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Basaltic glass: alteration mechanisms and analogy with nuclear waste glasses

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Abstract

A synthetic basaltic glass was dissolved experimentally at 90°C under static conditions in initially pure water. The basaltic glass dissolution rates measured near and far from equilibrium were compared with those of SON 68 nuclear waste glass. Experimental and literature data notably suggested that the alteration mechanisms for the two glasses are initially similar. Under steady-state concentration conditions, the alteration rate decreased of four orders of magnitude below the initial rate (r_0). The same alteration rate decrease was observed for basaltic and nuclear glass. These findings tend to corroborate the analogy of the two glasses alteration kinetics. The effect of dissolved silica in solution, observed through dynamic leach tests with silicon-rich solutions, cannot account for the significant drop in the basaltic glass kinetics. Hence, a protective effect of the glass alteration film was assumed and experimentally investigated. Moreover, modeling with LIXIVER argue for a significant effect of diffusion in the alteration gel. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Basaltic glasses of volcanic origin are considered as natural analogs of nuclear waste glasses used to condition fission product solutions. They provide data on the alteration behavior of vitreous materials over tens or hundreds of thousands years. The analogy between basaltic and nuclear glasses has been extensively documented with respect to the secondary products formed during alteration of these materials [1–5]. The present work demonstrates that the analogy also applies to the alteration mechanisms and kinetics. We discuss these alteration kinetics control. A synthetic basaltic glass was altered at 90°C under static conditions at various degrees of reaction progress to characterize the evolution of the dissolution rate as the solution becomes increasingly concentrated. The experimental findings were compared with similar data obtained under the same alteration conditions for SON 68 nuclear glass. The specific effect of dissolved silica on the dissolution kinetics was assessed by means of alteration experiments with silicon-enriched flowing solutions. A hypothetical protective effect of the alteration film on volcanic glass was also investigated experimentally by altering pristine glass and glass previously altered in a solution highly concentrated with respect to the material. The glass behavior was also modeled using the LIXIVER code [6,7], which takes into account the diffusion barrier role of the alteration film.

2. Experimental protocol and calculation parameters

2.1. Static-mode basaltic glass alteration in initially pure water

A synthetic basaltic glass (Table 1) doped with an alteration tracer (1% LiO_2) was altered in the laboratory at 90°C under static conditions in initially ultrapure

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Table 1
Basaltic glass compositions tested (oxide wt%)

Oxide	Doped glass	Undoped glass
SiO_2	49.3	49.8
Na_2O	2.67	2.70
Al_2O_3	14.8	15.0
MgO	7.9	7.97
CaO	10.9	11.0
Li_2O	**1.00**	**0.00**
Fe_2O_3	10.9	11.0
P_2O_5	0.10	0.10
SrO	0.36	0.36
MnO_2	0.19	0.19
K_2O	0.19	0.19
TiO_2	1.77	1.79

water. Tests were conducted at various glass-surface-area-to-solution-volume (S/V) ratios for periods (t) ranging from 9 to 281 days, covering alteration conditions near and far from equilibrium. Glass coupons measuring 16 cm^2 were placed in ultrapure ($pH_{25°C} = 5.6$) water and the volume was adjusted to obtain S/V ratios of 0.1 and 0.5 cm^{-1}. The test reactors were maintained under static conditions at 90°C for 9 days (0.1 cm^{-1}) and 112 days (0.5 cm^{-1}); at regular intervals, a 2 ml solution sample was taken from each reactor and the solution pH was measured within 0.05 unit at the test temperature by inserting an Orion 8103 RS combined electrode directly into the reactor through a small aperture. The time of the measurement (less than 3 min) is not great enough to allow an input of atmospheric CO_2 in test reactor [8]. Additional tests were conducted at a high S/V ratio (337 cm^{-1}) by altering 2 g of glass powder with a BET specific surface area of 842 $cm^2\,g^{-1}$ in 5 ml of initially ultrapure water; three test reactors for each time period were inserted into a sealed Pyrex tube and maintained at 90°C for up to 281 days, after which the solution was sampled and the pH was measured at the test temperature as before.

