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Review

Nature and role of natural alteration gels formed on the surface of ancient volcanic glasses (Natural analogs of waste containment glasses)

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Abstract

This paper provides an overview of the geochemical alteration of basaltic glass, considered for over 20 years as a suitable natural analogue for nuclear borosilicate glasses. The available data show that natural basaltic glasses may survive for million of years under subsurface conditions. Mineralogical studies show that an alteration layer called palagonite forms on the surface of the basaltic in response to the chemical attack by water. Under some environmental conditions, the alteration layer consists of an amorphous gel-like material, leading many authors to suspect hydration of the glass by water permeation and alkali interdiffusion. In other cases, the alteration layer is crystallized to some extent and contains clay minerals (smectite). Such layers are formed mainly on the younger natural glass samples (<1 My) by a process of coprecipitation of the elements dissolved from the glass. On samples older than 1 My, the alteration layers also contain zeolites. In the presence of these hydrated aluminosilicates, a hydrated residual glass is systematically observed, which thus forms as a consequence of interdiffusion processes. Leach tests conducted under controlled laboratory conditions at temperatures up to 200 °C on both natural glass samples and synthetic basaltic glass provide identical kinetic results and alteration mechanisms. When compared with the data for SON68 nuclear borosilicate glass, the initial dissolution rates show the same activation energy (about 72 kJ mol⁻¹) and consequently similar dissolution mechanisms. Moreover, when altered under static conditions at high reaction progress, both basaltic glass and nuclear glass have similar behavior characterized by a significant drop in the dissolution rate, up to three to five orders of magnitude lower than the initial dissolution rate. The time-dependence of the thickness of the altered layers measured on natural glass samples confirms this kinetic trend over time: the long-term dissolution rate is very low. This decrease may be related to diffusion mechanisms involving key chemical species and controlled by the mineralogy of the palagonite layer.

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1. Introduction

The long-term behavior of containment glass matrices for radioactive or non-radioactive waste cannot be predicted only on the basis of scientific laws using parameters experimentally measured in the laboratory.

The geological environment in which vitrified waste could be stored is complex, and most processes are subject to the variation of a large number of parameters including the nature of the fluids, climatic changes, etc.

Most of the parameters are interdependent; radionuclide behavior, for example, cannot be understood independently of phenomena such as coprecipitation or adsorption of other major or minor system constituents. Repository safety assessments are based on a series of calculation models used to examine the consequences of matrix alteration by water, and the dissemination of

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potentially toxic elements by migration in the environment.

The objective of this bibliographic review is not to discuss the validity of the concept of natural analogs, which has been thoroughly analyzed [1–6]. The objective is rather to examine the reasons for which the study of the alteration layers formed on the surface of basaltic glass is important in order to understand the processes determining the long-term chemical durability of glass.

Basaltic glass is considered as a natural analog of radioactive waste containment glass [2,7–14]. We have chosen to analyze the work carried out in recent decades. Only the data relative to glass behavior at low temperatures (below 100 °C) are considered here, as this is the pertinent temperature range for a long-term assessment of nuclear glass behavior.

Basaltic glasses recovered from the natural environment are the only tools capable of quantifying the consequences of aqueous alteration over the very long term. The structure of basaltic glasses is sufficiently like that of nuclear glasses, and their chemical compositions are relatively similar [8] for the major elements (silica content, presence of alkali and alkaline earth metals).

Although the repository sites considered for vitrified wasteforms are very different from the natural environment as found, for example, near the subglacial volcanoes of Iceland that produce basaltic glass, the systems are comparable in terms of their degree of complexity. Glass analogs can be used to test hypotheses on multi-parameter interactions [3,5–9].

It is important, however, not to expect more of analogs than they are capable of providing. Consider a single example: the literature abundantly illustrates a tendency of some authors to identify in the structure of the initial material a relation with the structure of the minerals formed by its alteration. Glass being amorphous, it is considered an excellent material for studying the transition between the initial amorphous phases and the crystallographically more organized products. Some experimental work, however, has shown that fully crystallized minerals can be obtained in a few days from basaltic glasses at 60 or 90 °C [15–18].

In addition to published data, this study concentrates on the results of laboratory investigations carried out in France by the Centre de Géochimie de la Surface de Strasbourg [16–24] and by the Commissariat à l'Énergie Atomique (Valrho-Marcoule) in collaboration with the University of Montpellier [14,25,26].

The first experimental work was performed to determine the nature of the mineralogical phases formed over the short term, to identify the alteration mechanisms, and to model the long-term behavior of these phases using geochemical calculation codes such as DISSOL or KINDIS. The experiments conducted by the CEA were intended mainly to measure the corrosion

kinetics of volcanic basaltic glass and obsidian, in comparison with SON68 nuclear glass. The effect of dissolved silica in solution on the alteration kinetics was examined in particular. Models were then developed using the KINDIS and LIXIVER calculation codes [25].

Icelandic subglacial basaltic glasses are highly suitable for these objectives. They constitute a series of glasses with very similar chemical compositions, altered under very similar conditions (subglacial meltwater or meteoric water at mean temperatures below 10 °C) for periods ranging from 2000 to 3 million years.

The natural glasses studied by Techer [25] and Techer et al. [14,26,27] originated in basaltic veins formed 1.4 million years ago in a clay sediment (Salagou massif, Hérault, southern France). The main objectives of this last study included the following:

- characterize the secondary phases formed by glass alteration in contact with clay (analogous to the clay barriers of a repository site),
- quantify the behavior and migration of glass constituents released into the clay barrier.

2. Palagonite

Palagonite, first described in 1845 by von Waltershausen [28], was named for Palagonia, a locality in the Iblei mountains of Sicily. Palagonite is an alteration product around the outer rind of basaltic glasses subjected to the action of water. Its structure and especially its chemical composition vary significantly from one sample to another. There is generally a very distinct border between the pristine glass, or sideromelane, and the alteration rind; observed by optical microscopy, the latter is characterized by its orange-yellow coloration in natural light and sometimes by slight birefringence in polarized light, while the glass itself is isotropic and honey-colored (Fig. 1).

No simple definition of this product was found in the literature. It was once considered a mineraloid distinct from species such as *korite*, *hyblite* or *notite* [28]. Des Cloizeaux [29] wrote in 1862:

‘Mr Sartorius de Waltershausen identified as korite a dark brown variety of palagonite disseminated in the Sudafell palagonitic tuff in Iceland and in the val di Nito; he finally acknowledged that a similar tombac-brown substance found in the Tonnara tuff of Cap Passaro consisted of 75% siderosilicite and 25% trinacrite. There is little need to point out that since palagonite is itself a rock rather than a well-defined mineral, all these names can be applied only to essentially variable mixtures’.

Penck [30] was of the same opinion: ‘*es existiert kein mineral Palagonite...*’. Nevertheless, Peacock [31] made a distinction between palagonite and chlorophaeite. Today its chemical composition is known to be largely dependent on the temperature, composition and flow rate of the alteration fluids, and on the time during which these solutions are in contact with the glass [14,18,25,26,32–44]. Honnorez [45,46] suggests that the term ‘palagonite’ is confusing and should no longer be used as it designates poorly defined and highly diverse products. He recommends the use of expressions such as *residual glass*, *altered glass* or *palagonitized glass* to designate alteration layers containing no clearly identifiable mineral. Some terms are difficult to get rid of, however, and ‘palagonite’ is often used in the literature.

It may also be noted that palagonitic layers do not form systematically in fresh water. Fieldes et al. [47] and Singer [48] noted that a palagonitic layer is systematically observed when the principal alteration mineral is montmorillonite. In this case, the layer itself consists of poorly organized montmorillonite. Conversely, when the principal alteration mineral is halloysite, it directly replaces the glass without forming an alteration layer per se that can be discriminated from the clayey intergranular material [49].

Many articles – particularly experimental studies – concern rhyolitic glass or obsidian. This bibliographical survey is limited to work on basaltic glass altered in seawater or meteoric water at temperatures below 100 °C. Indeed, it would appear that much of the confusion in the literature on this subject arises from comparisons of work involving glasses of different types or altered under different conditions; this is one of the limits of the ‘analog’ approach. Consider, for example, the article by Thorseth et al. [42]. Its authors see a conflict between the Berger’s conclusions [50] and our own [22] concerning the glass dissolution mechanism in a marine environment. Berger performed dissolution experiments with a basaltic glass at 200 and 320 °C in a solution resembling seawater: pH 4 and 2.8, with low magnesium, calcium

and sulfate concentrations to avoid precipitation (of anhydrite in particular). Berger et al. [50] concluded that under these conditions glass dissolution is selective, whereas we concluded that it is congruent between 0 °C and 60 °C in seawater, and that any subsequent incongruence arises from the precipitation of secondary phases. There is no contradiction here, only a difference in the alteration mechanism.

2.1. Structure and texture of palagonite

The spectra obtained by X-ray diffraction in these alteration rinds are those of amorphous or slightly crystallized products; they exhibit some characteristics of smectitic phyllosilicates [22,41,45,51–57]. Their crystallinity generally increases over time as shown, for example, by a study of basalt samples altered in the East Pacific Rise and in the North Atlantic Ridge [58]. In fact, these alteration layers often comprise multiple particles (glass fragments, amorphous products, oxides or hydroxides, phyllosilicates crystallized to some extent); the term *texture* is better suited than *structure* to characterize these layers.

For example, Fig. 2 shows the diffraction diagrams obtained for a palagonitized hyaloclastite sample from Hahryggur, Iceland. The alteration rind was separated from the pristine glass by grinding and suspending it in bromoform, then trimmed manually under a binocular magnifier.

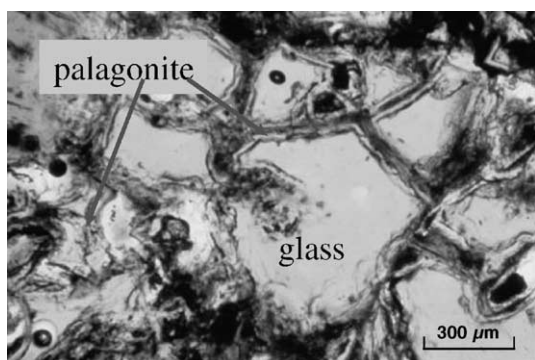


Fig. 1. Palagonitized Icelandic glass (Hahryggur) 90 000 years. Sample 86/26 (from [32]).

