175 done for each selected wavelength. Then, the elemental concentrations were calculated as the  
176 average of the results obtained for all wavelengths.

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

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

$$183 \quad NL_i(t) = \frac{c_i(t) \times V(t) + \sum_{j=1}^{t-1} [c_i(t) \times V_j]}{x_i \times S} \quad \text{with } V(t) = V_0 - \sum_{j=1}^{t-1} V_j \quad (1)$$

184 where:  $C_i(t)$  is the concentration of element  $i$  measured in solution at time  $t$  (in g.L<sup>-1</sup>);  $V(t)$  is the volume  
185 of solution remaining in the Savillex<sup>®</sup> reactor at time  $t$  (in L);  $V_j$  is the solution volume removed from  
186 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  
187 mass fraction of element  $i$  in the glass and  $S$  is the geometric surface area of the glass (in m<sup>2</sup>).

188 The alteration rate ( $r_i$ ) for a given element  $i$  corresponds to the time derivative of the normalized mass  
189 loss (equation 2). It is usually expressed in g.m<sup>-2</sup>.d<sup>-1</sup>.

$$190 \quad r_i = \frac{d(NL_i(t))}{dt} \quad (2)$$

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

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

196 The corresponding initial alteration rate of a monolith entirely irradiated with Au-ion,  $r(\text{Au\_glass})$ , was  
197 calculated using equation (3):

$$198 \quad r(\text{Au\_glass}) = \frac{r_{\text{effective}} - 0.1 \times r(\text{NI-glass})}{0.9} \quad (3)$$

199

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

203 The rate expressed in  $\mu\text{m}\cdot\text{d}^{-1}$  is calculated from the rate expressed in  $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  by multiplying this latter  
204 by the value of the ISG glass density,  $\rho$ , (expressed in  $\text{g}\cdot\text{cm}^{-3}$ ):

$$205 \quad r(\text{in } \mu\text{m}\cdot\text{d}^{-1}) = r(\text{in } \text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}) \times \rho(\text{in } \text{g}\cdot\text{cm}^{-3}) \quad (4)$$

