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Comparative effect of alkaline elements and calcium on alteration of International Simple Glass

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In the concept of deep geological repository for High Level Wastes, the chemical elements present in the media are expected to impact the long-term behavior of the glass. The effects of Ca, K, and Cs on International Simple Glass glass alteration are compared through long-term experiments (180–500 days). These elements limit glass alteration by their incorporation into the gel layer. The limiting mechanisms driving glass alteration appear to be mainly diffusive, at least during the first six months. The three cations are not equally efficient in limiting glass alteration: the effects of Ca are stronger than those of Cs and K. Multi-element experiments show that the effects of these elements are additive and proportional to the quantity of each element incorporated. When they play the role of charge compensator in the gel network, their incorporation is competitive and follows the order $\text{Ca} \gg \text{Cs} > \text{K}$. In addition, when Ca is added to the solution in excess, the quantity of elements incorporated into the gel layer is higher than the amount required for charge compensation. The incorporation of Ca in the gel nanopores as calcium carbonate could explain this phenomenon. These processes could slow the transport phenomena through the gel and enhance its protective properties.

npj Materials Degradation (2019)3:10; <https://doi.org/10.1038/s41529-019-0072-7>

INTRODUCTION

Interactions between glasses and solutions are of great interest in the field of material degradation, particularly to study the long-term behavior of high-level radioactive wastes. In deep geologic repository of high-level waste, the chemical elements present in the media (groundwater, near-field materials, metallic barriers, and the glass itself) are expected to have an impact on glass alteration.

During glass alteration, several concomitant or subsequent processes occur. First, glass hydration and interdiffusion induce ion exchange between protons from the solution and alkali from the glass, leading to a layer of hydrated glass.^{1,2} Simultaneously, the glass network is dissolved by the hydrolysis of the covalent bonds. As Si and Al are released from the glass, the solution reaches an equilibrium state and the rate of the hydrolysis reaction decreases. At this point, some elements (Si, Al, Zr, etc.) recondense to form a gel layer at the hydrated glass surface. Depending on its composition and porosity, this nanoporous layer may protect the underlying glass.^{3–6} Finally, the residual stage of alteration is controlled by the reactive diffusion of species from the glass and the solution through the hydrated glass and the gel, as well as the precipitation of secondary phases. During their formation, these secondary phases consume elements from the solution and the gel, particularly Si and Al, leading to a decrease in the protective properties of the gel.^{7,8} Under certain conditions, the glass alteration process may resume. This phenomenon has been observed during the precipitation of zeolites and hydrated calcium silicates.⁹

In our previous studies, we demonstrated that the addition of Zn, Mg, Ni, Co, and/or Fe to the alteration solution triggers the precipitation of secondary phases.^{10,11} These elements strongly increase glass alteration, and their effects are additive. The overall effect is proportional to the total concentration of these elements

in solution, even when a mixture of these elements is used. Depending on the conditions, these elements can also be incorporated into the gel layer as a replacement for Ca.¹²

The effects of Ca on glass alteration have been widely studied.^{13–18} When Ca is released through glass alteration or is added to the solution, it can be retained or incorporated into the gel layer.^{12,19} Ca^{2+} can participate in gel network formation as a charge compensator for the $[\text{AlO}_4]^-$ and $[\text{ZrO}_6]^{2-}$ units.²⁰ Ca can also condense via olation with the heavy elements in the gel, leading to a high degree of reticulation in the gel network.²¹ Under static conditions, Ca can act as a catalyst in the condensation reaction of silica responsible for the gel formation.^{22,23} Thus, the presence of Ca strengthens and densifies the gel network, thereby limiting the transport of water and elements through the gel layer and reducing the rate of glass alteration.^{22,23} In addition, some studies have demonstrated the precipitation of Ca carbonates in the pores of nanoporous silica and the altered glass gel layer.^{24,25}

Ambient conditions, especially the pH, can affect these processes.^{22,26,27} As the pH decreases, Ca becomes more concentrated in the solution and is less retained/incorporated into the gel layer, which in turn loses its protective properties. At $\text{pH} < 11$, Ca forms metallic surface complexes, weakening the Si–O bonds and thereby favoring their hydrolysis.^{26,28} At a high pH and for long-term experiments, the main drawback is the massive formation of secondary phases such as hydrated calcium silicates.^{29–31} The precipitation of these secondary phases consumes silicon and maintains a high glass dissolution rate.

Alkaline elements such as Cs and K are present in nuclear glasses and/or in the environment, near-field minerals, and groundwater. While the effects of Ca on glass alteration are well known,²⁶ the impacts of Cs and K have been poorly studied. The incorporation of K in the alteration layer was observed in natural

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Received: 9 August 2018 Accepted: 25 January 2019

Published online: 01 March 2019

analogs,^{32–36} archeological glasses^{37–41} and the International Simple Glass (ISG).^{4,42} Recently, Collin et al.⁴² studied gel layers formed during the alteration of ISG in Si-saturated solutions containing K, Cs, Li, or Na ions at pH 7. K, and to a greater extent, Cs, were incorporated in the gel layers as replacements for Ca. The exchange between Ca and alkali affects the total quantity of water inside each gel; this phenomenon is well correlated with the observed decrease in glass alteration.⁴²

The presence of K or Cs in secondary phases formed during the alteration of nuclear glasses and obsidian have been reported.^{31,43,44} However, these elements are incorporated as exchangeable cations in the structure of the secondary phases. Therefore, their presence in the media alone does not trigger precipitation, and no effect on glass alteration has been observed.⁴⁵ The formation of K or Cs carbonates is not favored during glass alteration since these minerals are highly soluble in solution.

In this work, we compare the effects of Cs, K, and Ca on the alteration of ISG glass to determine whether they are additive or competitive, similar to that done in our previous studies involving Zn, Mg, Ni, Co, and Fe.^{10–12} To achieve this goal, an extensive set of long-term experiments (180–500 days) was designed. The chloride salts of K, Cs, and/or Ca were added to the solution after one day of alteration in pure water at 50 °C. Two glasses were considered, ISG and its Ca-free equivalent, CJ7.⁴⁶ In addition, because the composition of the gel layer is strongly affected by the pH, experiments at fixed pH values were also conducted.

RESULTS

Scientific approach

First, to compare the effects of Ca originating from the glass with those of Ca added to the solution, the alteration of ISG in pure water (ISG test) was compared with that of CJ7 glass altered in CaCl₂ solution (4×10^{-3} mol L⁻¹ - CJ7-Ca test). This concentration was chosen to be representative of the maximum amount of Ca available in solution after one month of ISG glass alteration at a residual rate.⁴⁷

To study the effects of Cs and K, and to compare them with those of Ca, CJ7 glass was altered in CsCl or KCl solutions (4×10^{-3} mol L⁻¹ - CJ7-Cs and CJ7-K tests, respectively). This concentration fell in the range in which these elements are present in the media (i.e., the glass and the groundwater of the geological repository). To determine whether the effects of these elements were additive or competitive in nature, a multi-elemental experiment (CJ7-KCsCa test) was performed. In this experiment, all three elements were added together with an elemental concentration of 1.3×10^{-3} mol L⁻¹ each. The cumulative concentration ([K] + [Cs] + [Ca]) in the CJ7-KCsCa experiment was the same as the mono-elemental concentration used in the CJ7-K, CJ7-Cs, and CJ7-Ca tests, i.e., 4×10^{-3} mol L⁻¹.