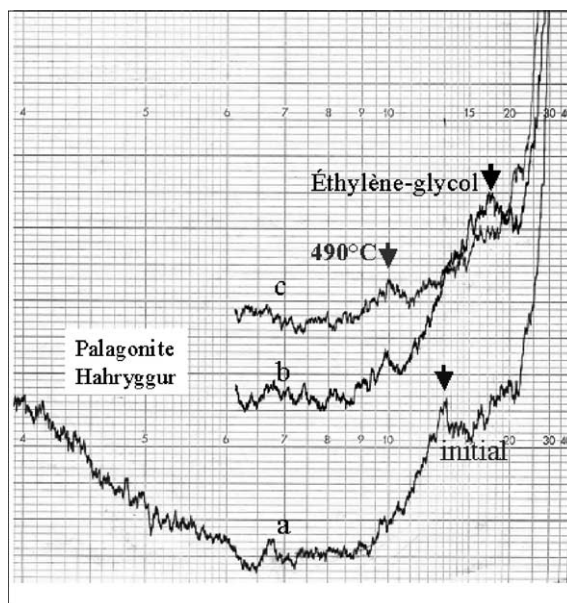


Fig. 2. Spectra obtained by X-ray diffraction in altered rind of a Hahryggur glass sample (Iceland). (a) As sampled; (b) after treatment with ethylene glycol; (c) after heating. Phillips 1120/90 diffractometer.

A broad, low-amplitude peak centered on 13 Å is visible in Fig. 2 (untreated sample). After treatment with ethylene glycol, the peak became broader and shifted to about 17 Å (Fig. 2(b)). Heating the sample to 490 °C caused the peak to collapse to about 10 Å (Fig. 2(c)). This behavior is characteristic of a poorly crystallized smectite. Some samples, such as one from the Contrada Acqua Amara (Palagonia, Sicily), were completely destroyed by heating [32,45,54].

In 1999, Techer [25] studied the palagonite on basaltic glass from the Salagou massif (France) with an estimated age of 1.4 million years. The palagonite was about 1 mm thick and consisted of nontronite.

In 1982, Eggleton and Keller [51] performed a transmission electron microscope study of the alteration rind of a limburgitic glass from Limburg (Kaiserstuhl, Germany) altered in meteoric water. Although the initial glass composition differed slightly from that of a tholeiitic glass, it is interesting to note that the authors clearly specified the clayey nature of the alteration layer (Mg–Al nontronite forming spherical aggregates).

Many samples have since been observed by transmission electron microscopy [20,22,32]. In the case of Palagonian palagonite, curled particles resembling smectite could be distinguished, but were poorly crystallized or were destroyed by the electron beam before an interpretable electron microdiffraction image could be obtained (Fig. 3). Qualitative chemical microanalysis discriminated between two main types of particles, one rich in silica and iron (nontronite?), the other consisting of silica, aluminum and magnesium (saponite?). The boundary between the pristine glass and its altered rind was sharply defined (Fig. 4) and no chemical concentration gradient was clearly visible from the interior to the exterior of the rind.

Subsequent studies of subglacial Icelandic glasses [32] generally revealed palagonites with the same textures: slightly or poorly crystallized smectitic clays (Figs. 5 and 6) for samples that had been in contact with water for less than 1 My and characterized by the absence of secondary minerals other than clays (no zeolites).

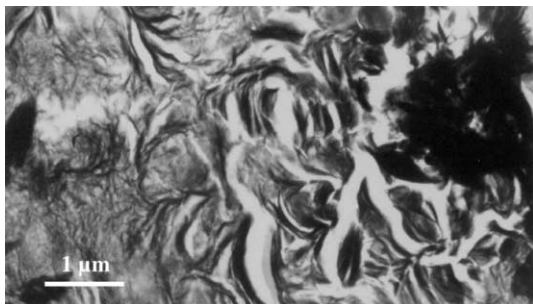


Fig. 3. Ultramicrotome cross-sectional view of the alteration layer on a basaltic glass from Palagonia, Sicily.

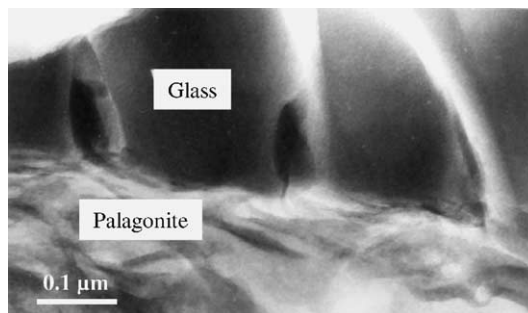


Fig. 4. Same as Fig. 3. Glass/palagonite interface [32].

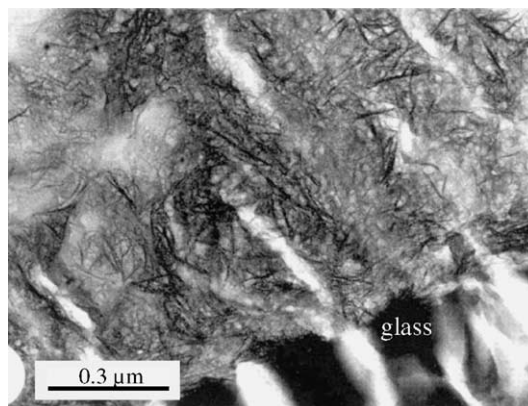


Fig. 5. Subglacial basaltic glass (Iceland: 0.1 My). Glass/palagonite interface [32].



Fig. 6. Same as Fig. 5. Electron diffraction image of palagonite [32].

In 1999, Le Gal et al. [43,44] studied older subglacial Icelandic glass samples (between 3 and 4 My) from the Vatnajökull region. In these hyaloclastite samples the gaps between the grains of glass were systematically filled with zeolites (mainly chabazite) and the palagonite layer or *gel* in Fig. 7 was fully isotropic, and identical with the pristine glass in polarized light. Under trans-

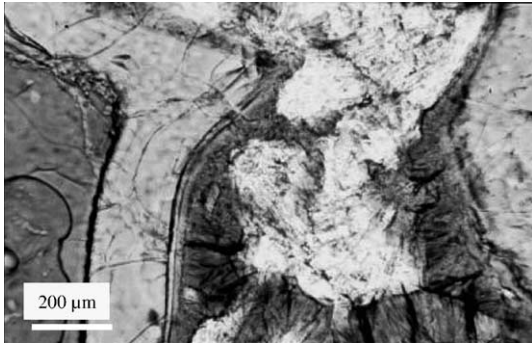


Fig. 7. Optical micrograph of subglacial Icelandic glass sample (3–4 My). Vatnajökull Region [43].

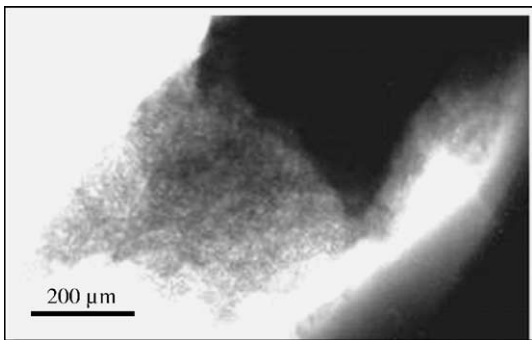


Fig. 8. Same as Fig. 7. Ultramicrotome cross-section observed by transmission electron microscopy [43].

mission electron microscopic observation, the palagonite layer was completely amorphous and microporous (Fig. 8).

2.2. Palagonite formation mechanism

Many hypotheses have been proposed to account for the development of the alteration layers surrounding basaltic glass subjected to the action of water.

2.2.1. Glass hydration

For Peacock [31], palagonite has basically the same chemical composition as the initial basaltic glass with the addition of 20–30% water. It is often considered obvious that the initial stage of palagonitization consists in ‘hydration’ of the glass. The hydrated glass is then assumed to crystallize slowly, forming clayey products. Some authors [59] refer to Marshall [60] or Friedmann et al. [61] for their work on the hydration of obsidian glass. In his essentially theoretical work, however, Marshall also assumes that the thickness of the perlite layer accurately reflects the depth of water penetration through diffusion into the glass network, and calculated

the water diffusion rate in obsidian by applying Fick’s laws. He acknowledges that the formation of alteration films is the same for all natural glasses. However, Bonatti [62] and Honnorez [45,54] were surprised at the thickness of the alteration layers formed in the natural environment compared with the low water diffusion coefficients given by Marshall [60] who considered, for example, that it would take 100 million years to form 5 μm of perlite at 50 °C. By way of comparison, the growth rate of some alteration rinds is 2–4 μm per thousand years for the basaltic glasses of the mid-Atlantic ridge (36 °N) altered at lower temperatures (0 °C) [63]. Marshall’s values [60] are implausible. Friedman et al. [61] reexamined this work and found a ‘hydration coefficient’ of 0.4 μm²/1000 years at 5 °C for the same glasses. Applying their proposed formula:

$$x^2 = k \cdot t,$$

(where x is the water penetration depth in μm, k the ‘hydration coefficient’ in μm²/1000 years, and t the time in thousands of years) yields a thickness of 2 μm in ten thousand years, still 10 times less than the thickness observed by Hékinian and Hoffert [63].

This comparison between obsidian and basaltic glass is probably unwarranted, considering the enormous difference in their chemical compositions. Obsidian glass contains about 75% silica, a glass network former, while basaltic glass contains only about 50% and is rich in ferrous iron and alkali and alkaline earth metals, glass network modifiers. There is thus no reason to assume that the alteration layer formation mechanisms are identical.