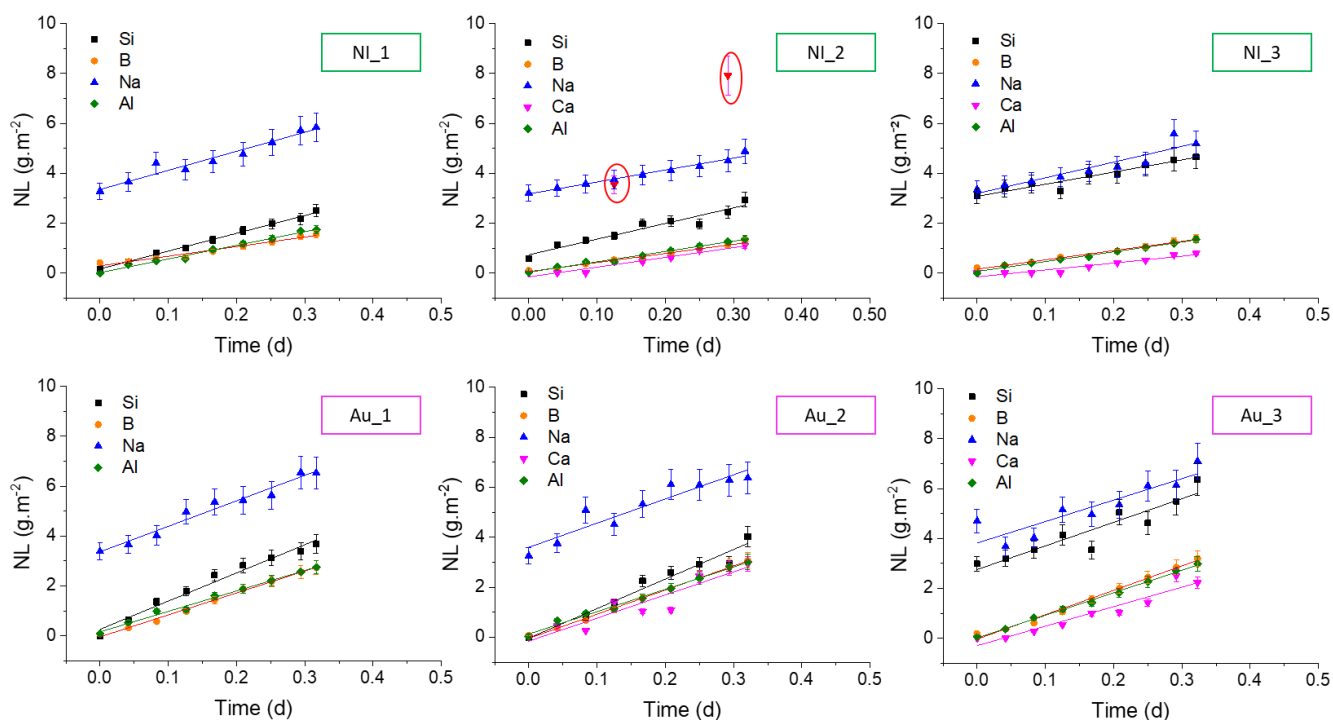
## 206 Results

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

210 From the releases in solution, the normalized mass losses were calculated for all the elements of the  
211 glass and plotted as a function of the alteration time for the 6 samples in Figure 2. It is worth noting  
212 that over a period of 8 hours, the evolution of normalized mass losses was linear, regardless of the  
213 element considered and the type of sample considered (NI\_glass or Au\_glass). Congruency was  
214 systematically observed for B, Al and Ca, while normalized mass losses in Na were systematically  
215 higher. For Ca, outliers were attributed to potential contaminations (points drawn in red and framed)  
216 and these data were not considered in the determination of the  $r_{\text{Ca}}$ . For NI\_1 (NI\_1 means Non-  
217 Irradiated glass, test number 1) and Au\_1 tests (Au\_1 means Au irradiated glass, test number 1), the  
218 releases of Ca were too scattered, therefore they were not considered in the subsequent calculations

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

223



224 *Figure 2 : Normalized mass losses (NL) of the different glass elements as a function of the leaching time*  
 225 *for the 3 experiments with NI\_samples (NI\_1,2,3) and with Au\_samples (Au\_1,2,3). The data circled in*  
 226 *red were not used in the calculation of  $r_{Ca}$ .*

227

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

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

235 alteration rate. This impact led to an increase in the average initial alteration rate by a factor  $F = 2.0 \pm$   
 236  $0.8$ . This higher initial alteration rate in the case of ISG glass samples irradiated with Au-ion indicated  
 237 a difference in chemical reactivity at the very first moments of alteration.

238

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

245

$r_i(\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1})$	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
$r_{\text{effective}}(\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1})$				$9.5 \pm 2.2$			
$r(\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1})$	<b><math>4.9 \pm 3.0</math></b>			<b><math>10.0 \pm 2.5</math></b>			
$r(\mu\text{m}\cdot\text{d}^{-1})$	$2.0 \pm 1.2$			$4.0 \pm 1.0$			

246

## 247 Discussion

248

### 249 Initial alteration rate values of ISG glass

250

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

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

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

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

267 Inagaki et al. [26] carried out leaching experiments at different pH and temperatures on ISG glass  
268 monoliths and determined a relation between the alteration rate at 90°C and the pH ( $\log r_{\text{Si}} = -1.56 +$   
269  $0.236 \times \text{pH}$ ). The use of this relation for pH = 9 gave  $r_{\text{Si}} = 3.7 \text{ g.m}^{-2}.\text{d}^{-1}$ .

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

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

277

278

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

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

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

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

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### 298 [Origin of the rate difference between NI\\_glass and Au\\_glass](#)

299 The initial alteration rate of Au\_glass samples was found to be higher than that of NI\_glass by a factor  
 300 of  $2.0 \pm 0.8$ . 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  $\text{BO}_4$  (B(+IV)) to  $\text{BO}_3$  (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  $\text{Q}^n$  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.



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

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

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### 339 [Comparison between ISG and SON68 complex nuclear glass](#)

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

350

## 351 Conclusion

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

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

## 365 Acknowledgments

366 The authors would like to thank Pascale Colombel and Laurent Duffours (Prime Verre company,  
367 Montpellier, France) for sample preparation, Jérôme Bourçois (CNRS-CSNSM, Orsay, France) and  
368 Olivier Cavani (Ecole Polytechnique, Palaiseau, France) for carrying out irradiations, Elodie Chauvet and  
369 Loan Lai (Tescan Analytics, Fuveau, France) and Laurent Dupuy (SERMA Technologies, Ecully, France)  
370 for the ToF-SIMS characterizations. This work was performed in the framework of the Vestale project  
371 co-funded by EDF, CEA and Orano and it was supported by INWARD coordinated research project [Ion  
372 Beam Irradiation for High Level Nuclear Waste Form Development, F11022] from IAEA.

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