In addition, the effects of K and Cs on ISG glass were studied in the ISG-K and ISG-Cs experiments, respectively. In these experiments, two of the three elements were present together: KCl or CsCl were introduced to the solution at a concentration of 4×10^{-3} mol L⁻¹, and Ca was provided by ISG glass alteration. The results of these were also compared with those of the ISG-Ca experiment, in which ISG was altered in the presence of 1×10^{-2} mol L⁻¹ of CaCl₂ in the solution. This test was initially conducted to compare the effects of Fe, Mg, and Ca on ISG glass alteration, and the detailed results are reported a previous paper.¹² All these tests were conducted without controlling the pH.

Finally, two ISG glass alteration tests were conducted at fixed pH values. The pH was expected to have a strong impact on the behavior of the elements and on their concentrations in solution. In the ISG-pH6.9 and ISG-pH7.6 tests, the pH was maintained by the addition of HCl or NaOH (10^{-3} to 1 mol L⁻¹). The measured pH

Table 1. References and characteristics of each experiment. All experiments were conducted at 50 °C, and the first element addition was carried out after one day of alteration in pure water

	Name	Glass	Element(s) present		[element] in solution		pH (50 °C)
			in solution	from glass	10^{-3} mol L ⁻¹	10^{-3} g L ⁻¹	
Glasses without Ca	CJ7-K	CJ7	KCl	–	4	156	Free
	CJ7-Cs	CJ7	CsCl	–	4	532	Free
	CJ7-Ca	CJ7	CaCl ₂	–	4	160	Free
	CJ7-KCsCa	CJ7	KCl	–	1.3	51	Free
			CsCl		1.3	173	
			CaCl ₂		1.3	52	
Glasses with Ca	ISG-K	ISG	KCl	Ca	4	156	Free
	ISG-Cs	ISG	CsCl	Ca	4	532	Free
	ISG-Ca	ISG	CaCl ₂	Ca	10	400	Free
	ISG	ISG	–	Ca	–	–	Free
	ISG-pH6.9	ISG	–	Ca			6.9
	ISG-pH7.6	ISG	–	Ca			7.6

variations and corrections are given in Supplementary Information 1. The target pH values were 6.5 and 7.5 (at 50 °C); however, the average pH values obtained were 6.9 and 7.6, respectively. In this study, the word “solubility” is used for chemical elements (K, Cs, Ca), even though it is normally applied to phases. The solubility of a chemical element means the solubility of the phase controlling the concentration of the element in solution. The names and the characteristics of each experiment are listed in Table 1.

Alteration kinetics and pH evolution

The normalized boron mass losses (NL(B)) and pH are shown as a function of time in Fig. 1. For the sake of clarity, Fig. 1 has been divided into several parts, in each of which only two to five experiments are compared. However, the results of all experiments are also plotted together in single figures in Supplementary information 2. From the NL(B) values, the alteration rates during several time periods were calculated (Fig. 1g, h).

Firstly, we studied the effect of Ca origin and pH, through experiments CJ7-Ca, ISG, ISG-pH6.9, and ISG-pH7.6. In pure water, glass alteration induces the release of alkali and boron, resulting in pH values of up to ~9 for ISG at 50 °C and ~8.7 for CJ7 at 90 °C.⁴⁶ The stabilization is due to the buffer effect of boron acid/borate, and the composition of the glass impacts the final pH value. When ISG was altered at lower fixed pH values (ISG-pH6.9 and ISG-pH7.6), the amount (NL(B), Fig. 1a) and rate (Fig. 1g, h) of glass alteration were higher than in the free-pH reference test (ISG). Thus, higher glass alteration quantities and rates were correlated with lower pH. This result can be attributed firstly to an increase in the hydration/interdiffusion rate and secondly, to a lower retention of Ca in the gel layer. In the fixed-pH tests, the NL(Ca) values were much lower than the NL(B) values (Supplementary information 1). Thus, when the fixed pH was decreased, the glass exhibited more alteration because the Ca was less retained in the alteration layer, and the alteration rate drop occurred later.

When Ca was added directly to the solution during the alteration of CJ7, the Ca-free glass (CJ7-Ca test), the NL(B) values, alteration rate, and pH (Fig. 1a, b, g and h) were lower than those observed when the Ca originated from the glass alteration (ISG test). As will be discussed later, this difference could be related to the availability of Ca. When Ca is added to the solution, a large amount is immediately available, whereas when it is provided by the glass, the glass network must first be hydrolyzed to make Ca available.