Bonatti [62] postulated that hydration occurs at high temperature during eruptions of molten lava in water. The author advanced this hypothesis to account for the relative rapidity of the formation of the alteration layers. It was also obvious to Walker and Blake [64] that palagonitization occurred when the hyaloclastites were formed. Honnorez [45,54] showed, however, that high-temperature hydration is negligible, and that the major phenomenon is post-eruptive alteration at low temperatures. He came to this conclusion by observing hyaloclastites that had been isolated at a very early date from contact with water by a carbonate cement, and which had sustained very little alteration. Studies [65–67] showed that in the case of recent samples there is no difference in the water content between the core and the outer edges of pillow lava rinds. Jakobsson [68,69] found no signs of palagonitization contemporary with recent phreatic eruptions (1963–1967) in studies of the Surtsey volcano in Iceland. The first signs of palagonitization and consolidation of Surtsey ash formed in 1964 were observed in 1969 [69] in a zone where the temperature was about 100 °C. At temperatures below 35 °C, no signs of palagonitization are visible under an optical

microscope. It is unanimously acknowledged today that palagonitization is essentially a post-eruptive phenomenon that can occur at very low temperatures. Measurements of $\delta^{18}\text{O}$ in Icelandic palagonites confirm this observation [43,44].

2.2.2. Role of glass texture

Trichet [70] noted that some basaltic glasses consist of spherules embedded in a matrix with a different chemical composition. Following this work, Honnorez [45] observed that the alteration reports for basaltic glass from the Contrada Acqua Amara (Palagonia, Sicily) can be explained by assuming selective extraction of spherules comparable to those described by Trichet, and containing most of the alkali metals and magnesium, a fraction of the silica and aluminum, and half the calcium in the glass. This explanation was also formulated by Staudigel and Hart [71] in 1983. This model was very tempting, since it accounted not only for the behavior of the elements during glass corrosion but also the rapidity with which alteration layers form at low temperatures (rapid dissolution of the matrix releasing virtually intact spherules). The basaltic glass studied by Trichet [70] appears to be something of a curiosity, however; it has proved impossible to find comparable spherules in other glass samples [22,72]. It is thus unlikely that a particular texture of basaltic glass can account for the rapid formation of alteration layers.

2.2.3. Dissolution-precipitation

Another mechanism was advanced by Hay and Iijima [33] for the formation of alteration layers. They studied the alteration rinds on tuffs from the Koko crater (Oahu, Hawaii). X-ray diffraction showed that they consist essentially of poorly crystallized montmorillonite. Electron microprobe analysis also revealed a sharp change in the chemical composition at the clearly delimited interface between the pristine glass and the alteration rind; no concentration gradient could be detected in the outer portion of the fresh glass. The authors concluded that palagonite could form by precipitation of montmorillonite on the surface of the glass from ions in solution after complete dissolution of the glass network. Melson and Thompson [73] reached the same conclusions after a study of basalt dredged from the vicinity of the Saint Paul Islands in the Atlantic Ocean.

Moreover, the $^{18}\text{O}/^{16}\text{O}$ ratios measured [74] in alteration rinds on basaltic glass samples from the Gordo Rise (Pacific Ocean) are compatible with a mechanism of this type. The measurements showed that all the oxygen atoms in the glass were replaced by oxygen from seawater during the formation of the alteration rind. The $\delta^{18}\text{O}$ ratios measured on Icelandic palagonites [43,44] also confirm this mechanism. The $^{87}\text{Sr}/^{86}\text{Sr}$ and K/Rb ratios measured in palagonitic layers [71] were found to

be near the values observed in seawater and in smectites, respectively.

Thus, as discussed below, a large body of experimental data on the dissolution rates of these glasses confirms the hypotheses regarding the rapid formation of palagonite at low temperatures.

3. Contribution of experimental work

3.1. Mechanisms

3.1.1. Experiments in seawater

Thomassin et al. [15,75–79] undertook a very thorough investigation of alteration layers formed on the surface of basaltic glass altered by seawater, using surface examination methods (photoelectron spectrometry, ion probe, electron microscopy). The experiments were carried out at 90 °C at 1 bar in Teflon reactors for periods ranging from a few minutes to nine months. The liquid/solid mass ratio was about 100. The authors showed that the alteration layers consisted of crystals. In seawater, hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) crystals develop after a few minutes of interaction, forming layers several micrometers thick after a few months. These crystals then tend to dissolve, and are replaced by magnesian and aluminous phyllosilicates (serpentine, then smectite). Over longer periods, an intermediate layer rich in silica, iron and magnesium develops toward the glass core. According to Thomassin et al. [76] palagonite is formed in seawater by two distinct mechanisms: precipitation of crystals (hydrotalcite and phyllosilicates) from solubilized elements, and the progressive modification of a residual hydrated glass (the intermediate layer).

These experiments represent a significant contribution toward understanding the palagonitization mechanism. They clearly demonstrate that the chemical and mineralogical composition of the alteration layers depends to a large extent on the chemical composition of the solution; they prove that the formation of the alteration layers is not the result of simple hydration of the glass.

In addition to this work, experiments were carried out by Crovisier et al. [16–23] under conditions similar to those reported by Thomassin, with the objective of investigating the effects of the temperature and pressure on the nature of the short-term alteration layers formed in seawater. The experiments were performed at 60, 50, 25 and 3 °C in polypropylene reactors for periods ranging from a few hours to 600 days at a pressure of 1 and 350 bars. The glass-surface-area-to-solution-volume ratio was 7 m^{-1} , and the solution was not renewed. The results showed that the mineralogical composition of the alteration layers at 50 and 60 °C did not differ appreciably from the composition observed by

Thomassin at 90 °C. However, an examination of the chemical composition of the solution and an electron microscope study of the intermediate layer between the pristine glass and the hydrotalcite crystals led us to conclude that the alteration layers were formed by a single mechanism: complete dissolution of the glass network followed by precipitation of amorphous or crystallized products from solubilized elements [22]. The alteration layers consist of crystals or amorphous products and their texture, observed by electron microscopy, systematically indicates a major reorganization of the initial glass structure that is incompatible with the persistence of a residual glass skeleton.

Figs. 9 and 10 show two examples of alteration layers formed experimentally and observed by transmission electron microscopy.

A pressure of 350 bars had no significant effect on the nature of the alteration products [16,23]. The products formed at 25 and 3 °C were radically different from those observed at 50 and 90 °C. Pyroaurite ($\text{Mg}_6\text{Fe}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) forms at 25 °C, while at 3 °C the alteration layer consists of iron hydroxide (βFeOOH) and illite (Fig. 10).

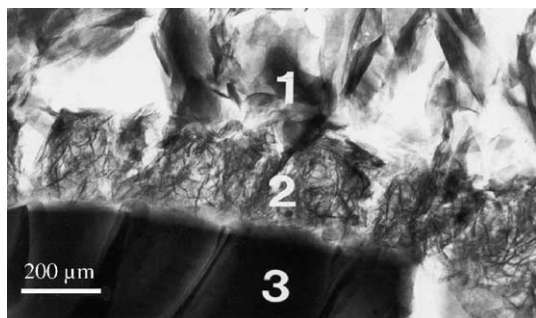


Fig. 9. Ultramicrotome cross-section showing the interface between the basaltic glass and the alteration layer formed in seawater at 50 °C after 120 days [22].

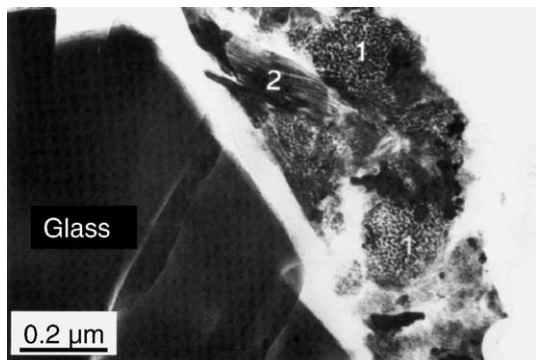


Fig. 10. Ultramicrotome cross-section showing the interface between the basaltic glass and the alteration layer formed in seawater at 3 °C after 600 days [43].

This experimental work has thus established that glass dissolution is initially congruent and that the alteration layers consist of precipitates, the nature of which is highly temperature-dependent. It therefore confirms the hypotheses proposed by Hay and Iijima [33] and by Melson and Thompson [73].

3.1.2. Experiments in pure water

Experimental work in pure water began with research by Trichet [70] and later by Decarreau [80]. These authors were more interested in the geochemical balances of glass alteration and in neoformed species observed in Soxhlet tests (halloysite, smectite), however, than in the nature of the alteration layers themselves.

Thomassin et al. [15,78] characterized the alteration layers that developed at 90 °C on the surface of a tholeiitic glass altered in deionized water. The experimental protocol was the same as for the experiments performed by the same authors in seawater. The experiments were carried out for periods ranging from 15 min to two months. Photoelectron spectrometry revealed that glass dissolution is initially selective, at least during the first six days [78]. Alteration layers rich in iron (ferrihydrite) and aluminum developed after only a few hours of interaction. Ferriferous and aluminous cryptocrystalline silicates were subsequently observed. After 6 days of interaction the alteration layer could be detached from the glass, revealing a surface with the chemical composition of the pristine glass, as analyzed by photoelectron spectrometry. The author concluded that a change occurred in the dissolution mechanism, resulting in simultaneous extraction of all the glass network constituents (congruent dissolution).

We also performed experimental dissolution of a tholeiitic glass in distilled water at 60 °C [23,24,81,82]. Two series of experiments were carried out: one in a confined medium (without solution renewal) and the second with periodic renewal of the alteration solution.

3.1.2.1. Experiments in confined media. The results of chemical analysis of the alteration solution are shown in Fig. 11. Glass dissolution was not stoichiometric during the first five days: the Na, Mg and Ca/Si ratios were much higher in solution than in the initial glass. The solution pH increased from 5.5 to 7.0. Subsequently, glass dissolution became stoichiometric. The solution pH reached 7.5 after 14 days and stabilized at this value up to 25 days.