2.2. Basaltic glass alteration in flowing solutions

A flowing solution of known composition was maintained in contact at a known constant flow rate at 90°C with basaltic glass coupons doped with 1% LiO_2 at an S/V ratio of 10 cm^{-1}. Four tests were carried out in initially ultrapure water at flow rates of 0.63, 0.12, 0.05 and 0.02 ml min^{-1}; seven additional tests were conducted at a constant flow rate of 0.01 ml min^{-1} with silicon-enriched solutions (15, 28, 38, 70, 90, 109 and 129 mg l^{-1}). The solution concentrations were measured before each experiment. Steady-state conditions were considered when the elementary concentration in solution were constant. After the time τ (days) required to reach these steady-state conditions, calculated for each test from Eq. (1), where V is the solution volume (l) and ϕ the solution flow rate ($l\ d^{-1}$), a 2 ml solution sample was taken from each reactor at regular intervals and the pH was measured at 90°C.

$$\tau = 4.6\frac{V}{\phi}. \tag{1}$$

2.3. Basaltic glass alteration in concentrated solution

A solution highly concentrated with basaltic glass constituent elements, at steady-state concentrations, was prepared by altering basaltic glass powder containing no lithium (Table 1) for 3 months at 90°C with an S/V ratio of 50 cm^{-1}. Leachate samples were taken at regular intervals and analyzed for Si and Na after ultrafiltration and acidification (Table 2). On completion of the test, the silicon-saturated solution was recovered and filtered. A basaltic glass coupon doped with 1% LiO_2 was placed in this solution for 91 days at 90°C at an S/V ratio of 10 cm^{-1}; lithium was not present in the initial saturated solution, and thus represented the only dissolution tracer element. At regular intervals, 2 ml solution samples were taken for analysis and the pH was measured at the test temperature.

2.4. Alteration parameters

The leachate samples were ultrafiltered and acidified with 1N HNO_3. The Si, Al, K, Ca, Mg, Fe, P, Sr, Mn and Ti concentrations were determined by ICP-AES; the Na and Li concentrations were determined by AAS. Glass alteration was characterized by the normalized mass loss (Eq. (2)) of lithium, the reaction tracer element, expressed in grams of glass per square meter

$$\mathrm{NL}(i) = \frac{C_i R_c}{i\frac{S}{V}}, \tag{2}$$

where C_i is the concentration of element i in solution (mg l^{-1}), R_c the oxide/element mass conversion ratio for the glass, i the mass fraction of oxide i in the glass, and S/V is the glass-surface-area-to-solution-volume ratio (m^{-1}). The same calculation was also performed for sodium to assess its tracer potential.

Table 2
Si (mg l^{-1} ± 3%) and Na (mg l^{-1} ± 5%) concentration and pH of solution during glass alteration at 50 cm^{-1}

Days	4	7	23	35	63	91	aF[a]
Si	18	20	21	21	22	22	22
Na	4.4	4.5	6.2	6.2	7.3	7.2	7.2
pH	8.6	8.7	8.8	8.9	8.8	8.8	8.8

[a] aF: after filtration.

The alteration rate, r, in g m^{-2} d^{-1}, was determined from the normalized mass loss $\mathrm{NL}_{(i)}$ by linear or logarithmic regression. The equivalent glass thickness of the alteration film was determined on the basis of a glass density ρ of 2.7 g cm^{-3} [9]

$$\mathrm{Th}_{\mathrm{eq}} = \frac{\mathrm{NL}_{(i)}}{\rho}. \tag{3}$$

The Si retention factor in the alteration film was calculated from the following relation:

$$f = 1 - \frac{\mathrm{NL}_{(\mathrm{Si})}}{\mathrm{NL}_{(\mathrm{Li})}}. \tag{4}$$

3. Basaltic glass alteration in initially ultrapure water

During basaltic glass alteration in initially pure water at 90°C, the pH rapidly became basic (8.4). As with SON 68 nuclear glass [10] dissolution was initially selective (preferential release of sodium) (Fig. 1). Further, the dissolution was incongruent with formation of secondary products and retention of Si in these phases (Na/Si ration increased with reaction progress). Two sections of the altered glass were analyzed by ionic beam (SIMS) which confirm the formation of Si secondary phases.