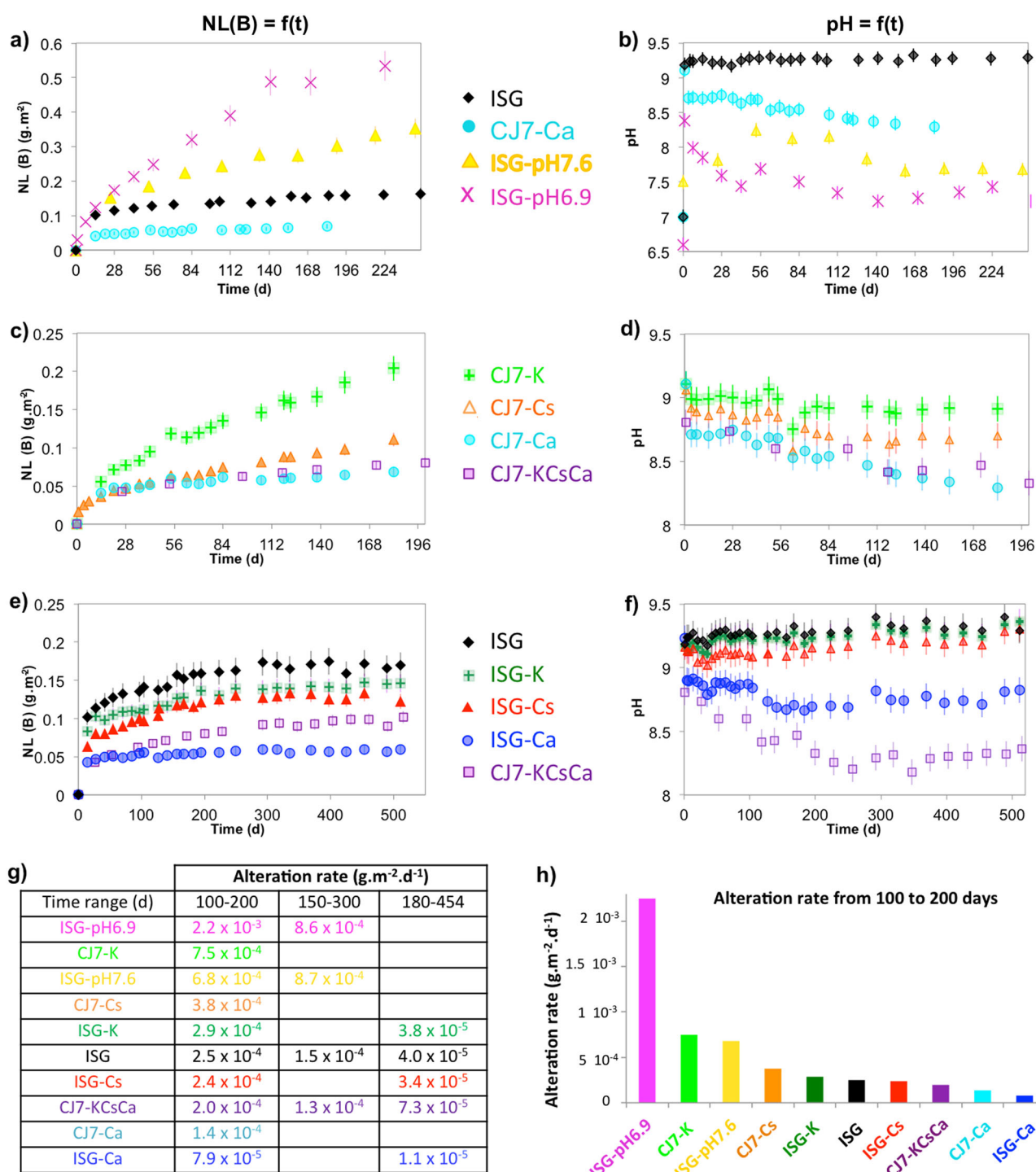


Fig. 1 NL(B) (left) and the pH (right) as a function of time. **a, b** show a comparison of the effect of Ca added to the solution (CJ7-Ca) and leached from the glass at free pH (ISG) and fixed pH (ISG-pH6.9 and ISG-pH7.6). **c, d** present the results of the experiments in which K, Cs, Ca, or K + Cs + Ca were added to CJ7 (experiments CJ7-K, CJ7-Cs, CJ7-Ca, and CJ7-KCsCa, respectively). **e, f** present the results of the multi-elemental experiments (Ca + K, Cs + Ca, K + Cs + Ca; experiments ISG-K, ISG-Cs, and CJ7-KCsCa, respectively) and the experiment ISG-Ca in which the concentration of Ca in the solution was higher. **g** Alteration rates calculated during different time ranges and **h** histogram of the alteration rates calculated between 100 and 200 days

Secondly, we studied the effect K, Cs, and/or Ca through the comparison between the elements and between the glasses. In the presence of K, Cs, and/or Ca, the NL(B) values for CJ7 (Fig. 1c) and ISG (Fig. 1e) and their alteration rates (Fig. 1g, h) were lower than in pure water. In both cases, the effects of Ca were stronger than those of Cs and K, partly because the rate drop occurred

sooner. Comparing the mono-elemental ISG experiments (ISG-K, ISG-Cs, ISG-Ca) with those using CJ7 (CJ7-K, CJ7-Cs, CJ7-Ca), the NL(B) values and glass alteration rates were lower for CJ7, except for the experiment CJ7-K. However, in pure water, CJ7 was significantly more altered than ISG, as has been reported in several studies.^{46,48}

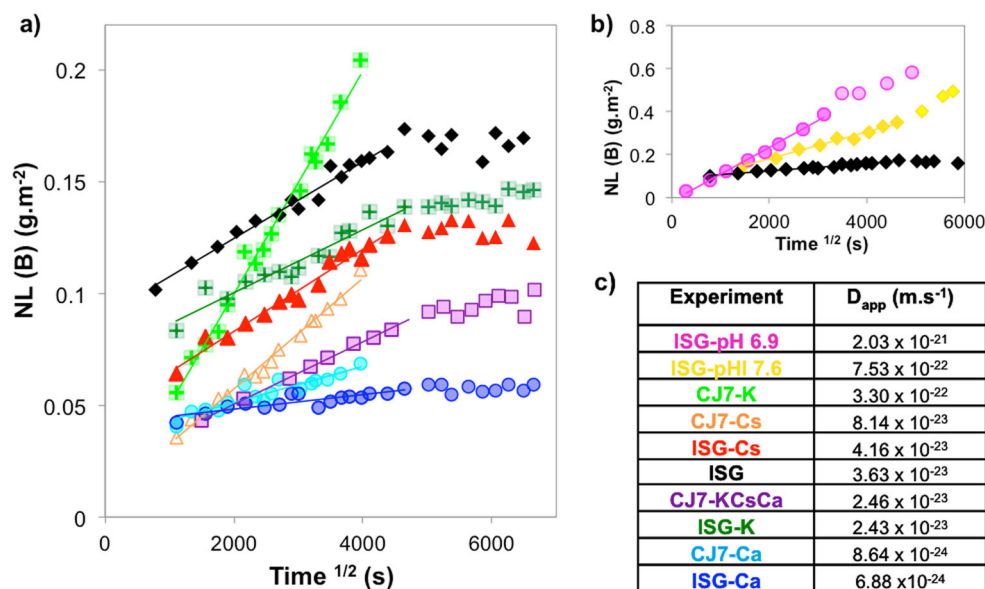


Fig. 2 **a, b** NL(B) as a function of $t^{1/2}$. **c** Calculated apparent diffusion coefficient D_{app} for each experiment

When all three elements were added together (CJ7-KCsCa), the results were very similar to those obtained for the experiment CJ7-Ca (Fig. 1c, g, h). The NL(B) values and alteration rates were much lower than those for ISG in pure water or even in the presence of K, Cs, or Ca (ISG-K, ISG-Cs, and ISG-Ca). As will be discussed later, this suggests that the effects of these elements are additive.

For CJ7, the pH remained relatively stable for the first 50 days of alteration, and decreased slightly afterwards (Fig. 1d). In the multi-elemental experiment CJ7-KCsCa, the pH values were similar to those of CJ7-Ca, and finally stabilized after 300 days (Fig. 1d). The pH values for ISG quickly became stable, and were higher than those observed for CJ7 (Fig. 1f). For both glasses, experiments involving Cs resulted in higher pH values than the Ca experiments, but lower ones than the K experiments. The pH values followed the same order as the NL(B) values; therefore, the alteration of a greater amount of glass induced a higher pH. This result can be explained by the release of alkali into the solution, which increased the pH.

Predominant processes

During the first 200 days of all the experiments, the NL(B) values increased linearly with the square root of time (Fig. 2a, b). Therefore, according to Fick's second law, the glass alteration was driven by a diffusive process during this period (see the methods section). The apparent diffusion coefficients D_{app} , which represent the diffusion rate of water (or other species) through the gel layer, were calculated at 50 °C and are presented in the table in Fig. 2c. These coefficients ranged from $10^{-25} \text{ m}^2 \text{ s}^{-1}$ to $10^{-21} \text{ m}^2 \text{ s}^{-1}$; these values fell within the range for the diffusion of water in glass.¹⁷ Moreover, the D_{app} coefficients followed the same order as the NL(B) and alteration rate values. Therefore, this diffusion process also controlled glass alteration at longer times. In the fixed-pH experiments, the coefficient D_{app} increased with a decrease in pH. This could be attributed to enhancement of the hydration/interdiffusion process and/or a decrease in Ca retention/incorporation, leading to a less protective gel layer.

After 200 days, glass alteration kinetics (NL(B)) no longer followed the relationship with the square root of time, and instead tended towards stabilization. This suggested a change in the rate-limiting processes, which were similar regardless of which cation (s) were added to the solution.

Cations concentrations

Figure 3 presents the concentrations of the cations measured before the monthly additions as a function of time. The setpoint values of the monthly additions are indicated by the dashed horizontal lines. Data points below the setpoint value indicate that the element was still being consumed, while stabilization of the data near the setpoint indicates that element consumption had stopped.

As shown in Fig. 3a, when the pH was fixed (experiments ISG-pH6.9 and ISG-pH7.6), the Ca concentrations in the solution were much higher than that in the free-pH test (ISG). In addition, the Ca concentrations increased regularly and then stabilized. This stabilization may be due to Ca reaching saturation in the solution under these conditions.

When Ca was added to the solution (ISG-Ca and CJ7-Ca), the values of the Ca concentrations were irregular, making their interpretation difficult (Fig. 3b). This variability could be due to calcite or other Ca carbonate precipitation/dissolution phenomena in solution and/or in the gel layer. Indeed, as indicated in Supplementary information 3, if the concentration is high enough, calcite could precipitate at the pH of the experiments.