During the initial selective dissolution phase, no alteration layer was visible on the surface of the glass when observed by electron microscopy. An alteration layer could be observed on the glass surface after 4 and 7 days (Fig. 12). X-ray microanalysis by electron microscopy indicated that this layer consisted of iron (85% Fe_2O_3) and titanium (15% TiO_2). Electron diffraction

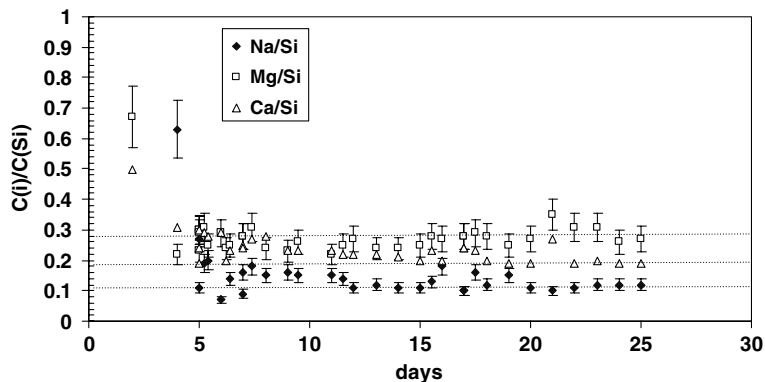


Fig. 11. Na, Ca and Mg/Si ratios versus time during dissolution of a tholeiitic glass in distilled water at 60 °C [24,82].

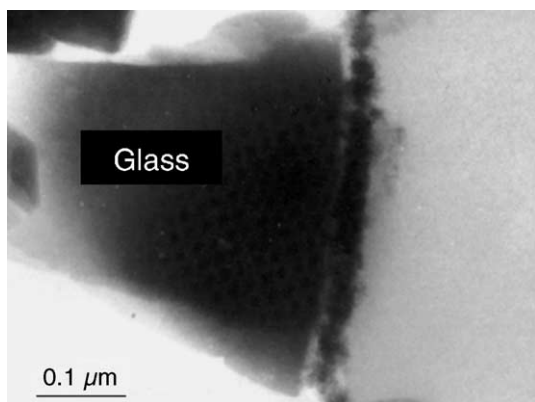


Fig. 12. Ultramicrotome cross-section showing the interface between the basaltic glass and the alteration layer formed in initially pure water at 60 °C after 7 days [24,82]. The layer consists mainly of iron hydroxides.

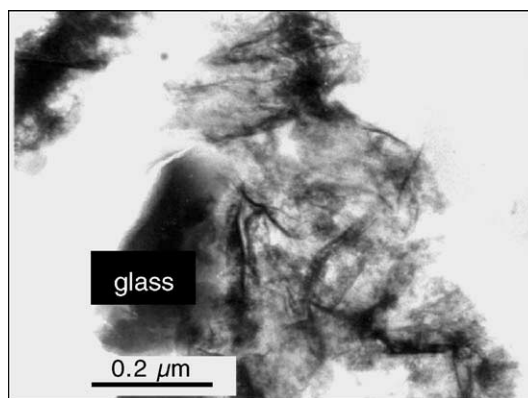


Fig. 13. Ultramicrotome cross-section showing the interface between the basaltic glass and the alteration layer formed in initially pure water at 60 °C after 25 days [24,81,82]. The layer consists mainly of iron hydroxides and an alumina silicate (*imogolite*).

analysis revealed the presence of crystalline microdomains. The images obtained were compatible with αFeOOH , but also with βFeOOH [24]. After 25 days, the alteration layer was up to 0.5 μm thick.

It consisted of zones of entangled filaments (Fig. 13), and its chemical composition was very different from that of the layer observed earlier. X-ray microanalysis showed that it consisted of an aluminous silicate similar to *imogolite* [23,24,81,82].

The glass dissolution rate calculated from the dissolved element mass during the congruent phase was $0.12 \text{ gm}^{-2} \text{ d}^{-1}$. This rate was very close to the rate measured at the same temperature in seawater ($0.09 \text{ gm}^{-2} \text{ d}^{-1}$).

These experiments at 60 °C thus lead in a different way to the same conclusions formulated by Thomassin and Touray [78] and Thomassin [15] after their work at 90 °C: glass dissolution is initially selective, then becomes congruent; any subsequent incongruence results from the precipitation of secondary phases. The transi-

tion between initially selective dissolution and congruent dissolution of the glass is probably attributable to the rise in the pH to 7.0, a threshold above which the number of hydroxyl ions in solution is sufficient to break the strong (Si–O–Si) bonds of the glass network at a rate equal to or greater than selective extraction of alkali metals and alkaline earth metals. The experiments carried out at 90 °C by Techer et al. [14] and Techer [25] confirm these conclusions, not only for basaltic glass but also for SON68 glass.

3.1.2.2. Experiments in renewed media. Experiments were carried out by Crovisier et al. [23] and Atassi [24] with a single specimen. The alteration solution was renewed daily for 7 days; it was then renewed twice at three-day intervals. The mass of elements extracted each day was observed to remain relatively constant. The solution pH did not exceed 6.2 during these experiments. The Na, Mg and Ca/Si ratios were higher in solution than in the

initial glass. When the alteration solution is renewed to prevent the pH from rising, the transition from selective dissolution to congruent dissolution does not occur. The rise in the pH thus appears to be responsible for the change in the mechanism.

In another study, Gislason and Eugster [83] also reached the same general conclusions. They experimentally dissolved a basaltic glass in distilled water at 25, 45 and 65 °C; the glass sample came from the Krafla volcano in northeastern Iceland (1981 eruption). The authors concluded that the glass dissolution rate was constant at any given temperature throughout their experiments. They also concluded that the dissolution was stoichiometric ('with a slight solution preference for Na and K at 25 °C') and that it became incongruent – notably at 45 and 65 °C – following the precipitation of silicate phases.

3.2. Kinetics

3.2.1. Relation between the dissolution rate and the temperature

Numerous alteration experiments have been carried out with basaltic glass in pure water and in very dilute solutions. The initial glass dissolution rates have thus been determined at temperatures ranging from 3 to 300 °C [14,16,23–25,83–88]. In this review we will not cover in detail the kinetic laws proposed by these authors; interested readers should refer directly to the studies cited, or to Techer [25]. The published data concerning basaltic glasses and SON68 nuclear glass are plotted in Fig. 14, excerpted from Techer [25].

The value of $\ln(r_0)$ can be seen to increase at a constant, linear rate with the temperature following an Arrhenius law. The activation energy value (73 kJ mol⁻¹) was constant over the temperature range studied (3–300 °C), indicating a single alteration mechanism for reactions at low or high temperatures. The activation energy value obtained suggests a predominant surface reaction mechanism during the initial dissolution of the basaltic glass (hydrolysis of the silicate network).

The activation energies of the basaltic glass and nuclear glass dissolution reactions are thus comparable. This similarity indicates that the aqueous reaction mechanisms for the nuclear glass and for its basaltic glass analog are identical in the initial instants of the reaction.

3.2.2. Evolution of the rate with the reaction progress

Fig. 15, also taken from [25], illustrates the well known fact that the alteration rate diminishes as the concentration of dissolved species increases in solution.

At the most advanced stage of reaction progress at 90 °C (281 days at an S/V ratio of 337 cm⁻¹), the glass alteration rate was 4 orders of magnitude below r_0 . The initial alteration rate of the basaltic glass at 25 °C was estimated equal to 4×10^{-3} g m⁻² d⁻¹. The rates measured during the tests at 346 cm⁻¹ ranged from 2×10^{-4} to 2×10^{-6} g m⁻² d⁻¹ from 7 to 364 days. The alteration rate thus diminished by at least 3 orders of magnitude at 25 °C compared with r_0 .

3.2.3. Role of dissolved silica in solution

In 1986, Grambow and Coll [87] have studied natural basaltic glasses altered in seawater. These authors have suspected that 'the rate of reaction is high in solutions low in silica and about two orders of magnitude lower in silica saturated solutions'. Specific experimental approaches were then conducted to quantify this important finding, on both natural and nuclear waste glasses.

In 1997, Daux et al. [88] investigated in the laboratory the behavior of synthetic tholeiitic basaltic glass in the presence of dissolved silica; the maximum Si concentration was 73 mg l⁻¹. Techer [25] carried out additional tests, notably at high dissolved silica concentrations (up to 129 mg l⁻¹). The basaltic glass alteration rates measured in highly Si-enriched media were lower than the initial alteration rate determined in 90 °C in a basic medium ($r_0 = 0.75$ g m⁻² d⁻¹); the difference ranged from a factor of 2.3–200 (i.e. up to two orders of magnitude, as suspected by Grambow et al. [87]). The rate was inversely proportional to the Si

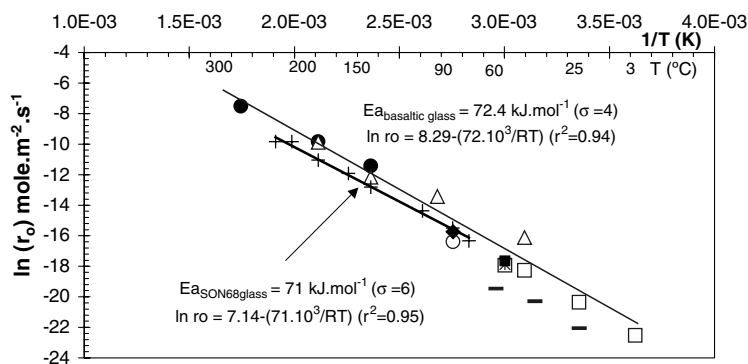


Fig. 14. Initial alteration rate (r_0) of basaltic glass and SON68 nuclear glass versus the reciprocal of the temperature (from [25]).