The altered glass quantity based on Na and Li increased in a linear manner over the first 4 days. The maximum alteration rate (i.e., the 'initial rate' r_0) of 0.78g m^{-2} d^{-1} was measured by linear regression over these data points; this value is comparable to the result obtained for SON 68 glass at 90°C (1.03 g m^{-2} d^{-1}) [11]. The initial alteration rate of basaltic glass in aqueous media at various temperatures (from 3°C to 300°C) has been widely reported in the literature [12–17]. All refer to basaltic glass of tholeiitic composition, close to the studied basaltic glass one. These literature data were corrected to a same value of pH of 8.4 (value obtained in our experiments), using Guy and Schott data on the evolution of r_0 with pH for temperatures ranging from 50°C to 200°C [15]. The logarithm of the corrected data is plotted versus the reciprocal of the temperature in Fig. 2. At the same temperature, for equivalent pH, the r_0 values for volcanic glass are comparable to those of nuclear glass [11]. Over a wide temperature range (from 3°C to 300°C), $\ln(r_0)$ exhibits a linear variation for basaltic glass following an Arrhenius law:

$$\ln(r_0) = \ln(A) + \frac{-E_\mathrm{a}}{RT}, \tag{5}$$

where A is the pre-exponential factor (g m^{-2} d^{-1}), R the ideal gas constant, T the temperature (K) and E_a the activation energy (J mol^{-1}) (Fig. 2). The activation energy of the alteration reaction, calculated on the basis of all the literature data reported, was constant over the temperature range and equal to 72.4 kJ mol^{-1}. The value of $\ln(A)$ was equal to 24 g m^{-2} d^{-1}. The activation energy of the basaltic glass alteration reaction is comparable with the value of 71 kJ mol^{-1} for the initial alteration of SON 68 glass [11] between 80°C and 250°C (Fig. 2). The similarity of the two values obtained suggests that the alteration mechanisms are identical for aluminosilicate basaltic glass and alumino-borosilicate nuclear glass.

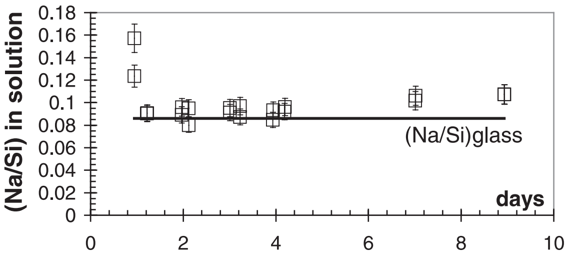

Fig. 1. Na/Si ratio in basaltic glass leachate (at 0.1 cm^{-1}) and in the glass as a function of time.

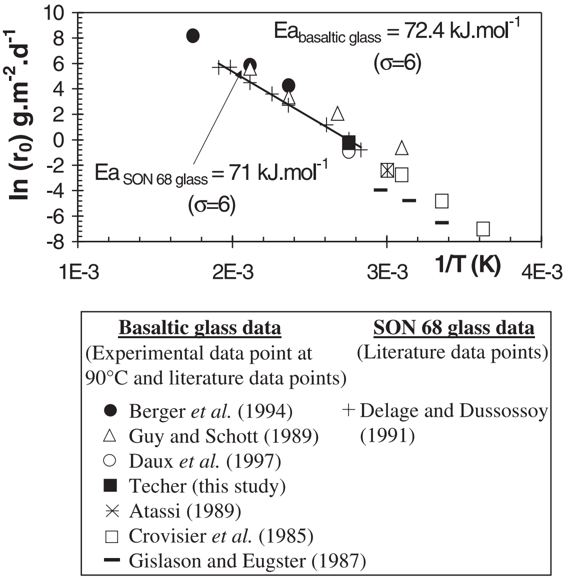

Fig. 2. Initial alteration rate for ballastic glass and SON 68 nuclear glass as a function of temperature.

The rates calculated from the lithium and sodium release were comparable within the experimental error margin. In the absence of lithium, sodium can thus be considered as a suitable basaltic glass alteration tracer at 90°C. The alteration rate diminished as the reaction progressed (Fig. 3), reaching $r_0/3$ after 9 days of alteration at 0.1 cm^{-1}. At the highest degree of reaction progress, it was 20 000 times (over four orders of magnitude) lower than r_0. A very strong inhibition of