When Cs or K was added to the solution during ISG alteration, the element was partly consumed during the first two to three months, after which the consumption stopped (Fig. 3c). When K, Cs, or Ca was added to the solution during CJ7 alteration, the element was partly consumed each month throughout the entire experiment (Fig. 3d). The concentration remaining in solution at the end of each month slightly increased, but the consumption did not stop. Finally, when all three elements were added together (Fig. 3e), the Ca concentrations were lower than those of Cs, which in turn were lower than those of K. At the end of the experiment, only Ca was still being consumed, and the concentration remaining of K exceeded the setpoint value.

Elemental incorporation/retention ratios

The consumption of K, Cs, and Ca from the solution was used to calculate the ratio R_x between the quantity (n_x) of the element retained and/or incorporated into the gel layer and the NL(B) (Eq. 1). The word "incorporation" refers to elements added to the solution and integrated into the gel layer assuming that no secondary mineral precipitation occurs at the gel surface, and the word "retention" refers to Ca provided by the ISG alteration that is

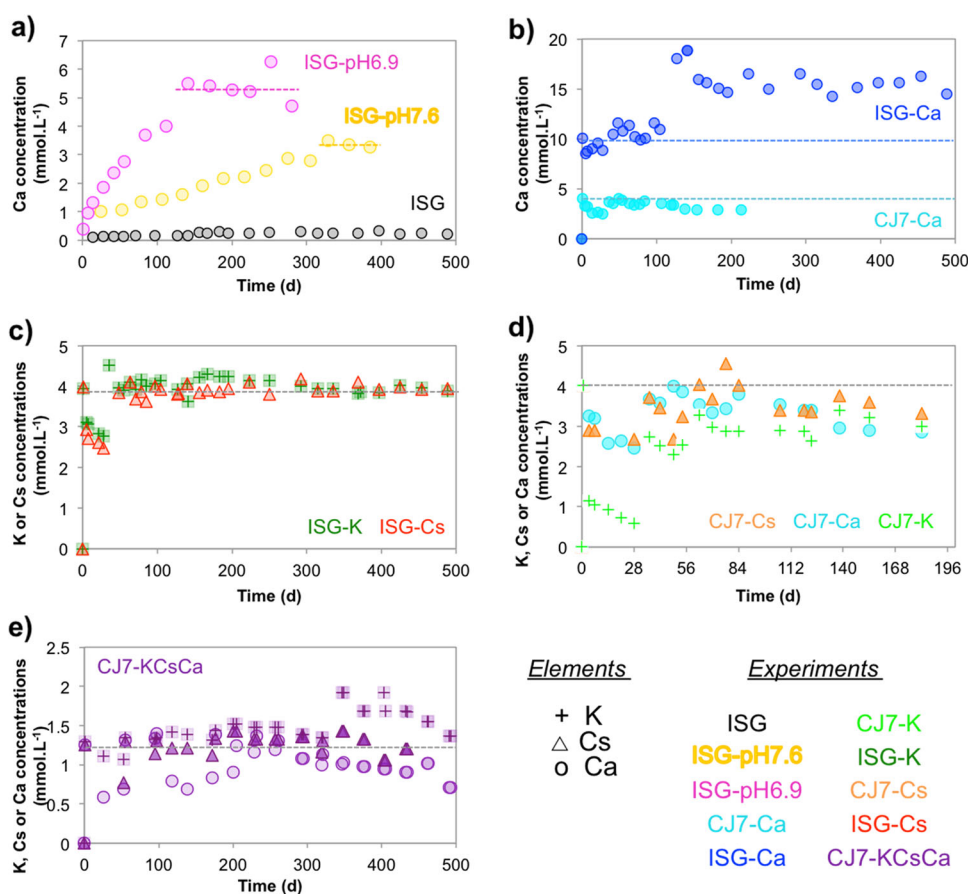


Fig. 3 Ca, Cs, and K concentrations in solution before the monthly additions as a function of time in selected experiments. Horizontal lines are included as a guide for the eyes to highlight the data stabilization in **a**, and to show the setpoint value for the monthly addition in each experiment in **b–e**.

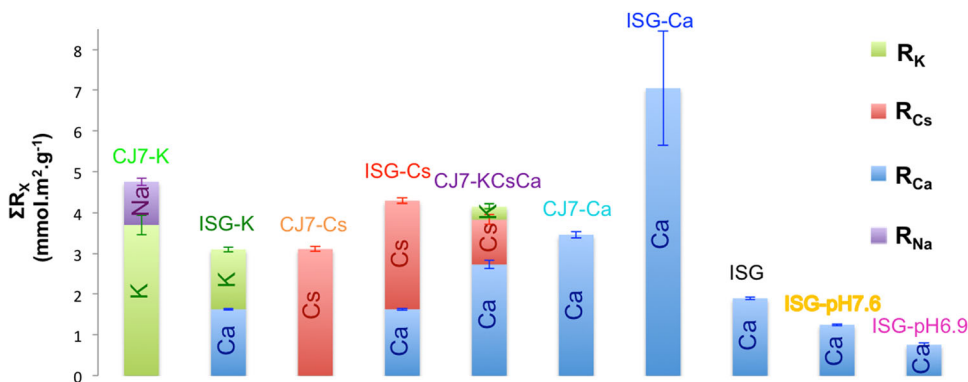


Fig. 4 Proportions of the elements incorporated/retained in the gel layer represented by the ratio R_X between the quantity (n_X) of the element retained and/or incorporated into the gel layer and the $NL(B)$ value. The error bars are based on the standard deviation calculated for the R_X values during the last 100 days

not released into the solution, and is therefore retained in the gel layer.

$$R_X = \frac{n_X}{NL(B)} \quad (1)$$

where $X = K, Cs, \text{ or } Ca$, and n_X is the quantity of the element X incorporated or retained in the gel layer (mmol).

The Na present in both the CJ7 and ISG glasses could behave as a charge compensator. In all experiments except CJ7-K, Na was released congruently with B, indicating that it was not retained in

the alteration layer. Therefore, Na was only considered in the calculations for experiment ISG-K. Because the R_X values remained constant as a function of time (Supplementary Information 4), an average value of R_X was selected for each element of each experiment (Fig. 4).

As presented in Fig. 4, R_{Ca} was higher for experiment CJ7-Ca than for experiment ISG. Therefore, the incorporation of Ca from the solution into the CJ7 gel layer was higher than the retention of Ca in the ISG gel layer. In experiments with a fixed pH (ISG-pH6.9 and ISG-pH7.6), R_{Ca} was much lower than in the free-pH ISG

reference test (ISG). Therefore, Ca retention increased with the pH. As discussed above, the Ca consumption data for experiments CJ7-Ca and particularly, ISG-Ca, are highly variable and difficult to interpret. Nevertheless, when Ca was provided via monthly additions, its concentration in the solution was high enough to enable a high R_{Ca} and thereby high incorporation of Ca into the gel layer.

The Ca retention was equal (same R_{Ca}) in the experiments ISG-K and ISG-Cs, but a much greater proportion of Cs was incorporated in ISG-Cs than K in ISG-K ($R_{Cs} > R_K$). In the multi-elemental experiment CJ7-KCsCa, the R_X values followed the order $Ca > Cs > K$. The R_{Cs} values were similar in the CJ7-Cs and ISG-Cs experiments, but lower in the experiment CJ7-KCsCa. The R_K values varied greatly depending on the experiment: in the presence of Cs and Ca (CJ7-KCsCa), barely any K was incorporated, while its incorporation was greater in the presence of Ca (ISG-K test) and even more when K was alone in the solution (CJ7-K test).