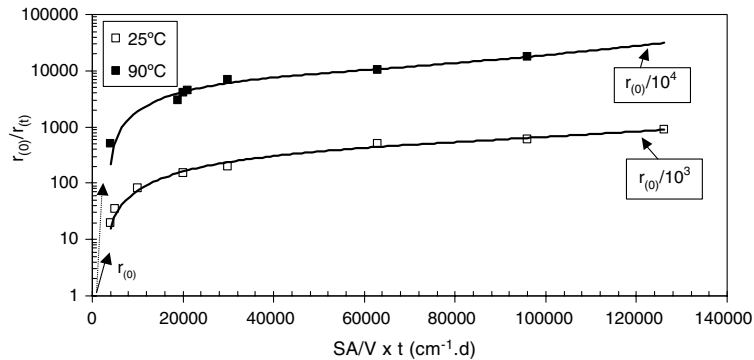


Fig. 15. Alteration kinetics reduction factor (r_0/r) of a basaltic glass at 90 and 25 °C versus the $S/V \times t$ parameter (tests at 337 and 346 cm^{-1} , respectively) (from [25]).

concentration, or the orthosilicic acid activity, in solution. However, even at very high silicon concentrations in solution, the basaltic glass alteration rate did not drop to the order of magnitude measured during static tests at high S/V ratios after several months of interaction (i.e. up to four orders of magnitude).

Techer [25] and Techer et al. [26] examined the evolution of the basaltic glass alteration rate in the context of kinetic laws involving the concept of reaction affinity (see for example [87,89]). These authors have calculated the dissolution rates of basaltic glass by applying the different rate equations, such as those postulated by Grambow et al. [87] and Daux et al. [88]. The calculated rates were then compared with the experimental values obtained during leaching tests in the laboratory. Techer [14,25,26] concluded that: ‘*The basaltic glass alteration kinetics under static conditions in a closed system, whether near or far from equilibrium, are not governed by the solution chemistry alone. The chemical affinity as well as the inhibiting effect of dissolved silica are not sufficient to account for the experimentally observed drop in the alteration rate by several orders of magnitude. Clearly a process other than the solution chemistry accounts for over 90% in controlling the alteration kinetics*’.

3.2.4. Protective role of the alteration layer

Techer [25] also studied the dissolution kinetics of a pristine glass specimen and of a glass specimen previously altered in the same type of aqueous solution, and thus already covered by an alteration film. She observed that after 91 days in solution at steady-state Si and Na concentrations, the basaltic glass, which had developed an alteration film 20 nm thick, was altered at a rate over 4 orders of magnitude lower than the initial rate calculated under the same pH and temperature conditions. In this solution, a pristine glass specimen without an alteration film was altered at a rate near r_0 (lower by a factor of 15). These observations clearly

reveal the minor role of the solution chemistry in controlling the alteration kinetics during the initial stages of glass/water interactions. The author then postulated that the alteration film formed on the glass surface had a protective role leading to the low observed rates.

A more comprehensive demonstration of such controlling factor would imply more specific experimental approaches on palagonite, such as tracer experiments with ^{32}Si or ^{29}Si . Such methodologies have started on gel-like alteration products obtained by leaching of simulated SON68 nuclear waste glass [90,91]. The obtained results show a direct correlation between the apparent diffusion coefficient of ^{29}Si and the porosity of the gel-like alteration product [91]. A clear inhibition of ^{29}Si diffusion is observed for gel-like material formed during aqueous corrosion of SON68 glass under high SA/V ratio, where the glass dissolution rate is 10^4 lower than the initial dissolution rate $r_{(0)}$. Under these experimental conditions, the gel-like alteration product is dense, and the network of the internal porosity clearly reduces the velocity and the penetration of dissolved silica.

4. Contribution of natural specimens

4.1. Historical background

Many authors have used a simple relation between the palagonite thickness and the age of the glass to determine the time-dependence of the alteration reaction. The glass is assumed to have been subjected to alteration processes since its formation. The alteration time is thus assumed equal to the age of the volcanic formation. The *apparent alteration rate* is then determined and expressed in micrometers of altered glass versus time. This approach also implies that palagonitization is a constant-volume process.

4.1.1. Alteration in fresh water

Icelandic basaltic hyaloclastites, hyaloclastites from British Columbia, and pillow lava from the Columbia River were studied [32,41,87,89,92,93]. The Icelandic basaltic glasses were exposed to meteoric water during the interglacial periods, and are subjected today to alteration by meteoric water at a mean temperature not exceeding 4 °C, according to Crovisier [32].

Crovisier [32] examined hyaloclastites from the Húsafell and Hengill volcanic series dated to 0.09 and 2.4 million years. Depending on the sample origin, age and grain size, the alteration film – consisting of palagonite associated with intergranular secondary minerals (clays and zeolites in the oldest samples) – was of variable thickness. No trend with respect to the grain size was observed, however. Moreover, there is no simple relation between the specimen age and the altered glass thickness (e.g. the older the sample, the greater the quantity of palagonite): only 10 µm of palagonite were measured on the surface of the oldest sample (2.4 million years), for example, compared with 29 µm at the surface of a sample 0.5 million years old. The mean alteration rates determined by equating the alteration time with the sample age range from 0.004 to 0.33 µm/1000 years. The lowest rates were obtained for two samples from Húsafell (0.004 and 0.06 µm/1000 years); they were 2–40 times lower than those measured on the Hengill samples. The alteration rates obtained for this series were relatively homogeneous (mean: 0.16 µm/1000 years).

Other Icelandic samples from the Mosfell, Midalsfjall, Raudafell, Blafell, Valafell, Eyrarfjall and Tungufell regions were studied by Byers et al. [92] and Jercinovic and Ewing [41]. The first few of these volcanic formations were formed during the middle and late Pleistocene (0.8–0.008 million years ago). The Eyrarfjall and Tungufell eruptions occurred earlier, during the Plio-Pleistocene (3.1–0.7 million years ago). No accurate chronological data are available, however, concerning these volcanic formations. The authors considered a minimum age and a maximum age, in some cases over 2 million years apart. Moreover, the thicknesses of the alteration films – palagonite, smectite or saponite clays, and zeolites in the Eyrarfjall and Tungufell formations – varied considerably within the same volcanic series. Under these conditions (uncertainty on the age, major differences in the alteration thicknesses), only a range can be determined between the minimum and maximum rates. This range extends from 0.002 to 10 µm/1000 years.

Hyaloclastites from Ash Mountain, southern Tuya, and Tuya Butte in British Columbia were studied by Grambow et al. [87], Byers et al. [92], Jercinovic et al. [41,93]. They also originated from subglacial eruptions during the late Pleistocene (15 000–10 000 years ago). These glasses were initially altered by glacial water, then by meteoric water. The thicknesses of the altera-

tion films on these glasses (palagonite, clays, calcite, zeolite) are highly variable: from 2 to 138 µm. The films on the Tuya Butte hyaloclastites were highly developed (50–138 µm) compared with those from Southern Tuya and Ash Mountain (3–12 µm). The apparent alteration rates based on the assumption that these volcanic formations were subjected to alteration processes from the outset are relatively high for the Tuya Butte system: 2.1–13.8 µm/1000 years compared with 0.1–0.8 µm/1000 years for the Ash Mountain and Southern Tuya systems. The considerable difference between nearby volcanic systems can be attributed to the fact that the upper Southern Tuya and Ash Mountain formations were the result of more recent eruptions. The hyaloclastites were not exposed to the subaqueous lacustrine environment, and were altered essentially by percolating water [93].

Byers et al. [92] examined Columbia River samples that differed from the previous ones by their greater age (14–12 million years) and their formation mechanism (in this case, pillow lava and breccias formed by the interaction between a basalt flow and the water of a river or lake). These volcanic products have probably been submitted to alteration by surface or infiltration water since their formation. The palagonite thicknesses measured on the surface of the glassy rinds on the pillow lava samples varied from a few tens to over 350 µm.

The measured basaltic glass alteration rates were low, ranging from 0.025 to 0.03 µm/1000 years. For the Columbia River samples, the altered surfaces included not only authigenic clays but also calcite and barite rich in strontium. Precipitated barite is widely observed in the free spaces of the formations and in the vesicles, while calcite appears as a film in fractures within the basalt. These late precipitates may have played a significant role in obstructing water flow and limiting or even inhibiting glass alteration; this could account for the low rates.

4.1.2. Alteration in seawater

Jercinovic and Ewing [41] as well as Grambow et al. [87] and Furnes [94] studied the alteration of basaltic glasses from boreholes in the Reykjanes and mid-Atlantic ridges. The samples ranged in age between 2.4 and 119 million years. It would be inappropriate in this case to determine the alteration rates from the palagonite thicknesses (which ranged from 0.002 to 0.3 µm/1000 years) and the age of the materials. This approach does not take into account the possibility that the glass may have been isolated by sedimentation processes. The time interval between the formation of the basalt and the sediment deposits is a critical parameter that must be determined. Similarly, the stages of precipitation of phases such as calcite, observed on many samples, must be situated in the geological history of the glass. Both sedimentation and calcitization isolate the glass from

water. The protectiveness of calcitic cement was observed in particular [54,87]. Modeling by Grambow et al. [87] clarified the conditions under which alteration products were formed. It has thus been demonstrated that phillipsite (zeolite) forms at high glass-surface-area-to-solution-volume ratios, or under static or low-flow alteration conditions. Phillipsite was observed on the borehole samples studied here, and is thus indicative of development in a confined system. Borehole sampling methods tend to scrape off some of the alteration film [41] making any determination of the alteration rate using this method inexact.

Jercinovic and Ewing [41] also studied the alteration of basaltic glasses dredged from oceanic ridges: Reykjanes, the Galapagos, Gorda, and the mid-Atlantic ridge. The age of formation of some of these basaltic glasses are known from magnetic anomalies associated with suboceanic spreading. This method is not always very accurate, however, and only a maximum age can be obtained. This age and the palagonite thicknesses thus provide a basis for determining a minimum alteration rate. The values obtained in this way are low, less than $0.1 \mu\text{m}/1000$ years (from 0.0003 to $0.1 \mu\text{m}/1000$ years). Maximum rates of approximately $0.1 \mu\text{m}/1000$ years were obtained for samples from the Reykjanes and Galapagos ridges.