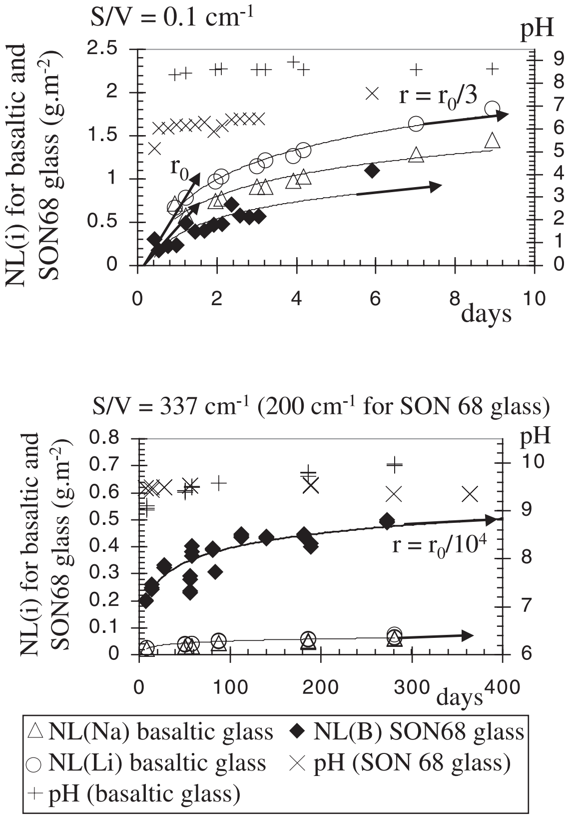

Fig. 3. Normalized mass losses for ballastic glass and SON 68 nuclear glass as a function of the reaction progress.

comparable magnitude has been observed [18] during the alteration of nuclear glass (Fig. 3). The nuclear french glass and the basaltic one have the same kinetic behavior. However, in the same alteration conditions, the leachate pH measured during the dissolution of the two glasses was different (Fig. 3). In the first stage of the reaction, basaltic glass leachate was more basic due to the high alkali and earth alkali concentrations of the glass. Hence, dependence of initial rate with pH has been determined [15,19]. As with SON 68 glass, the initial basaltic glass dissolution rate, r_0, can be expressed as a function of the H^+ concentration in solution together with a coefficient n and an initial rate constant k^+:

$$r_{0_{\mathrm{g\,m^{-2}d^{-1}}}} = k^+ \cdot [H^+]^n = 2 \times 10^{-4}[H^+]^{-0.44}. \qquad (6)$$

The solution pH difference was observed only in the first days of the reaction. Farther, the two glasses alteration leachates had identical pH.

Basaltic glass alteration at 90°C is thus characterized by a major drop in the rate as the reaction progresses, i.e., as the solution approaches saturation with respect to the glass. This behavior is similar to that of SON 68 nuclear glass at the same temperature.

4. Specific effect of dissolved silica in solution

The alteration rate of basaltic glass diminishes as the solution becomes increasingly concentrated with glass constituent elements, notably silicon. The specific inhibiting effect of this element on the reaction was assessed by alteration experiments in flowing ultrapure water and silicon-enriched solutions. The concentrations of the elements in solution after interaction with the glass were higher at low flow rates, and when the silicon concentration was low in the feed solution. The basaltic glass alteration rate calculated for each test from $NL_{(Na)}$ is plotted in Fig. 4(a) versus the orthosilicic acid activity in solution ($[H_4SiO_4^0]$ was determined from the total Si concentrations and from the equilibrium constants [1] K_1 and K_2, equal to $10^{-9.17}$ and $10^{-10.7}$, respectively [20]). The kinetics diminished as the $H_4SiO_4^0$ activity increased. The effect of dissolved silica in solution can be expressed by an empirical law determined on the basis of experimental data presented:

$$\frac{r}{r_0} = 8 \times 10^{-3} \times \left[H_4SiO_4^0\right]^{-0.62}. \qquad (7)$$

Basaltic glass behavior in the presence of silicon-rich solutions is comparable to that of nuclear glass (Fig. 4(b)) at the same temperature [21]. The minimum rate, measured in a solution highly enriched in silicon, was $5 \times 10^{-3} \pm 7 \times 10^{-4}$ g m^{-2} d^{-1}, a value less than 200 times lower than the initial alteration rate r_0.

The specific effect of silica in solution is not sufficient to account for the experimentally observed drop in the alteration rate by four orders of magnitude. Moreover, a recent study [19] on the application of the kinetic laws of dissolution of nuclear glasses [22], basaltic glasses [17] or silicate minerals [23] to the alteration of the basaltic glass studied revealed that the effect of the solution chemistry alone, in the form of an affinity term, cannot explain the major inhibition of the kinetics at high reaction progress. The affinity effect must be coupled with one or more additional parameters to account for the glass alteration kinetics.

