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Impact of gold ions 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 ions.

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 ions 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

27 alteration rate was found to be (2.0 ± 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. In order to find a management solution suitable to each type of nuclear waste, they are
33 classified according to their level of radioactivity and lifetime. High-level waste (HLW) are packaged
34 into a vitrified form and are intended for long-term disposal in a deep geological repository (Cigeo
35 project). Once the waste packages are introduced into the disposal site, the glass will initially evolve
36 into a closed system and will be subjected to its own self-irradiation due to the fission products and
37 minor actinides incorporated in the glass structure. Fission products produce β decays accompanied
38 by γ transitions that predominate with respect to the total activity of the waste in the short term (first
39 500 years), while α decays coming from actinide decays are the main contributor to the activity for the
40 long-term [1]. α decays are responsible for the production of recoil nuclei (with an energy of about 100
41 keV) and α particles (with an energy of about 5 MeV). The glass is therefore submitted to dose rate
42 and cumulative dose caused by these radiation sources, which can damage the glass by accumulation
43 of radiation effects into the glass structure.

44

45 There are many studies [2-5] on the impact of irradiation on the structure and the macroscopic
46 properties of borosilicate glasses including ISG glass (reference glass chosen by the international
47 scientific community). These studies have shown that nuclear effects are predominant and that
48 coupled effects between nuclear and electronic collisions can exist. Indeed, the α particles induce a
49 partial annealing of the damage generated by the heavy ions. In addition, Angeli et al [6] studied the
50 effect of hyperquenching on ISG glass fibers and reported a disordered structure similar to that of
51 induced by irradiation.

52

53

54 After a few hundred or even a few thousand years, water will access the cells containing the waste
55 packages. Then, the glass will evolve into an open system, which represents a risk of dissemination of
56 radionuclides by water. It is thus of primary importance to assess the glass chemical durability. Once
57 the glass package is in contact with the groundwater, exchanges of chemical species take place at the
58 solid/solution interface leading to changes in the properties of the glass [7-9]. Several successive
59 mechanisms occur at the glass/solution interface with different kinetics. Glass hydration by diffusion
60 of water in its structure precedes the interdiffusion step, which consists of an ion exchange between
61 the protons from the solution and the alkaline elements contained in a layer of a few angstroms at the
62 glass surface. Then, hydrolysis of the vitreous network consists of a nucleophilic attack of a hydroxide
63 ion OH^- on a bridging bond leading to a congruent dissolution of the glass [10]. The maximum alteration
64 rate (called r_0) in a given environment is observed during the hydrolysis stage.

65 The impact of the recoil nuclei of α decays on the glass initial alteration rate regime has already been
66 partially addressed in the literature. Most studies are dedicated to glasses of complex composition and
67 are rather descriptive and did not show any effect of radiation on the initial alteration rate [11, 12].
68 Recent studies, rather focused on simplified glasses, seem to indicate an impact of this type of
69 irradiation at short alteration times [13-15]. However, these studies did not fill all the gaps. Indeed,
70 the ISG glass irradiated with heavy ions studied by Karakurt, has been altered more deeply than the
71 irradiated zone, the rate obtained is therefore not characteristic of the irradiated zone only. Zhang et
72 al. studied a simple 3-oxide glass, as well as Lonartz et al. In addition, the ions used have a high energy
73 whose representativeness of the effects of self-irradiation by α decay is not yet fully demonstrated
74 and the alteration conditions do not quite correspond to an initial alteration regime. That's why this
75 study focused on ISG glass (reference glass chosen by the scientific community), irradiated with 7 MeV
76 gold ion irradiation in order to simulate the nuclear damage caused by recoil nuclei of α decays. In
77 addition, the structural evolution of ISG submitted to this type of irradiation has already been
78 described in the literature [3-5]. Leaching tests have been performed using low surface over solution
79 volume ratio to determine the initial leaching rate of irradiated and non-irradiated ISG glass samples.

80 The current article presents the experimental conditions, the results of the leaching tests and discusses
81 the origin of the effect of the external irradiation on the leaching rate.

82

83 Materials and methods

84 Glass samples preparation

85 In this study, the alteration experiments were carried out on the International Simple Glass (ISG)
86 provided by MoSCI Corporation (Rolla, Missouri, USA). Its composition is given in Table 1 [8].