For these authors, the glassy hyaloclastite or pillow lava samples with glassy rinds were altered under open-system conditions. However, they noted the presence of detrital and authigenic cements (iron-rich saponites, iron–aluminum oxides) regularly associated with the palagonite. These deposits could have sealed the hyaloclastic formations, isolating them from direct contact with seawater. The rate determined above may thus be significantly underestimated.

In a study of hydrothermal alteration of basaltic glasses from Surtsey Island, Jakobsson and Moore [95] compared them with a vitreous basalt sample dredged from the ocean bottom southwest of the island. This recent sample was very accurately dated: it was formed in June 1964. The palagonite thicknesses formed over 18.4 years (the sample was taken in November 1982) indicate alteration rates of $27.2\text{--}0.9 \mu\text{m}/1000$ years. These values are significantly higher than those obtained earlier. Moreover, the sample was not covered by sediments (the author noted only partial biological crusting). In this case alteration occurred in an open system from the outset.

Hékinian and Hoffert [63] studied the alteration of pillow lava dredged from the Rift Valley. These basaltic products were formed on the ocean floor several tens of thousands of years ago. The authors measured the thickness of the manganese deposits on the samples to determine the age of these volcanic formations. The age of glass was calculated based on a growth rate of $3 \mu\text{m}/1000$ years for these deposits, assumed constant for all

the oceans. Some samples were also dated by fission tracks.

A major discrepancy was observed between the two ages. Only the ages obtained on sample DR 11-315X by fission tracks and by manganese dating were comparable. These results show that the manganese growth rate cannot be used as a dating method. The problem with this approach is related to the assumption of a single constant Mn growth rate for all the oceans irrespective of the depth.

The alteration film thicknesses on basaltic glass samples altered in continental or oceanic environments are indicated in Fig. 16 according to the sample age, considered equal to the duration of alteration. This representation corresponds to the *apparent* alteration rate of the glass. The indicated parameter values are subject to error, arbitrarily estimated at $\pm 50\%$ for the film thickness and -50% for the alteration time. It may be assumed that the palagonite thickness is not always equal to the dissolved glass thickness. Crovisier [32] demonstrated this experimentally for Icelandic glass samples. The reported error value also takes into account possible damage to the alteration film during sampling. The basaltic glass alteration time is assumed not to exceed 50% of the age of the formation, thus taking into account possible variations in fluid access to the glass over geological time.

The result is thus a very wide range of values, from about 50 to $10^{-3} \mu\text{m}/1000$ years. In continental and oceanic environments the glass dissolution rates are generally less than $50 \mu\text{m}/1000$ years. In addition, the rate tends to diminish over time. The older the glass or the longer the glass/fluid interaction time, the lower the alteration rate. In an oceanic environment, for example, the highest rates (about $10 \mu\text{m}/1000$ years) correspond to the most recent samples (Surtsey, Rift Valley); rates of about $10^{-3} \mu\text{m}/1000$ years were obtained for glass samples older than 1 million years. This observation is not always true for individual samples, but remains the general trend. Nevertheless, although the glass/fluid interaction time cannot be reliably determined, the alteration rates estimated by this method – the only available method for investigating volcanic glass alteration kinetics – indicate an order of magnitude for the alteration rate in the natural environment.

The geological systems investigated (continental and oceanic environment) are characterized by low temperatures; the mean temperature in Iceland, for example, does not exceed 4°C [32]. Seabed temperatures have been determined in a few cases. The basaltic glass from Surtsey was sampled at a depth where the prevailing temperature is about $7\text{--}10^\circ\text{C}$ [95]. The mean temperature was about 4°C for the Rift Valley glass samples studied by Hékinian and Hoffert [63]. No data are available concerning the sampling depths and temperatures of the samples studied by Jercinovic and Ewing

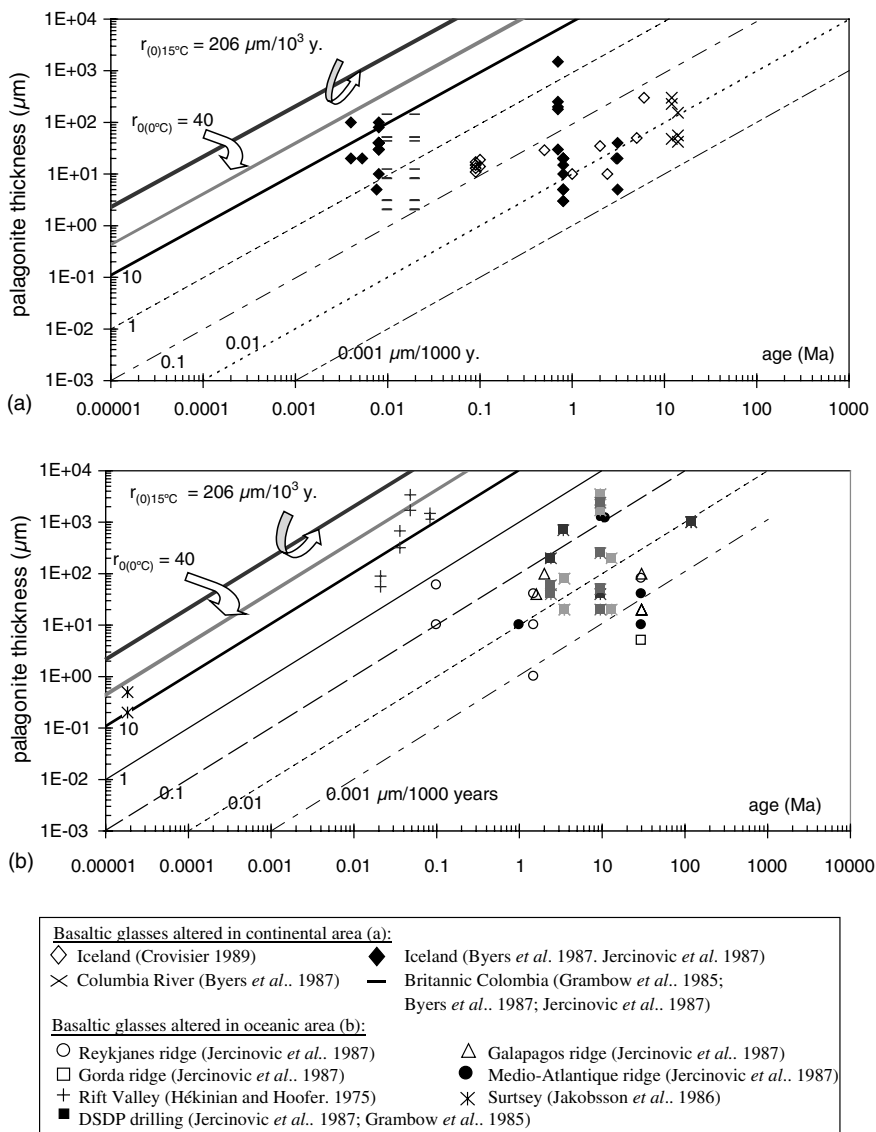


Fig. 16. Palagonite thickness versus glass age (considered to represent the alteration time) for basaltic glasses altered in a continental (a) or oceanic (b) environment. The alteration rates determined from this relation are represented by broken lines and expressed in μm per 1000 years. The initial alteration rates r_0 (in μm per 1000 years) are calculated for 0 and 15 °C (from [25]).

[41] and Grambow et al. [87], but they can reasonably be estimated to be below 15 °C.

The initial glass alteration rates were calculated for a minimum temperature of 0 °C and a maximum temperature of 15 °C representative of the context of the studies. The values are based on knowledge of the evolution of r_0 with the reciprocal of the temperature, and on the activation energy of the reaction (Fig. 14):

$$\ln(r_0) = 24 - \left(\frac{73 \times 10^3}{RT} \right),$$

where T is the temperature in kelvins and R is the ideal gas constant. The rates are expressed in $\mu\text{m}/1000$ years, assuming a mean glass density of 2.7 g cm^{-3} [33,93].

The initial alteration rates calculated for temperatures of 0 and 15 °C are 40 and 209 $\mu\text{m}/1000$ years, respectively. These initial rate values are compared with the apparent rates measured on the natural samples in Fig. 16. The mean alteration rates for basaltic glass appear to be lower than the initial alteration rate, especially for long reaction times. In the case of glasses less than 10 000 years old (e.g. Rift Valley and Surtsey oceanic glass and some Icelandic continental glass) the