5. Protective role of the alteration film

5.1. Naturally altered volcanic glasses

Low-temperature alteration of volcanic basaltic glass in oceanic and continental environments, over periods ranging from tens of thousands to millions of years, has been investigated by numerous authors [3,24–28]. Alteration is characterized by the development of

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[1] $K_1 : H_4SiO_4^0 = H_3SiO_4^- + H^+ ; K_2 : H_3SiO_4^- = H_2SiO_4^{2-} + H^+$.

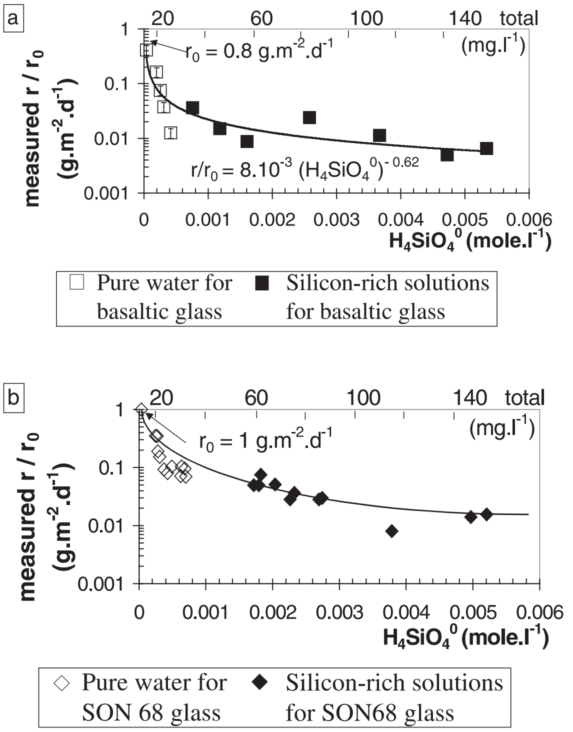

Fig. 4. Basaltic glass alteration rate as a function of orthosilicic acid activity, [$H_4SiO_4^0$], in solution.

amorphous or crystallized secondary products (palagonite, clay, zeolite, etc.) of variable thicknesses. The mean alteration rates for these natural glasses estimated from the thickness of the alteration films and the age of the glass (with the age assumed equal to the duration of the reaction) ranging from 10^{-4} to 70 μm per thousand years. These values are four to five orders of magnitude lower than the initial rate representative of such systems (r_0 equal to 40 and 206 μm/1000 years at 0°C and 15°C, respectively, considering Eq. (5) and a glass density of 2.7 g cm^{-3} [19]. The presence of an alteration film several micrometers thick on the glass surface could be responsible for the very low estimated kinetics. The alteration film could constitute a protective barrier against alteration of the glass. This assumed protective effect was examined by experimental alteration of basaltic glass in a saturated leaching solution.

5.2. Alteration of basaltic glass in a concentrated leaching solution

A lithium-free basaltic glass specimen was altered in initially ultrapure water. As in previous experiments, pH increased rapidly and became basic. Si and particularly Na concentrations in solution increased until about 60 days. Farther a steady-state stage was reached with Si and Na concentrations equal to 22 and 7.2 mg l^{-1}, respectively. The reaction was maintained until 91 days; at this time, the alteration rate diminished by a factor of about 7000 with respect to r_0 (Fig. 5). The alteration film that formed on the glass was 27 nm thick, containing over 70% Si. The altered specimen was then removed from the leaching solution and replaced by a pristine glass specimen doped with Li_2O. The absence of lithium in solution made it possible to assess the alteration kinetics of the fresh specimen in the concentrated solution.