87 *Table 1: ISG glass composition.*

Oxide	SiO ₂	B ₂ O ₃	Na ₂ O	Al ₂ O 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

88

89 Glass monoliths were obtained from a glass cylinder of 2 cm in diameter that was cut into monoliths
90 which were polished to optical grade on both sides (up to reach a sample thickness of 700 μm) and on
91 the edge (Prime Verre company, Montpellier, France). Indeed, surface roughness may influence glass
92 alteration therefore, it is necessary that the samples would be completely polished. The geometric
93 surface area of the polished monoliths was considered in calculations of the normalized alteration rate.

94 Irradiation scenario

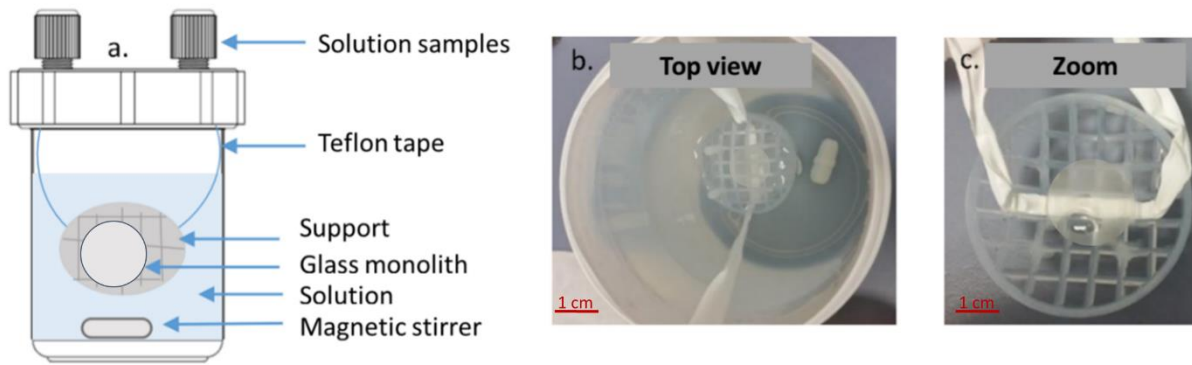
95 ISG glass monoliths were irradiated on both sides with 7 MeV Au³⁺ ions on the 2MV Aramis accelerator
96 at the SCALP facility (CNRS-CSNSM, Orsay, France) to induce a significant nuclear damage in the glass
97 structure as demonstrated in numerous studies that has been recently reviewed in [3]. A fluence of
98 2×10^{14} at.cm⁻² was used, which induces a minimum nuclear dose of around 40 MGy in the all the
99 damaged depth [4] and thus to reach the saturation damage. The Au implantation profile was
100 measured by negative ions analysis by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

101 and was also obtained by simulation with the Stopping and Range of Ions in Matter (SRIM) software
102 [16]. It was shown that the 7 MeV Au³⁺ ions stop after a range of around 2 μm within the glass [4],
103 creating thus a damage depth of 2 μm thick. It is worth noting that the alteration protocol was chosen
104 to generate an altered depth less than or equal to the damaged depth so that the non-irradiated glass
105 does not contribute to the initial alteration rate value. However, in addition to the two main irradiated
106 faces, the edges of the sample which had not been irradiated and represented 10 % of the geometrical
107 surface area contributed to the release of elements in solution. Thus, a correction was achieved when
108 calculating the alteration rate (see equation 3).

109

110 Alteration protocol

111 The leaching experiments were carried out in PFA (Perfluoroalkoxy) reactors, Savillex® brand. These
112 experiments were conducted on the non-irradiated ISG glass (named NI_glass later) and on the ISG
113 glass irradiated with Au ions (named Au_glass later). The alteration experiments were performed in an
114 oven at 90°C and at a pH_{90°C} of 9.0 ± 0.1. The solution was continuously stirred thanks to a magnetic
115 stirrer. The volume of solution was adapted to the surface area of the coupon to reach the chosen
116 surface over solution volume ratio (SA/V) of 0.01 cm⁻¹. The pH 9 solution was prepared by adding 9.53
117 mg of lithium hydroxide (99.995% purity, Alfa Aesar) into 1 L of deionized water. The pH was measured
118 once the solution was prepared, at 90°C, under strong stirring and reached 9.0 ± 0.1. Then, the lithium
119 hydroxide solution was introduced into the Savillex® reactor that was placed for the night in an oven
120 at 90°C the day before the start of the experiment. At the beginning of the experiment, a PFA sample
121 holder was held in the middle of the leachate, using a Teflon ribbon. The glass monolith was finally
122 placed on this sample holder so it would be completely immersed in the solution. The complete set-
123 up is shown in Figure 1.