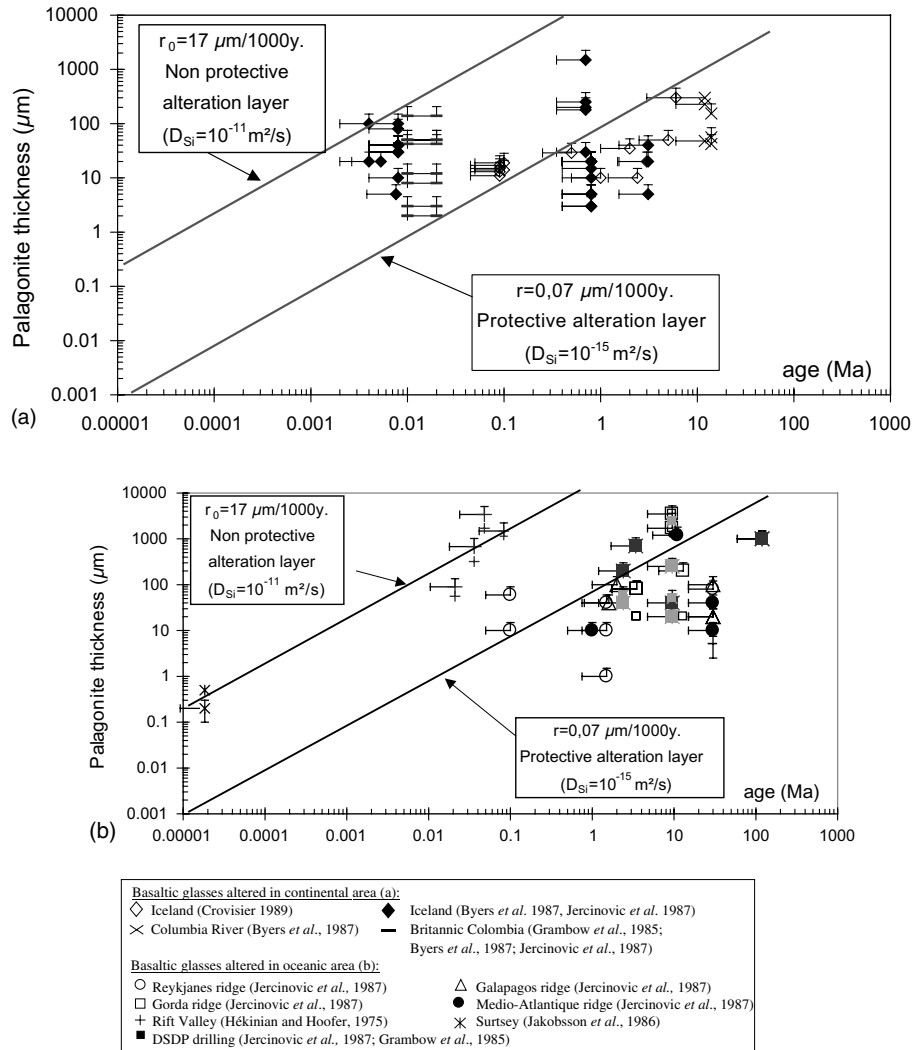


Fig. 17. Apparent alteration rates of basaltic glasses measured in a continental (a) and oceanic (b) environment, compared with the alteration rates calculated by PREDIVER for diffusion coefficients D_{Si} of 10^{11} and $10^{15} \text{m}^2 \text{s}^{-1}$ (from [25]).

alteration rate appears to remain near r_0 . This conclusion is in agreement with the results of laboratory experiments that confirm a drop in the alteration rates over time.

Several parameters can account for the increasing difference between r_0 and the apparent rate as the alteration time increases:

1. The older the volcanic formations, the more difficult it is to constrain the alteration conditions, and thus the water/glass contact time. Major natural phenomena in particular can influence the conditions of fluid access to the glass: changing seasons, the alternation of glacial and interglacial periods, sedimentation processes, deposition of detrital or authigenic phases, etc.

All these phenomena tend to isolate the glass from fluids, and thus shorten the alteration time. Grambow et al. [87] noted the effect of the water concentration related to sedimentation in oceanic conditions. In the presence of sediments, which generally contain biogenic silica, the silica concentration of the interstitial water ($5\text{--}25 \text{mg l}^{-1}$) exceeds that of seawater ($0.4\text{--}4 \text{mg l}^{-1}$). According to Grambow's hypothesis that the alteration kinetics are governed by silica in solution, this high concentration should contribute to a reduction in the glass alteration rate. Grambow spoke of final rates ($0.02\text{--}0.2 \mu\text{m}/1000 \text{years}$) measured on 'isolated' glass borehole samples. Conversely, the initial rates determined for dredged glass samples embedded to varying degrees in the sed-

iments exceeded $3 \mu\text{m}/1000$ years ($3\text{--}20 \mu\text{m}/1000$ years). Allowing for a 50% error on the age of the glass could be insufficient if the glass was isolated relatively early compared with the age of the materials. The calculated rates would be underestimated in this case.

- Similarly, the older the volcanic formations, the more difficult it is to obtain representative data. Assuming a basaltic glass alteration rate of $100 \mu\text{m}/1000$ years (near the initial rate), a palagonite thickness of 10 cm should be observed after 1 million years. The initial diameter of the hyaloclastite grains is not sufficient to obtain altered glass thicknesses of this order today.
- The palagonite film may have a protective role with respect to alteration. This film would constitute a diffusion barrier that slows or even inhibits glass alteration. The role of this barrier varies over time. It would have a slight or negligible effect during the initial stages of the reaction. This would account for the r_0 values measured on recent glass samples. As the reaction progresses, however, the protective role could become the controlling factor leading to the low measured alteration rates ($r_0/10^3$ to $r_0/10^4$).

Techer [25] examined the third hypothesis using the PREDIVER calculation code [96,97]. The code is based on the first-order law coupled with a Si diffusion law in the alteration film, and was applied to the reference nuclear glass by integrating two extreme values for the diffusion coefficient: $D_{\text{Si}} = 10^{-11}$ and $D_{\text{Si}} = 10^{-15} \text{ m}^2 \text{ s}^{-1}$. A D_{Si} coefficient of $10^{-11} \text{ m}^2 \text{ s}^{-1}$ was determined for alteration conditions with a non-protective gel. D_{Si} values below $10^{-13} \text{ m}^2 \text{ s}^{-1}$ are considered to correspond to a protective gel [97]. The alteration rates obtained at a temperature of 4°C were $16.8 \mu\text{m}/1000$ years for a coefficient of $10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $0.07 \mu\text{m}/1000$ years and 10^{-15} [97]. The apparent rates determined for natural glasses lie between these two theoretical values (Fig. 17).



Fig. 18. View of contact between the basalt dike with glassy rind (black) covered by palagonite (brown fringe) and the argillaceous pelite host formation (red).

The older the basaltic glass, the closer the mean alteration rate is to the value defined with a diffusion coefficient of $10^{-15} \text{ m}^2 \text{ s}^{-1}$. These results suggest that the alteration film does indeed have a protective role with respect to alteration, and that this role becomes increasingly important as the reaction advances.

4.2. Salagou palagonite (Hérault, France)

Techer [25] studied basaltic veins with glassy rinds formed 1.4 million years ago in the Salagou massif (Lodève Basin, Hérault, France) in an argillaceous (pelite) sediment with an age of 258 million years (Fig. 18). By studying the alteration of these natural glasses in a clay environment, she was able to examine palagonitization in the presence of clay; this enhances the utility of the analog since the sites under consideration for the disposal of radioactive waste containment glass will include multiple engineered barriers notably containing clay.

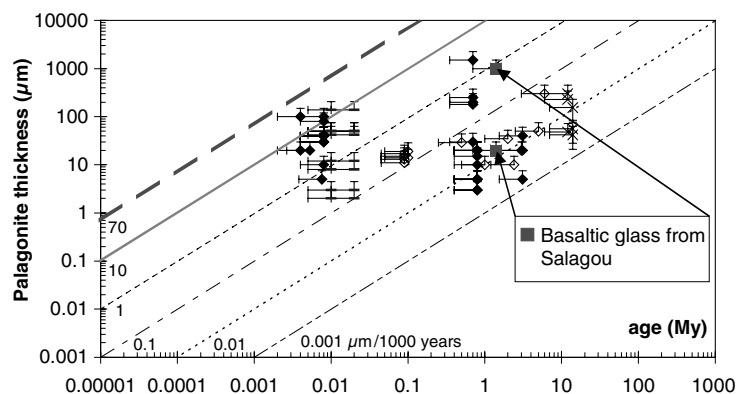


Fig. 19. Alteration kinetics of Salagou basaltic glass in pelite medium [25].

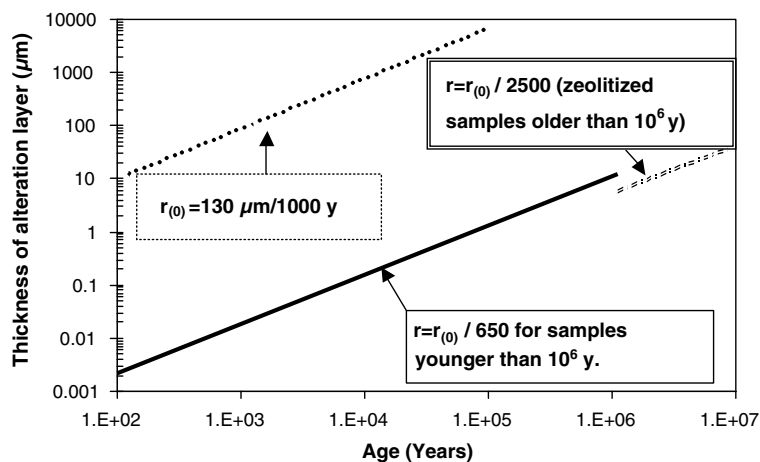


Fig. 20. Alteration rates of zeolitic (green) and non-zeolitic (red) Icelandic basaltic glasses compared with the initial rate r_0 measured in the laboratory (from [43,44]).

The estimated alteration rate for these glasses ranges from 0.014 to 2.14 $\mu\text{m}/1000$ years, assuming an arbitrary error of $\pm 50\%$ on the age of the glass (water–glass contact time shorter than the geological history of the glass) and a $\pm 50\%$ error on the palagonite film thickness (due to surface damage during sampling). These values are within the range defined using the same approach for numerous basaltic glasses altered in continental or oceanic environments. Despite the uncertainties on the rates determined in this way, it may be noted that the alteration kinetics of basaltic glass in contact with Permian pelite are comparable to those measured immediately in contact with the glass in aqueous media without clay material. Over a period of 1 million years, no more significant alteration of the glass was observed in the presence of Permian pelite.

The initial alteration rate of basaltic glasses at 25 °C (Fig. 14) is $3.5 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$ (473 $\mu\text{m}/1000$ years for a basaltic glass density of 2.7 g m^{-3}). The rates estimated from the palagonite thicknesses are thus at least 220 times lower than r_0 (Fig. 19).

4.3. Vatnajökull palagonite (Iceland)

In 1999, Le Gal [43,44] studied altered Icelandic glass samples from the Vatnajökull region. These are the most ancient subglacial formations of Iceland, with an estimated age of 3 or 4 million years. The glass grains were surrounded by a thick and fully isotropic palagonite rind (Fig. 7). X-ray diffraction and transmission electron microscope observation revealed that the palagonite was completely amorphous and microporous, unlike any of the more recent subglacial palagonites observed by Crovisier et al. [98]. The initially empty gaps between the glass grains were entirely filled with compact zeolites (mainly analcime). The estimated alteration rates were

2500 times lower than the experimental values, whereas they were 650 times lower for the samples without zeolites (Fig. 20). This was attributed to the presence of the zeolites, which constitute a diffusion barrier. It also implies a different mechanism: a transition occurred from complete dissolution of the glass network for recent samples to selective dissolution for the older samples in which zeolites precipitated [44].