At the outset (Fig. 5), the alteration rate was near the r_0 value measured in initially ultrapure water ($r_0/15$). The rate then diminished to a value three orders of magnitude lower than r_0 after 273 days cm^{-1}. The evolution of the alteration kinetics in the concentrated solution was comparable to that observed in initially pure

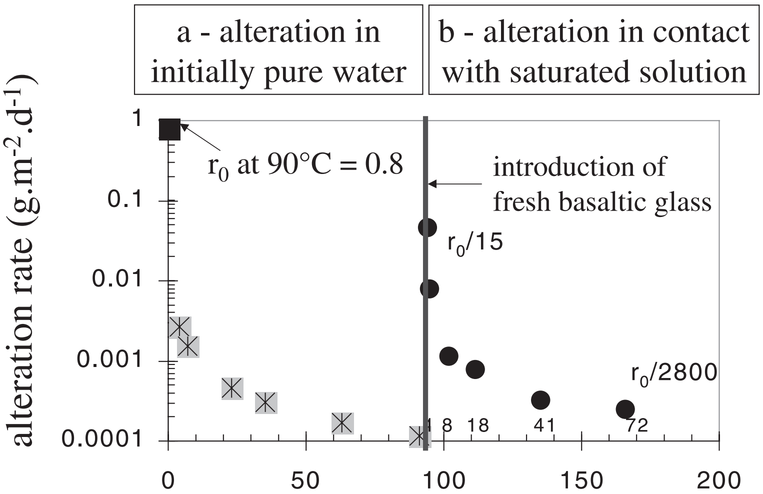

Fig. 5. Basaltic glass alteration rate in initially pure water and in "saturated" solution as a function of time.

water, within a factor of 15. The solution chemistry alone did not strongly inhibit the kinetics; this is consistent with the preceding remarks. One of the parameters that could account for the drop in the rate is the presence of the alteration film. In the same solution, a glass specimen protected by a film relatively rich in silica was altered at a rate nearly four orders of magnitude below r_0, while a pristine glass specimen was altered nearly at r_0.

5.3. Modeling with the LIXIVER mechanistic code

The protective effect of the alteration film was evaluated by modeling the glass behavior using the LIXIVER mechanistic code, which is based on the following assumptions:

(1) The alteration kinetics are controlled by the silicic acid activity in solution and are expressed by the first order law [22]

$$r = r_0\left(1 - \frac{C_{\mathrm{int}}}{C^*}\right), \tag{8}$$

where r is the dissolution rate, C_{int}, the total silicon concentration at the glass/alteration film interface and C^* the total silicon concentration at saturation with respect to the glass. This later parameter is deduced from alteration experiments with high S/V ratios.

(2) The silicon released by dissolution of the glass diffuse into the alteration film. The Si concentration gradient is assumed to be linear and is described by the Fick law

$$C_{\mathrm{int}} = s(x) + C, \tag{9}$$

where s is the concentration gradient, x the alteration layer thickness and C the silicon concentration in the leaching solution.

The silicon flow in the alteration layer (J_l) is expressed as a function of a silicon diffusion coefficient, D

$$J_l = D\frac{\partial C}{\partial x}, \tag{10}$$

(3) A part of silicon released by dissolution of the glass is retained in the alteration layer. The retention factor is defined as a linear function of the silicon concentration in the leachate

$$f = a + (bC). \tag{11}$$

The values of a and b are experimentally determined.

(4)The quantity of silicon released and not retained in the alteration film is equal to the quantity of silicon diffusing through this layer.

$$D \times \frac{\partial C}{\partial x} = r\left[\left(C_{\mathrm{g}}(1-f)\right) - C_{\mathrm{int}}\right], \tag{12}$$

where C_{g} is the silicon concentration in the glass.

The alteration rate equation used in LIXIVER is based on the combination of Eqs. (8)–(12) and on a silicon mass balance which takes into account parameters such as the glass surface area (S), the solution volume (V), the solution renewal rate (F) and Co the initial silicon area concentration in solution [6]. The entire mathematical formalism is not detailed here as it has already published [6]. The alteration rate is then given by the following reaction:

$$r = r_0\frac{1 - C/C^*}{1 + r_0((C_{\mathrm{g}}(1-f)x)/(DC^*))}, \tag{13}$$

and the altered glass thickness is expressed by the equation

$$\mathrm{d}x = r\,\mathrm{d}t. \tag{14}$$

The code LIXIVER was applied to the basaltic glass studied experimentally at 90°C. The calculation parameters were the following:

1. temperature: 90°C;
2. initial surface-area-to-solution-volume ratio: 0.1, 0.5 and 337 cm^{-1};
3. glass solubility value: $C^* = 22$ mg Si l^{-1}. This value was determined, as for the reference nuclear glass, in steady-state Si concentrations conditions at high S/V ratio;
4. no leaching solution renewal rate (static conditions);
5. parameters for silicon retention: $a = -0.15$, $b = 0.035$. The values were determined experimentally considering data obtained at 0.1, 0.5 and 337 cm^{-1};
6. $r_0 = 0.78$ g m^{-2} d^{-1}.