Moreover, in all the experiments except ISG-pH6.9 and ISG-pH7.6, the sum of the R_X values was higher than the R_{Ca} value for ISG alteration in pure water. This indicated that ISG and CJ7 can incorporate a greater amount of the tested elements (K, Cs, and/or Ca) into their gel layer than the quantity of Ca provided by ISG alteration.

DISCUSSION

The Discussion section is divided into five parts. First, we discuss the pH dependence, followed by the impact of the origin of Ca. Afterward the effects of K, Cs and Ca are compared in terms of quantity and efficiency, and we determine if their effects were additive or competitive in nature. Finally, we discuss the quantity of cations required for charge compensation.

The results reported in this study confirmed that the pH is a key parameter in glass alteration. In static conditions, when the pH decreased (through deliberate adjustment of the solution pH or passively due to the glass alteration process), glass alteration increased. Similar results were reported for ISG glass alteration at 90 °C and pH values ranging from 7 to 9.⁴⁸ Two explanations for this phenomenon can be proposed.

The first is that the hydration/interdiffusion and diffusion reactions are favored when the pH decreases. Several studies^{5,49–51} have demonstrated that in silicon-saturated solutions (in which the hydrolysis process is highly disfavored), glass alteration increases as the pH decreases. Under these conditions, the predominant processes driving glass alteration are the hydration/interdiffusion and diffusion reactions. These processes are usually predominant at the very beginning of the alteration, and also occur during the residual stage of alteration.^{5,49–51}

The second is that the solubility of Ca in solution increases as the pH decreases (Supplementary information 3). Therefore, Ca is less retained in the gel layer, reducing the protective effect of the gel. The rate drop was less intense, leading to an increase in the amount of altered glass.³ In the experiments ISG-pH6.9 and ISG-pH7.6, after the Ca concentration in the solution reached a certain value, it stabilized and the glass alteration slowed. After this point, the Ca retention increased, making the gel layer more protective. The value at which the Ca concentration stabilizes depends on the pH and may follow the trend of Ca solubility in the solution depending on the phases involved in the experimental system (an example is given using calcite in Supplementary information 3).

Additionally, although no secondary phases were observed on the altered glass samples, it should be noted that pH has also strongly affects the precipitation of secondary phases. The precipitation of smectites has been reported in similar experiments involving ISG glass in the presence of Zn, Mg, Ni, Co, or Fe.^{10–12} The precipitation of smectites decreases the pH by consuming hydroxyl ions; when the pH is low enough, the precipitation is inhibited. At this point, other elements such as Zn,

Ni, Fe, or Mg can be incorporated into the gel layer as a replacement for the Ca, whose solubility in solution increases due to the pH decrease.^{11,12}

Regardless of its origin, i.e., via the addition of Ca to solution or the diffusion of Ca out of the glass, the Ca had the same overall effect on glass alteration: it limited glass alteration by its incorporation/retention into the gel layer, thereby increasing the protective properties of the layer. However, this effect was stronger when Ca was added to the solution (CJ7-Ca) than when it was provided by glass alteration (ISG). In experiment CJ7-Ca, the pH values were lower than those in experiment ISG; thus, the interdiffusion and diffusion processes must have been enhanced, and the solubility of Ca in solution must have been higher. Despite this, the NL(B) values were lower. The Ca incorporation ratio in the CJ7 gel layer was almost twice the retention ratio of Ca in the ISG gel layer (Fig. 4). Therefore, the CJ7-Ca gel layer was more protective, and the alteration rate drop was greater and/or occurred earlier.

Several hypotheses can be suggested to explain these results. Firstly, Ca can play two roles in the gel layer. When it is provided by the glass, Ca can be incorporated into the gel network as a former and/or as a charge compensator for the $[AlO_4]^-$ and $[ZrO_6]^{2-}$ units. When it is added in the solution, it can be incorporated into the gel layer both as a charge compensator and as nano-precipitates in the gel nanopores. The probable presence of dissolved carbonates in the solution may favor the incorporation of Ca through the precipitation of calcium carbonates in the gel nanopores. This type of precipitation is more strongly favored in confined media than in the bulk solution.⁵² It could induce pore clogging, which would limit the transport of water and other species through the gel, thereby limiting the glass alteration. This hypothesis is supported by the work of Rebisoul et al.,²⁴ who demonstrated the presence of a carbon gradient from the solution to the glass associated with Ca enrichment in the gel, and suggested the presence of calcium carbonates into the gel layer.²⁴ When Ca is only provided by glass alteration, the precipitation of Ca carbonates into the nanopores is less probable; therefore, the quantity of Ca in the gel layer is lower.

Secondly, in most of the experiments, the sum of the R_X values was higher than the R_{Ca} value obtained in the experiment ISG. This result shows that the gel layer formed during the ISG experiment was capable of incorporating more cations than the amount of Ca that would be provided by its alteration based on its composition. Moreover, the amount of Ca supplied by ISG glass alteration in pure water is limited by the hydrolysis of the network. This situation was different in the CJ7-Ca experiment, in which the quantity of Ca available in solution was largely sufficient to compensate for all $[AlO_4]^-$ and $[ZrO_6]^{2-}$ units present in the gel network.

Finally, when the Ca is provided by the glass (ISG test), its availability is driven by the hydrolysis of the glass network and Ca recondensation to participate in the gel network.³ When Ca was added directly to the solution (CJ7-Ca test), although the first addition was made after one day of alteration in pure water, the Ca was immediately available in a large and sufficient quantity.

All these explanations are supported by the D_{app} values obtained from the ISG and CJ7-Ca experiments (Fig. 2). The D_{app} value was higher when Ca originated from the glass (ISG-test) than when it was added to the solution (CJ7-Ca test). Moreover, when a large excess of Ca with regard to the amount required to compensate the charges in the gel (ISG-Ca) was present in the solution, D_{app} was lower. This may be due to the precipitation of Ca carbonates limiting the transport of species in the gel.

The addition of K, Cs, and/or Ca limited the alteration of both CJ7 and ISG. These elements were incorporated/retained in the gel layer, enhancing its protective properties. However, although these elements had the same effect, their incorporation/retention differed in quantity and efficiency.

The amount of K incorporated was reduced in the presence of Ca (experiment ISG-K) and even further reduced in the presence of Cs and Ca (experiment CJ7-KCsCa) compared to their absence in experiment CJ7-K. In contrast, the incorporation of Cs was not affected by the presence of Ca and/or K (experiments CJ7-Cs, ISG-Cs, and CJ7-KCsCa). As expected, in the gel layer, the retention of Ca from the ISG glass was lower when K or Cs were present in the solution (experiments ISG-K and ISG-Cs) than in pure water (experiment ISG). In experiment ISG-Cs, this lower Ca retention can be explained by the lower pH and therefore higher Ca solubility in the solution. However, in experiments ISG-K and ISG, the pH values were similar. Therefore, it was the incorporation of K into the gel layer rather than the pH conditions that limited the Ca retention. Thus, the presence of K and Ca affected the incorporation/retention of the other element, but Cs was not affected. When all the three elements were added to the solution (experiment CJ7-KCsCa), the amount of each element incorporated followed the order $\text{Ca} \gg \text{Cs} > \text{K}$. The much higher incorporation of Ca could be explained by its role as a charge compensator/network former and its possible participation in calcium carbonate precipitation.

The alkali Na was also present in the system. As shown in the work of Gin et al.⁴⁶ which is shown in Supplementary information 5, when CJ7 glass is altered in pure water, Na is not released congruently with B; the NL(B) is twice the NL(Na) . Some of the Na is retained in the gel layer as a charge compensator. On the contrary, in experiments CJ7-K, CJ7-Cs, and CJ7-Ca, Na is released more congruently with B. Thus, the incorporation of K, Cs, or Ca in the gel layer occurs at the expense of Na retention.