124

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

127

128 The alteration experiment lasted 24 hours but the initial alteration rate was calculated over the first 8
 129 hours to guarantee a concentration in silicon less than 1 mg.L^{-1} . This choice was made to avoid the
 130 influence of saturation phenomenon of the solution with respect to silica on the alteration rate [17].
 131 In addition, for Au_samples, beyond 8 hours of alteration, the altered thickness became greater than
 132 the irradiated depth ($2 \mu\text{m}$). Moreover, to limit disruptions of the system, the number and the volume
 133 of solution were adapted to limit the total sampled volume (less than 20 % of the total volume).
 134 Experiments on NI_glass and Au_glass were repeated 3 times each.

135 [Solution analyses](#)

136 Under these conditions, all the elements coming from the glass are expected to be released in solution
 137 (except zirconium which is very poorly soluble at a pH of 9.0) [18] and can be used to determine the
 138 alteration rate. Measurements of the elemental concentrations were conducted using both UV-visible
 139 spectrophotometry (Cary Varian 50 Scan) and ICP-AES (Spectro Arcos EOP). For UV-visible
 140 spectroscopy measurements, commercial Spectroquant® kits were used to prepare the standard
 141 solutions and unknown samples. The absorbance was measured at a wavelength of 665 nm for silicon
 142 and 405 nm for boron using a UV-visible spectrophotometer. The absorbance measurement was
 143 repeated 5 times to check the stability of the signal and an average of the 5 measurements was

144 retained. Calibration was done using several standard solutions prepared by dilution in deionized
 145 water of commercial standard solutions at 1 g.L⁻¹ (ARISTAR® single element calibration standard for
 146 ICP-AES 1000 mg L⁻¹, VWR). The concentrations of the standard solutions were in the range from 0.1
 147 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
 148 measurements and the remaining leachate sample (1 mL) was then acidified by adding a small amount
 149 (about 70 µL) of 14 N nitric acid (Suprapur®, 14 N, 65%) to reach [HNO₃] = 1 mol.L⁻¹ and analyzed by
 150 ICP-AES. All analyses were carried out the day after the end of the experiment. 2 to 4 wavelengths per
 151 element were selected to measure the elemental concentration with ICP-AES. For each wavelength,
 152 calibration curves were determined from the analysis of several standard solutions prepared by
 153 dilution in 1 mol.L⁻¹ HNO₃ solution of certified standard solutions at 1 g.L⁻¹ (PlasmaCAL single element
 154 calibration standard for ICP-AES 1000 mg L⁻¹, SCP-Science). 3 measurements were done for each
 155 selected wavelength. Then, the elemental concentrations were calculated as the average of the results
 156 obtained for all wavelengths.

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

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

$$163 \quad NL_i(t) = \frac{C_i(t) \times V(t) + \sum_1^{t-1} [C_i(t) \times V_j]}{x_i \times S} \quad \text{with } V(t) = V_0 - \sum_1^{t-1} V_j \quad (1)$$

164 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
 165 of solution remaining in the Savillex® reactor at time t (in L); V_j is the solution volume removed from
 166 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
 167 mass fraction of element i in the glass and S is the geometric surface area of the glass (in m²).

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

$$170 \quad r_i = \frac{d(NL_i(t))}{dt} \quad (2)$$

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

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

176 The corresponding initial alteration rate of a monolith entirely irradiated with Au ions, $r(\text{Au_glass})$, was
177 calculated using equation (3):

$$178 \quad r(\text{Au_glass}) = \frac{r_{\text{effective}} - 0.1 \times r(\text{NI-glass})}{0.9} \quad (3)$$