The concentrations, rates and alteration film thickness measured during static-mode experiments at 0.1 cm^{-1} were satisfactorily reproduced by the code by assuming a silicon diffusion coefficient in the film equal to 3.2×10^{-13} m^2 s^{-1}, constant on the time reaction (Fig. 6). Only the first experimental data point was not reproduced with this value. This is probably due to the fact that in the initial stage of the reaction, the alteration film is poorly protective. Data calculated by LIXIVER for a S/V ratio of 0.5 cm^{-1}, were fitted with a silicon diffusion coefficient equal to 3.2×10^{-15} m^2 s^{-1} (Fig. 6). However data were more and more scattered with the increase of the reaction time. This could be avoid with a lower silicon diffusion coefficient.

For the highest S/V ratio, experimental data could be reproduced only by taking into account a decrease of the silicon diffusion coefficient with time: from 5×10^{-20} to 9×10^{-21} m^2 s^{-1} (Fig. 6). This decrease correspond to a change in the structure of the alteration film.

The application of LIXIVER to the alteration of the basaltic glass suggested that under the initial stage of the alteration reaction the film is considered as a porous gel through which elements readily diffuse ($D = 3.2 \times 10^{-13}$ m^2 s^{-1}). During the initial phases the alteration layer has no protective power and the first-order law is sufficient to account for the kinetics [19]. As the solution

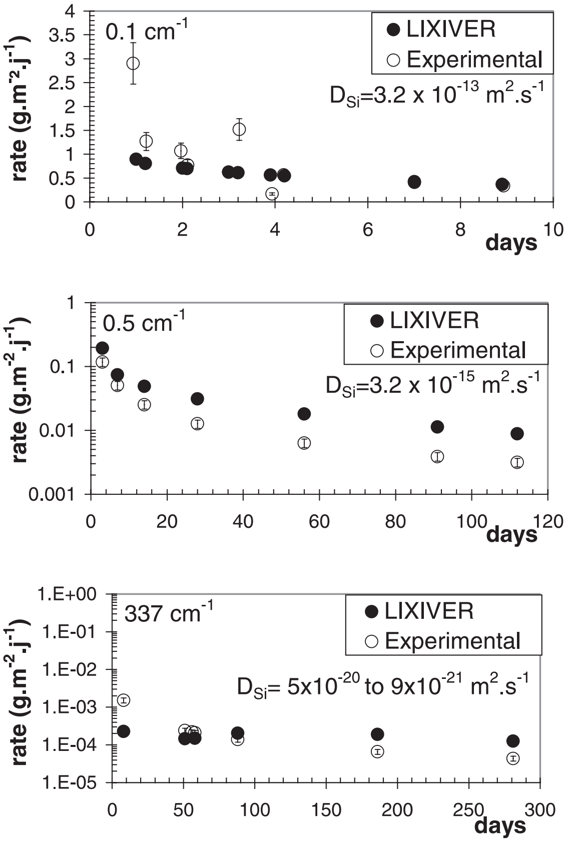

Fig. 6. Alteration rates calculated by LIXIVER as a function of time.

becomes concentrated in element notably in silicon the alteration film increasingly constitutes a barrier with regard to diffusion (D increases between 3×10^{-15} and 10^{-20} m^2 s^{-1}). The low alteration rates measured experimentally at high reaction progresses were reproduced by the code only by taking into account a low diffusion of silicon in the alteration layer. Therefore, with time, this layer becomes more and more protective towards the glass dissolution.

6. Conclusion

The alteration of basaltic glass was characterized under conditions near and far from equilibrium. The mechanisms and kinetics of volcanic glass alteration are comparable to those of SON 68 nuclear glass. As the leaching solution becomes saturated, the alteration rate diminishes by over four orders of magnitude with respect to the maximum rate measured during the first moments of alteration. This inhibition of the alteration kinetics is not controlled by the solution chemistry alone; the alteration film has a major role in controlling the reaction by constituting a diffusion barrier. The importance of this barrier role increases as the reaction progresses.

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