Thien et al.⁵³ showed that Na, which acts as a charge compensator into the gel layer, is immediately replaced by Mg when this element is added in the solution. Similarly, Debure et al.⁵⁴ reported that when both Ca and Mg were added to the solution during the alteration of CJ7 glass, more Ca than Mg was incorporated. All these cations are exchangeable, depending on their affinity.

Therefore, the amount of cations incorporated/retained in the gel layer followed the order $\text{Ca} \gg \text{Cs} > \text{K} > \text{Na}$. This order does not follow the trend suggested by the properties of the ions in solution. According to Ohtaki et al.⁵⁵ Ca^{2+} is the most hydrated ion on this list (8 water molecules), and due to its thick hydration shell, has the largest hydrated radius. Therefore, it has the lowest self-diffusion coefficient and is the least mobile of the ions considered in the present study. Nevertheless, Ca was the most-incorporated element. This could be explained by the possible precipitation of calcium carbonates into the gel nanopores.

To evaluate the efficiency of the incorporation/retention of each element, we considered the slope of the total quantity of the element mobilized as a function of NL(B) (Supplementary Information 6-a). A higher slope corresponds to a lower NL(B) value for the same amount of incorporated/retained element. For both series of glasses, the slopes were lower with Cs than with Ca, but higher with Cs than with K. Therefore, their efficiency in limiting glass alteration followed the order $\text{Ca} \gg \text{Cs} > \text{K}$. In light of the fact that these elements behave as charge compensators,²⁰ it is not surprising that Ca is more efficient than K or Cs. The Ca ion is bivalent and Cs and K are monovalent; thus, one Ca^{2+} can compensate for two negative charges, whereas Cs^+ and K^+ can only compensate for one. In addition, one Ca^{2+} forms two bonds and constrains the gel network more than two K^+ or Cs^+ , thereby limiting transport through the gel layer (D_{app} is lower for experiments in presence of Ca).

The results obtained in this study indicate that K, Cs, and/or Ca limit glass alteration. However, at this point, it is not clear whether the effects of these elements on glass alteration were additive or competitive. From the results of the mono-elemental experiments (CJ7-Ca, CJ7-K, CJ7-Cs, and ISG), we used linear combinations to calculate the normalized boron mass losses that would be

obtained if the effects of these elements were additive (2). This calculation was successfully applied to the effects of Zn, Mg, Ni, Co, Fe, and Ca in previous papers;^{11,12} the effects of Zn, Ni, Co, Mg, and Fe were found to be additive, and those of Fe, Mg, and Ca were competitive. Here, we took into account the differences in elemental consumption between the three cations.

$$\text{NL(B)}_{\text{cal}} = \sum_X (\text{NL(B)}_{X \text{ mono}} * c_X) \quad (2)$$

where,

X: Element of interest (K, Cs, or Ca);

$\text{NL(B)}_{\text{cal}}$: Calculated normalized boron mass loss;

$\text{NL(B)}_{X \text{ mono}}$: Normalized boron mass loss reported for each element X in its mono-elemental experiment. To simulate the contribution of Ca in the ISG-K and ISG-Cs experiments, two cases were considered: the $\text{NL(B)}_{\text{cal}}$ from experiment CJ7-Ca and from experiment ISG. For experiment CJ7-KCsCa, only the case of $\text{NL(B)}_{\text{cal}}$ from the experiment CJ7-Ca was considered, since ISG was not involved in this experiment.

c_X : Proportion of the element X in the overall quantity of elements mobilized into the gel layer, calculated from the elemental consumptions.

The results are presented in Fig. 5a.

In experiment CJ7-KCsCa, the calculated values fit well with the experimental ones. Therefore, the effects of K, Cs, and Ca on Ca-free glass were additive and proportional to their elemental consumption. In experiment ISG-K, the values calculated using the $\text{NL(B)}_{\text{cal}}$ from experiment ISG only fit the experimental values during the first month, before the alteration rate drop. At longer times (from day 100 onward), the best fit was obtained for the values calculated using $\text{NL(B)}_{\text{cal}}$ from experiment CJ7-Ca. In experiment ISG-Cs, the values calculated using $\text{NL(B)}_{\text{cal}}$ from experiment ISG fit the experimental data well, while the values calculated using $\text{NL(B)}_{\text{cal}}$ from CJ7-Ca were much lower. Therefore, to take into account the effects of the Ca from the ISG, the results calculated from the ISG experiment are more useful than those of experiment CJ7-Ca. Again, the effects of these elements seem to be additive and proportional to the quantity of element mobilized into the gel layer.

Although only Ca could be incorporated in the gel nanopores as Ca carbonates, the three cations in this study could act as charge compensators. To determine the differences in charge compensation between the ions, we calculated the Q ratio, which corresponds to the quantity of positive charges (n_{z+}) retained and incorporated into the gel layer divided by the altered glass percentage according to Eq. (3). In this part, all the incorporated/retained Ca was taken into account, whether it acted as a charge compensator, a network former, or precipitated Ca carbonate. In experiment CJ7-K, the release of Na was not congruent with that of B (see Supplementary Information 5), i.e., some of the Na was retained in the gel layer. Therefore, the positive charges of Na were also taken into account.

$$Q = \frac{n_{z+}}{\text{AG}\%} \quad (3)$$

In all cases except the CJ7-K and CJ7-Ca tests, after a sufficient period of time, the variation of Q with time became linear and remained within in the same range (Supplementary information 6-b). Therefore, the phenomena involved in all the experiments may be similar and remain stable in the long term. The average values of Q are reported in Fig. 5b).

Using the compositions of the ISG and CJ7 glasses, the quantity of charge compensators needed in their gels was calculated based on one negative charge for each Al and two for each Zr. The concentrations of Al and Zr in solution were too low to be detected by solution analyzes, therefore, it can be assumed that these elements were fully retained in the gel layer, probably forming $[\text{AlO}_4]^-$ and $[\text{ZrO}_6]^{2-}$ units. The Q values needed were