179

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

183

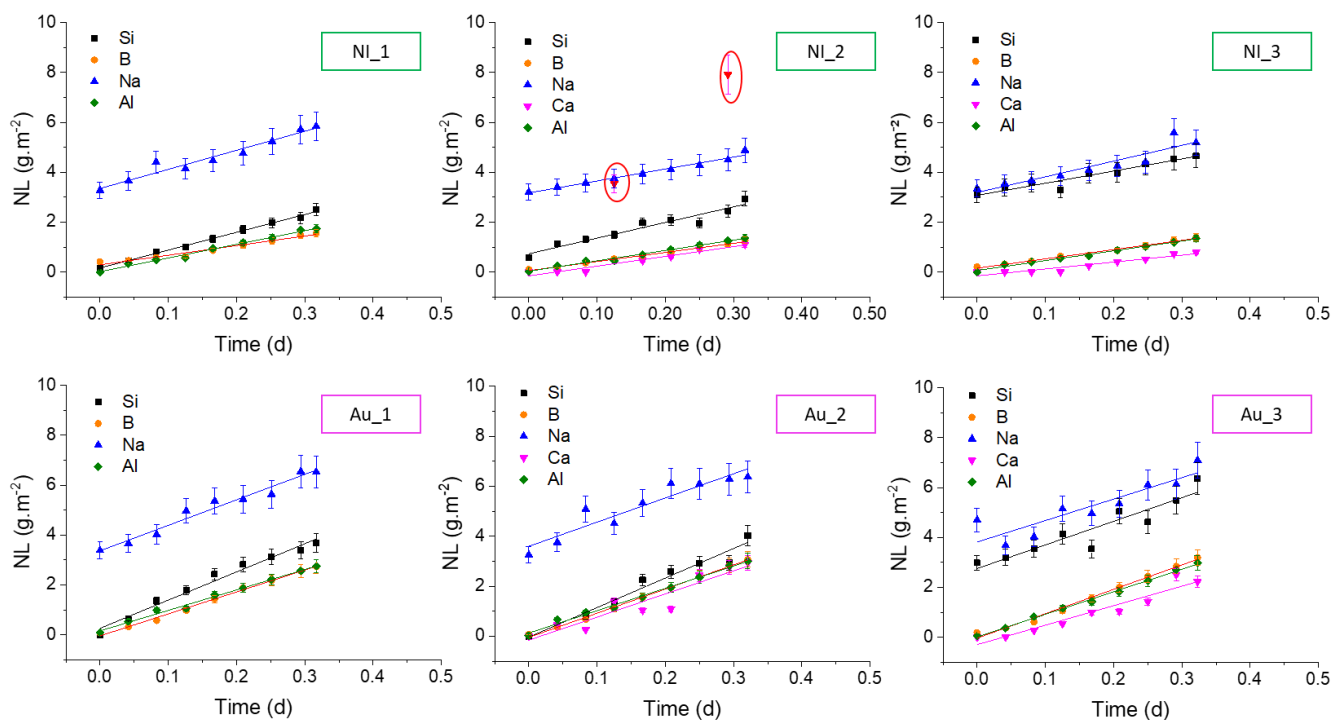
184 Results

185 The study of the initial alteration rate regime allows to focus on the first moments of the glass
186 alteration. This regime is controlled by hydrolysis of the vitreous network [10] and corresponds to a
187 maximum rate of alteration of a glass in a given medium.

188 From the releases in solution, the normalized mass losses were calculated for all the elements of the
189 glass and plotted as a function of the alteration time for the 6 samples in Figure 2. It is worth noting
190 that over a period of 8 hours, the evolution of normalized mass losses was linear, regardless of the

191 element considered and the type of sample considered (NI_glass or Au_glass). Congruency was
 192 systematically observed for B, Al and Ca, while normalized mass losses in Na were systematically
 193 higher. For Ca, outliers were attributed to potential contaminations (points drawn in red and framed)
 194 and these data were not considered in the determination of the r_{Ca} . For NI_1 and Au_1 tests, the
 195 releases of Ca were too scattered, therefore they were not considered in the subsequent calculations
 196 of r_{Ca} . For Si and Na, the initial concentrations are variable. It was thus assumed that an initial
 197 contamination in the Savillex® reactor could have induced an initial offset of the concentrations. This
 198 initial offset had virtually no impact on the slope of the $NL_{Si}(t)$ and $NL_{Na}(t)$ curves. Thus, these data were
 199 used to determine r_{Si} and r_{Na} .

200



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

204

205

206 Linear regression was performed on the NL obtained for each element and the slopes corresponding
 207 to the initial rates are reported in Table 2. We observed that, regardless of the element considered
 208 and the series, the results of the various experiments were not significantly different. The initial
 209 alteration rates calculated were systematically lower for NI_glasses than for irradiated Au_glasses. For
 210 NI_glasses, an average initial rate of $(4.9 \pm 3.0) \text{ g.m}^{-2}.\text{d}^{-1}$ was obtained compared to (10.0 ± 2.5)
 211 $\text{g.m}^{-2}.\text{d}^{-1}$ for the glasses irradiated with Au ions. Therefore, there is a significant impact of Au ions
 212 irradiation on the value of the initial alteration rate. This impact led to an increase in the average initial
 213 alteration rate by a factor $F = 2.0 \pm 0.8$. This higher initial alteration rate in the case of ISG glass samples
 214 irradiated with Au ions indicated a difference in chemical reactivity at the very first moments of
 215 alteration.