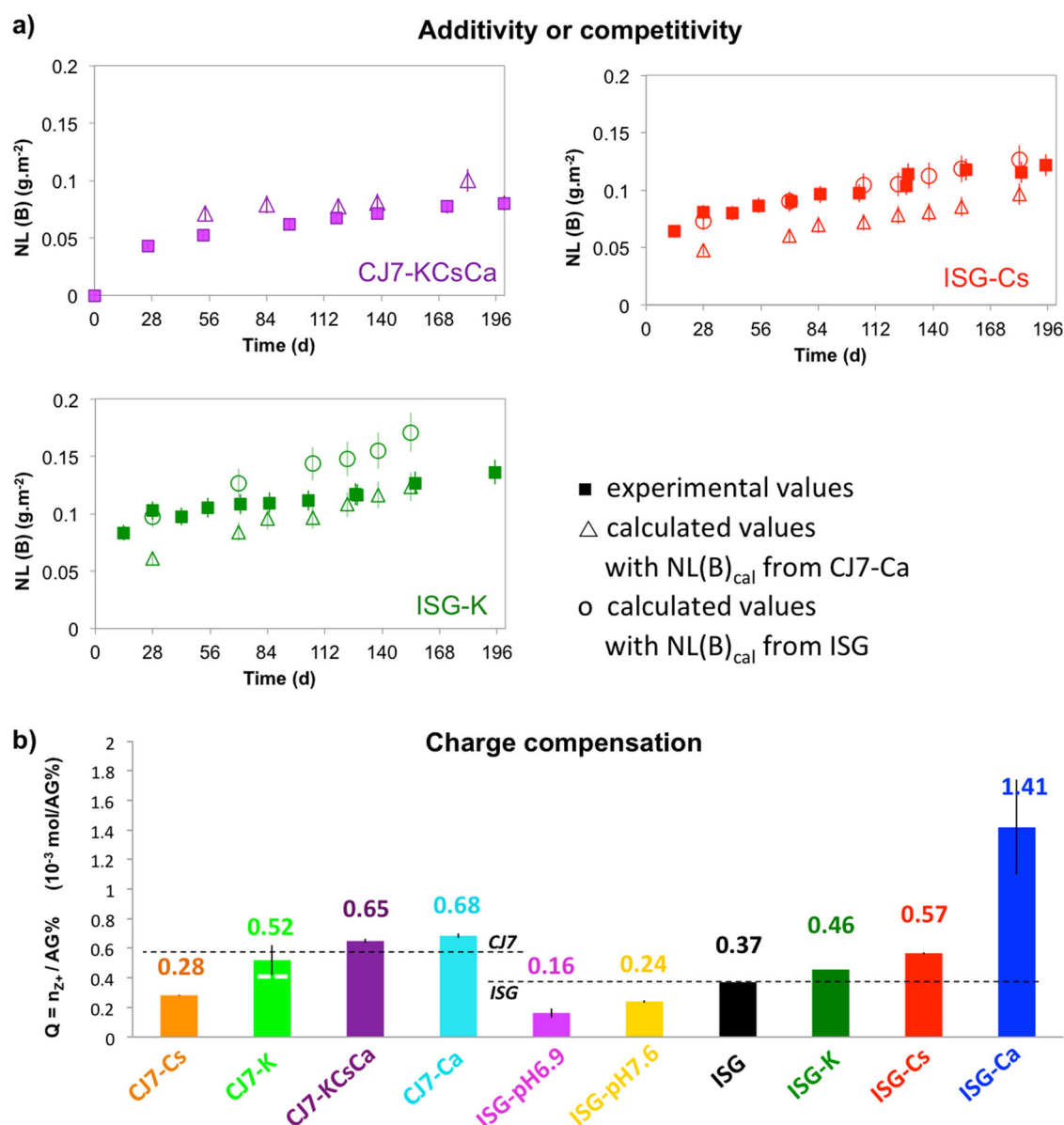


Fig. 5 **a** Comparison between the experimental $NL(B)$ values and the $NL(B)_{cal}$ values calculated using equation (2) as a function of time. **b** Q , the quantity of positive charges retained and/or incorporated into the gel layer for 1% of altered glass. The dashed horizontal lines represent the value of Q theoretically needed to compensate for all $[AlO_4]^-$ and $[ZrO_6]^{2-}$ units in the gel layer (0.58 for CJ7 and 0.39 for ISG). In experiment CJ7-K, the white line represents the Q value reached without taking into account the Na charges retained in the gel layer (0.34)

0.39 and 0.58 mmol of negative charges to compensate for 1% of altered ISG and CJ7 glass, respectively. However, it should be specified that depending on the experimental conditions, the gel layers formed may be different. They may be more or less polymerized and contain non-bridging oxygens. Thus, the amount of charge compensators required can vary.

When CJ7 was altered in the presence of K or Cs and without Ca (CJ7-K and CJ7-Cs tests), the Q values were lower than the quantity theoretically required for the CJ7 gel (0.58), even when taking into account the Na retained in the CJ7-K gel layer. The formation of K carbonates or Cs carbonates is unlikely, since these phases are highly soluble under the conditions of this study. Therefore, all the K or Cs incorporated into the gel layer should act as charge compensators. The availability of K or Cs in solution is not the limiting factor, since the amount consumed was compensated by the monthly additions. Thus, the Zr and Al atoms may have eventually changed their coordination to limit their need for

charge compensators. A recent study of the Zr environment in gel layers reported a strong distortion of the Zr octahedral geometry when the gel lacks charge compensators.⁵⁶

In the presence of Ca in solution (CJ7-Ca and CJ7-KCsCa), the Q value was much higher (0.65–0.68), even higher than the amount theoretically needed (0.58). This result could be explained by the precipitation of Ca carbonates into the gel nanopores. In the CJ7-KCsCa test, if all the K and the Cs are assumed to be mobilized as charge compensators, their incorporation represents a Q value of 0.26, which is less than the amount theoretically needed. Therefore, the incorporated Ca would consist partly of charge compensators and partly of Ca carbonate.

When ISG was altered in pure water, the Q value was 0.37. The amount of Ca retained was close to the theoretical Q value of charge compensators required (0.39). As demonstrated in the ISG-pH6.9 and ISG-pH7.6 tests, the increase in the Ca solubility with a decrease in pH leads to lower Q values. In these experiments, Na is

Table 2. Composition and grain size of ISG and CJ7 glasses

Glass	Oxide	SiO ₂	B ₂ O ₃	Na ₂ O	Al ₂ O ₃	ZrO ₂	CaO
ISG	%mass	56.2	17.3	12.2	6	3.3	5
	%at	44.3	35.4	11.8	4.9	0.8	2.8
	Grain size:	40–63 μm		BET Sa = 0.1060 m ² g ^{−1}			
CJ7	%mass	59.1	18.2	12.8	6.4	3.5	–
	%at	45.6	36.4	12.1	5.1	0.8	–
	Grain size:	63–125 μm		BET Sa = 0.0570 m ² g ^{−1}			

not retained in the gel layer; therefore, it can be suggested that the Zr and Al atoms changed their coordination or distorted their geometry to compensate for this lack of charge compensators. When K and Cs were added to the solution during ISG alteration (ISG-K and ISG-Cs tests), the *Q* values increased. K and Cs were incorporated to complete the charge compensation, which was partly accomplished by Ca. Again, in this case the availability of K and Cs was not limited, therefore, the *Q* values corresponded to the maximum amount of charge compensator needed for the gel layer formed in these conditions. As the *Q* values reached were higher than those theoretically predicted, the gel layer may contain non-bridging oxygens requiring compensation. Finally, when Ca was provided by both glass alteration and addition to the solution (ISG-Ca), the *Q* value reached a high value of 1.41, which could be explained by the precipitation of Ca carbonates into the gel nanopores, for example.

In the present study, the effects of K, Cs, and Ca on the alteration of ISG and Ca-free ISG (CJ7) were studied through long-term experiments. The three elements have the same overall effect: they enhance the protective properties of the gel layer, and thereby limit the alteration of the glass. This effect is stronger when the element is directly added to the solution than when it is present in pristine glass and released by glass alteration. During ISG alteration, Ca must first be released from the pristine glass in the pore solution before being incorporated into the gel layer. In contrast, when Ca is added to the solution, it can be incorporated into the gel network and may also react with dissolved carbonates to precipitate as Ca carbonates in the gel nanopores. The pH conditions are a key factor influencing the Ca retention in the gel layer; lower pH induces lower Ca retention. The addition of K or Cs to the solution limits ISG alteration; these elements are incorporated into the gel layer in addition to the retained Ca and also as a replacement for the Ca mobilized into the solution due to the solubility of Ca. When K, Cs, and Ca are added together to the solution during Ca-free ISG (CJ7 glass) alteration, they are incorporated into the gel layer; their incorporation follows the order Ca ≫ Cs > K. The formation of Ca carbonates could also explain this relative order. Moreover, Ca seems to be more efficient in limiting glass alteration than Cs and K. This may be due to the bivalency of Ca²⁺, which makes it twice as efficient at compensating the negative charges in the gel layer. The effects of these elements are additive, but the elements are not equally efficient. The effects are proportional to the amount of each element incorporated into the gel layer. In the case of Ca, additional incorporation as Ca carbonates is possible. Additional characterization would be necessary to validate this hypothesis and provide a better understanding of the processes involved. Additionally, it would be interesting to extend this study to other divalent cations present in groundwater and/or in glasses, such as barium or strontium, following the same procedure to obtain a more complete understanding of processes involved in glass alteration and gel formation. Finally, as the pH has an impact on

Ca retention, it could be interesting to test the addition of K or Cs at fixed pH values to see if they behave similarly to Ca.