216

217 *Table 2: Initial alteration rate in $\text{g.m}^{-2}.\text{d}^{-1}$ for each element of the glass and for each test (r_i). The ratio*
 218 *of the average initial alteration rates of irradiated samples to non-irradiated samples ($F =$*
 219 *$r(\text{Au_glass})/r(\text{NI_glass})$) is given in the last column of the table. The final rate (given in $\text{g.m}^{-2}.\text{d}^{-1}$ and*
 220 *$\mu\text{m}.\text{d}^{-1}$) is the average of all the elements and all the tests. The $r_{\text{effective}}$ value is the calculated leaching*
 221 *rate without considering the non-irradiated edges. All uncertainties correspond to twice the standard*
 222 *deviation except for $r(\text{Au})$ where $\Delta r(\text{Au}) = \Delta r_{\text{effective}} + 0,1 \times \Delta r_{\text{NI}}$.*

223

$r_i (\text{g.m}^{-2}.\text{d}^{-1})$	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
$r_{\text{effective}} (\text{g.m}^{-2}.\text{d}^{-1})$				9.5 ± 2.2			
$r (\text{g.m}^{-2}.\text{d}^{-1})$	4.9 ± 3.0			10.0 ± 2.5			
$r (\mu\text{m}.\text{d}^{-1})$	2.0 ± 1.2			4.0 ± 1.0			

228

229

230

231

232

233 Discussion

234

235 Initial alteration rate values of ISG glass

236

237 This study allows to determine the initial alteration rate of ISG at 90°C. It is important to note that
238 only few data regarding the value of the initial alteration rate of ISG glass exist in the literature and
239 that the published data are variable (see Table 2).

240 Most of these data concern non-irradiated ISG specimens. Some studies were conducted on ISG glass
241 powder (the surface area was measured by the BET method or using the geometric surface of the
242 powder) and others on monoliths. In order to be able to compare the initial alteration rate values
243 obtained for powders and for monoliths, it is necessary to use corrective factors as assessed by
244 Fournier et al. [17]. Indeed, the initial alteration rate obtained from the powder should be multiplied
245 by a factor of 0.8 when the surface area considered is the geometric one and by 1.9 when the surface
246 area is measured by the BET method.

247 Jegou [19] studied the initial alteration rate of non-irradiated ISG glass powder altered in pure water
248 at 90°C, with $SA/V = 0.1 \text{ cm}^{-1}$ and $pH = 9$, over 2 days. Jegou reported an initial alteration rate of $r_0 = 1.7$
249 $\text{g.m}^{-2}.\text{d}^{-1}$, which becomes $r_0(\text{monolith}) = 3.2 \text{ g.m}^{-2}.\text{d}^{-1}$, using the corrective factor recommended by
250 Fournier et al.

251 Gin et al. [20] also altered ISG glass powder in initial rate regime in pure water at $pH = 9$, 90°C, with a
252 SA/V ratio of 0.076 cm^{-1} 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
253 appropriate corrective factor of 0.8, the corresponding average rate for a monolith is $6.6 \text{ g.m}^{-2}.\text{d}^{-1}$.

254 Inagaki et al. [21] carried out leaching experiments at different pH and temperatures on ISG glass
255 monoliths and determined a relation between the alteration rate at 90°C and the pH ($\log r_{Si} = -1.56 +$
256 $0.236 \times pH$). The use of this relation for $pH = 9$ gave $r_{Si} = 3.7 \text{ g.m}^{-2}.\text{d}^{-1}$.

257 Thus, considering data from the literature, the initial alteration rate of a non-irradiated ISG glass in
 258 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-
 259 irradiated ISG monoliths (i.e. 4.9 ± 3.0 g.m⁻².d⁻¹) is well included in this range. This observation led to
 260 the conclusion that the experimental protocol and the data treatment were reliable.

261

262

263 *Table 2: r₀ values of ISG glass reported in the literature and from the current study.*

264

References	pH	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
This study	9	90	0.01	Monolith		Static	0.33	4.9 ± 3.0

265

266

267 To the best of our knowledge, there are only two studies reporting results on the initial alteration rate
 268 of ISG glass whose structure was damaged before alteration. Angeli et al. [6] studied ISG glass fibers
 269 hyperquenched (simulating structural disorder close to the one induced by irradiation) and therefore
 270 structurally more disordered. They showed that the silicate network, was hydrolyzed 1.4 to 1.8 times
 271 faster than for annealed fibers. This result is close to the increase factor obtained in this study, which
 272 is 2.0 ± 0.8. However, the second study of Karakurt et al. [13] on the initial rate of ISG glass irradiated
 273 with gold ions cannot be considered since the glass was altered deeper than the irradiated zone.

274 Thus, the results obtained in our study brings new information and showed an effect of the glass
 275 disorder on its initial alteration rate and is consistent with the literature: the r₀ of an irradiated or
 276 hyperquenched ISG glass is increased compared to the one of a non-irradiated ISG glass.

277

278 Origin of the rate difference between NI_glass and Au_glass

279 The initial alteration rate of Au_glass samples was found to be higher than that of NI_glass by a factor
280 of 2.0 ± 0.8 . This observation means that the chemical reactivity of the Au_glass with respect to the
281 solution (pure water) is greater than that of the NI_glass during the hydrolysis step. Several authors
282 [5, 6, 22, 23] showed that there is a link between the structural disorder of glass, whether thermally
283 induced [6] or by irradiation [5, 22, 23], and its chemical durability in the long term alteration rate
284 regime. The current study demonstrated that this is also true for the initial alteration rate of ISG glass.
285 Several explanations could be proposed to explain the increase of r_0 due to the glass disorder induced
286 by Au ions irradiation.

287 Firstly, radiation damage as well as high quenching rate induce a modification of the glass short range
288 order with the creation of punctual defects and non-bridging oxygen atoms that induce a decrease of
289 the polymerization of the glass network. Moreover a partial conversion of BO_4 in BO_3 species [2, 4-6,
290 14, 24] is observed that also participates to the decrease of the glass polymerization degree which
291 could induce a higher hydrolysis of the silicate network and result in an increase in glass alteration
292 rate. Overall, the general depolymerisation of the glass network results in a lower number of bridging
293 bonds between network former atoms. The initial rate regime is controlled by the hydrolysis of the
294 vitreous network through the breaking of its bridging bonds (Si-O-Si, Si-O-Al or Si-O-Zr for example)
295 by protonation or hydroxylation of reactive surface sites [10]. Thus, the hydrolysis of the glass can be
296 favoured by a low degree of polymerization of the vitreous network. This was recently confirmed by
297 Monte Carlo simulations which showed that the primary cause for the increase of glass alteration rate
298 was the extent of the depolymerization of the glass network introduced by these local structural
299 changes (boron coordination, number and nature of Q^n species, and angular distribution of Si-O-Si
300 linkages) [25]. Moreover the reactivity of B(III) was shown to be higher than that of B(IV). Kapoor et al.
301 [26] showed that the boron (+III) could be seen as a Lewis acid, with water acting as a Lewis base.

302 Moreover, by considering the Lewis acido-basicity of borate species, an increased reactivity of the
303 B(+III) compared to B(+IV) can be assumed to increase the glass network hydrolysis.

304 Secondly, the radiation damage generated by nuclear collisions also induces a modification of the glass
305 medium range order (MRO) with mainly a broadening of the ring size and angle distribution [5, 27], as
306 indicated by the increase of three membered silicate rings and the shift of R band. The MRO
307 modification was also observed by molecular dynamic simulation of radiation damage and high
308 quenching rate in simple borosilicate glasses [28]. This modification of the ring size distribution directly
309 affects the glass free volume and thereby the accessibility of the water into the glass network [28],
310 that may also favour its hydrolysis.

311 Finally, these mechanisms can occur either upstream of the hydrolysis step, the water penetrates
312 faster into the glass and therefore leads to a deeper hydrolysis [29] or are directly related to the
313 increase of B(III), more reactive towards water [24, 26]. These two mechanisms can effectively act
314 concomitantly and synergistically.

315

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

317 In the literature, it was shown for SON68 glass that irradiation with Au ions had no significant impact
318 on the initial alteration rate [11]. Indeed, the initial rate of SON68 glass was about $2 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, whether
319 the glass was irradiated with Au ions or not [11]. This result was also observed for SON68 glasses doped
320 with actinides [11, 12, 30]. The more complex chemical composition of SON68 glass compared to ISG
321 glass could certainly explain the weaker impact of Au ions on the glass structure and thus on the initial
322 alteration rate [3]. More experiments on complex SON68 glass are needed to quantify its structural
323 evolution versus irradiation and compare it to the one of ISG glass so as to try to explain the lower
324 sensitivity of SON68 glass initial alteration rate under irradiation.

325

326

327 Conclusion

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

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

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