METHODS

Leaching experiments

Two simple glasses based on the French SON68 inactive reference glass composition were chosen: the six-oxide ISG and its Ca-free equivalent, CJ7.^{46,57} The composition of these glasses is given in Table 2.

The Ca-free ISG equivalent (CJ7) was prepared at 1400 °C during for three hours and annealed at 450 °C for one hour. The ISG originated from a 50 kg international batch.⁵⁸ Both glasses were ground and sieved to recover the 40–63 μm and the 63–125 μm size grain fractions.

The glass powders were cleaned several times in acetone and ethanol and recovered by sedimentation to remove fine particles remaining on the surface. The specific surface areas of the powders were measured by krypton adsorption-desorption according to the Brunauer–Emmett–Teller (BET) model, and were 0.1060 m² g^{−1} and 0.0570 m² g^{−1} for ISG and CJ7, respectively.

Long-term static glass alteration tests were performed in PTFE reactors with a glass surface area-to-solution volume ratio (*S/V*) of 20,000 m^{−1} at 50 °C. K, Cs and Ca were brought into contact with the glass via the monthly addition of chloride salts (Normapure prolabo) to the leaching solution. Each month, a maximum volume of 1.5 mL of solution was sampled to perform analyzes and to determine the concentration of K, Cs, and/or Ca remaining in the leachate. The sampling frequency varied slightly from one experiment to another. To compensate for K, Cs, and/or Ca consumption and for evaporation, 1 mol L^{−1} KCl, CsCl and/or CaCl₂ solutions and pure water were added once a month, on the day after the last sampling and after the results of the analyzes were available. In all experiments, the renewal rate was approximately 15% vol/year.

Solution analysis

The pH was measured at 50 °C before each sampling using a *Metrohm 827 pH lab* using *NIST 7* and *NIST 9* buffers for the calibration of the electrodes. The samples were then subjected to ultrafiltration through a 10,000 Dalton cutoff filter and acidified by the addition of 0.5 N HNO₃. The concentrations of Si, B, Na, Al, and Zr in the solution were determined from an ICP-AES analysis conducted by the “FILAB” laboratory with an analytical uncertainty of 3–5%. The Ca, K, and Cs concentrations were measured using ionic chromatography (*Metrohm Professional IC*) with an analytical uncertainty of 5%.

Boron was chosen as the glass alteration tracer because it is a network former that is not retained in the alteration products. From the boron concentrations [B] (g m^{−3}) obtained from the solution analyzes, the altered glass fraction %AG and the normalized mass losses NL (g m^{−2}) were calculated using equations (4) and (5), respectively (for more details regarding the calculation method, please refer to⁴⁶ and²²

$$\%AG(B)_t = \frac{[B]_t V_{bs,t} - [B]_{t-1} V_{bs,t-1}}{m_g w_B} * 100 + \%AG(B)_{t-1} \quad (4)$$

$$NL(B)_t = \frac{3}{S} \left(1 - \sqrt[3]{\frac{100 - \%AG(B)_t}{100}} \right) \quad (5)$$

A correlation between the NL(B) and the square root of time suggests that the glass alteration is limited by a diffusion process. Because boron is a good alteration tracer, the apparent diffusion coefficient of the limiting species through the alteration layer *D*_{app} can be calculated from the NL(B) data. Equation (6) is derived from Fick's second law and was applied between 0 and 200 days. The nature of the limiting species is still under discussion in the literature (hydrogenated species, water, silicon, etc.). In any case, the coefficient *D*_{app} indicates the diffusion mechanism(s) and the protective nature of the gel layer.

$$NL(B) = \frac{2\rho}{\sqrt{\pi}} \sqrt{D_B^{\text{Fick}} \cdot t} \quad (6)$$

In Eqs. (4) to (6), *V*_{bs} is the volume of the alteration solution before sampling (m³), *S* is the specific surface area of the powder (m² g^{−1}), *m*_g is the mass of glass in the experiment (g), *w*_B is the weight fraction of boron in the glass composition, and *ρ* is the mass density (2.43 × 10⁶ g m^{−3} and 2.50 × 10⁶ g m^{−3} for CJ7 and ISG, respectively).

The glass alteration rate (*r*_g) was calculated by linear regression of four to five successive values of NL(B) versus time. The monthly consumption (*n*_c

in mol) of the element X (X = K, Cs or Ca) was obtained using Eq. (7):

$$n_c = n_{l,t-1} + n_a - n_{l,t} - n_s = [X]_{L,t-1} V_{L,t-1} + [X]_{CS} V_{CS} - [X]_{L,t} V_{L,t} - \sum_{\text{month}} [X]_s V_s \quad (7)$$

where n is the quantity of X:

present in the leachate before the addition ($n_{l,t-1}$)
added to the leachate at the beginning of the month (n_a),
remaining in the leachate after the last sampling of the month ($n_{l,t}$)
and contained in all the samples taken throughout the month (n_s)

calculated from the concentrations of the element X ($[X]$, mol·m⁻³) and volumes V (m⁻³) of the concentrated solution ($[X]_{CS}$, V_{CS}), the leachate after sampling ($[X]_L$, $V_{L,as}$), and the samples ($[X]_s$, V_s).

The total consumption is the sum of all monthly consumption values at time t ($n_{\text{consumed},t}$).

The amount of Ca released by glass alteration and retained in the gel layer at time t ($n_{\text{Ca retained},t}$) can be calculated using equation (8). The amount of element X incorporated in the gel layer at time t ($n_{\text{X incorporated},t}$) was calculated using Eq. (9).

$$n_{\text{Ca retained},t} = \frac{\%AG_t \%m_{\text{CaO}} m_{\text{glass}}}{M_{\text{Ca}}} - n_{l,t} - n_s \quad (8)$$

$$n_{\text{X incorporated},t} = n_{\text{X consumed},t} = n_{\text{X consumed},t-1} + n_{l,t-1} + n_a - n_{l,t} - n_s \quad (9)$$

At the end of the experiments, the altered glass powders were rinsed twice with pure water. SEM observations were conducted on the altered glass grains. In all experiments, the altered glass surface had a gel-like appearance without any secondary phase, and the altered layer was too thin to be measured or analyzed. Therefore, the solid characterization was not presented in further detail.

ACKNOWLEDGEMENTS

The authors are grateful to Emmanuelle Garcès and Géraldine Parisot for technical support. We would like to thank Renaud Podor, Marie Collin, Pierre Frugier, and Patrick Jollivet for scientific discussions. This work was funded by CEA, ORANO, and EDF.

AUTHOR CONTRIBUTIONS

H.A. was responsible for the experimental analysis and for writing the paper. N.G. and D.R. supervised the study. All the authors participated in editing of the paper.

ADDITIONAL INFORMATION

Supplementary information accompanies the paper on the *npj Materials Degradation* website (<https://doi.org/10.1038/s41529-019-0072-7>).

Competing interests: The authors declare no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

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