Zeolite precipitation was also observed during nuclear glass alteration experiments [99,100]. Crystallization of the zeolites caused an acceleration of the nuclear glass corrosion rate. This kinetic effect was attributed mainly to the consumption of silicon and aluminum during their formation, as these elements directly influence the chemical affinity. This appears to be in contradiction with the observed behavior of zeolitic basaltic glasses.

All these observations of basaltic glass and nuclear glass indicate that the formation of alteration minerals has a decisive influence on the kinetics. The relative importance of the solution chemistry and of physical effects related to the location of the zeolites with respect to the glass surface must therefore be investigated in greater detail.

5. Conclusions

The data summarized in this paper indicate that dedicated petrographic examination of natural basaltic glasses and leach tests conducted on synthetic glasses can shed light on the geochemical alteration mechanisms and kinetics.

Palagonite is an alteration layer surrounding basaltic glass altered by water. It consists of products that vary according to the environment, but may be classified into

two broad categories. The first is characterized by an amorphous gel, suggesting to many authors that it results from simple hydration of the glass. In other cases it consists of smectitic clay minerals, crystallized to some extent. Palagonite may form by coprecipitation of glass constituent elements that are initially solubilized, as generally observed for non-zeolitic samples usually less than a million years old. Palagonite may also form by interdiffusion processes in a residual hydrated glass: this is generally the case for zeolitic samples that are almost always more than a million years old.

Laboratory leaching experiments indicate that glass dissolution is congruent in seawater between 0 and 60 °C. The subsequent incongruence is due to the precipitation of secondary minerals. An initial selective dissolution phase has been evidenced experimentally in fresh water. In confined media, the pH becomes alkaline as a result of glass dissolution; dissolution then ceases to be selective and becomes congruent. The noteworthy point is that the dissolution rate of basaltic glass at 60 °C is practically the same in seawater and in fresh water.

The activation energies associated with the initial alteration reactions of basaltic glass and glass nuclear are identical (73–71 kJ mol⁻¹). This similarity indicates that similar mechanisms are involved during aqueous dissolution, including hydrolysis of the silicate network. Laboratory leaching experiments have also shown that the basaltic glass alteration rate diminishes very rapidly with the reaction progress. The drop in the dissolution kinetics may reach several orders of magnitude at advanced stages of reaction progress. A similar trend is observed for nuclear borosilicate glass altered under the same experimental conditions (temperature, water/glass ratio and interaction time). The protectiveness of the alteration layer could account for the drop in the alteration rate. At the same time, the chemical composition the alteration solution influences the alteration reaction processes. Measurements of the thickness of the alteration layers on volcanic glasses weathered in the natural environment (palagonites) have shown that the long-term alteration rates are very low, of the same order of magnitude as those measured in the laboratory.

A specific area that should be addressed in future work includes the measurement of the permeability of palagonite. The idea is to quantify the effectiveness of palagonite in limiting the transport of the chemical species (H₂O, H₄SiO₄^o, etc.) that kinetically activate the transformation of glass into palagonite.

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References

- [1] D.G. Brookins, *Environ. Geol.* I (1976) 225.
- [2] R.C. Ewing, M.R.S. Conference Proceedings, Scientific Basis for Nuclear Waste Management I, 1979, p. 57.
- [3] J.C. Petit, *Appl. Geochem. Supplementary Issue 1* (1992) 9.
- [4] N.A. Chapman, I.G. McKinley, A.T. Smellie Jr., The potential of natural analogues in assessing systems for deep disposal of high-level radioactive waste, Swedish Nuclear Fuel and Waste Management, Technical Report SKB 84-16, 1984, p. 103.
- [5] B. Miller, R. Alexander, N.A. Chapman, I.G. McKinley, A.T. Smellie Jr., Natural analogues revisited, Fourth International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, 1994, p. 545.
- [6] W. Miller, R. Alexander, N. Chapman, I. McKinley, S. John, *Natural Analogue Studies in the Geological Disposal of Radioactive Wastes*, Elsevier, Amsterdam, 1994.
- [7] G. Malow, R.C. Ewing, *Materials Research Society Symposium Proceedings, Scientific Basis for Nuclear Waste Management III*, 1981, p. 315.
- [8] W. Lutze, G. Malow, R.C. Ewing, M.J. Jercinovic, K. Keil, *Nature* 314 (1985) 252.
- [9] G. Malow, W. Lutze, R. Ewing, *J. Non-Crystal. Solids* 67 (1984) 305.
- [10] R.C. Ewing, M.J. Jercinovic, in: J.K. Bates, W.B. Seefeldt (Eds.), *Materials Research Society Proceedings, Scientific Basis for Nuclear Waste Management X*, vol. 84, Pittsburgh, Pennsylvania, 1987, p. 67.
- [11] W. Lutze, B. Grambow, R.C. Ewing, M.J. Jercinovic, in: B. Côme, N.A. Chapman (Eds.) and sponsored by the Commissions of the European Communities, *Proceedings Symposium on 'Natural Analogues in Radioactive Waste Disposal'*, Brussels, Graham and Trotman, Brussels, 28–30 April 1987, p. 142.
- [12] B. Grambow, W. Lutze, R.C. Ewing, L.O. Werme, in: M.J. Apted, R.E. Westerman (Eds.), *Material Research Society Proceedings, Scientific Basis for Nuclear Waste Management XI*, vol. 112, Pittsburgh, Pennsylvania, 1988, p. 531.
- [13] 'Glass as a Waste Form and Vitrification Technology: summary of an International Workshop', Board on Radioactive Waste Management, Commission on Geosciences, Environment, and Resources, National research council: National Academy of Science Press, 1996, p. 143.
- [14] I. Techer, T. Advocat, J. Lancelot, J.-M. Liotard, *J. Nucl. Mater.* 282 (2000) 40.
- [15] J.H. Thomassin, *Étude expérimentale de l'altération des verres silicatés dans l'eau douce et en milieu océanique: apports des méthodes d'analyse de surface des solides*, Thèse Doc. ès Sci., Université d'Orléans, 1984, p. 215.

- [16] J.L. Crovisier, Dissolution du verre basaltique dans l'eau de mer: approche expérimentale et thermodynamique, Doctorat d'Université, Université Louis Pasteur, Strasbourg, 1985, p. 178.
- [17] J.L. Crovisier, J.P. Eberhart, J.H. Thomassin, T. Juteau, J.C. Touray, G. Ehret, Interaction eau de mer-verre basaltique à 50 °C, Formation d'un hydroxycarbonate et de produits silicatés amorphes (Al, Mg) et mal cristallisés (Al, Fe, Mg), Étude en microscopie électronique et par spectrométrie des photoélectrons (ESCA), C.R. Acad. Sci. Paris, vol. 294(II), 1982, p. 989.
- [18] T. Murakami, R.C. Ewing, B.C. Bunker, in: M.J. Apter, R.E. Westerman (Eds.), Materials Research Society Proceedings, Scientific Basis for Nuclear Waste Management XI, vol. 112, Pittsburg, Pennsylvania, 1988, p. 737.
- [19] J.L. Crovisier, G. Ehret, J.P. Eberhart, T. Juteau, Sci. Géol. Mém. 36 (1983) 197.
- [20] J.L. Crovisier, J.H. Thomassin, T. Juteau, J.P. Eberhart, J.C. Touray, P. Baillif, Geochim. Cosmochim. Acta 47 (1983) 377.
- [21] J.L. Crovisier, B. Fritz, B. Grambow, J.P. Eberhart, Materials Research Society Conference Proceedings, Scientific Basis for Nuclear Waste Management IX, 1985, p. 273.
- [22] J.L. Crovisier, J. Honnorez, J.P. Eberhart, Geochim. Cosmochim. Acta 51 (1987) 2977.
- [23] J.L. Crovisier, H. Atassi, V. Daux, J.P. Eberhart, Hydrolyse d'un verre basaltique tholéitique à 60 °C, Dissolution sélective puis congruente par élévation du pH, Comptes Rendus-Académie des Sciences, Série II: sciences de la Terre et des Planètes, vol. 310, 1990, p. 941.
- [24] H. Atassi, Évaluation de la résistance à la corrosion en solution aqueuse de quelques verres silicatés, Thèse de l'Université Louis Pasteur, Strasbourg, 1989, p. 173.
- [25] I. Techer, Apports des analogues naturels vitreux à la validation des codes de prédiction du comportement à long terme des verres nucléaires, Thèse de l'Université de Montpellier, Université des Sciences et Techniques du Languedoc, 1999, p. 206.
- [26] I. Techer, T. Advocat, J. Lancelot, J.-M. Liotard, Chem. Geol. 176 (2001) 235.
- [27] I. Techer, J. Lancelot, N. Clauer, J.M. Liotard, T. Advocat, Geochim. Cosmochim. Acta 65 (no. 7) (2001) 1071.
- [28] S. von Waltershausen, Göttingen Studien I (1845) 371.
- [29] A. Des Cloizeaux, Manuel de Minéralogie, Dunod Ed., Paris, 1862, p. 572.
- [30] A. Penck, Zei. Deut. Geol. Ges. 31 (1879) 504.
- [31] M.A. Peacock, Geol. Mag. 67 (1930) 170.
- [32] J.L. Crovisier, Dissolution des verres basaltiques dans l'eau de mer et dans l'eau douce, Essai de modélisation, Thèse de Doctorat de l'Université Louis Pasteur de Strasbourg, 1989, p. 253.
- [33] R.L. Hay, A. Iijima, Geol. Soc. Amer. Mem. 116 (1968) 331.
- [34] M.N. Bass, in: R.S. Yeats et al. (Eds.), Initial Report. D.S.D.P., vol. 34, US Government Printing Office, 1976, p. 392.
- [35] C. Mevel, Initial Report DSDP, vol. LI, LII, LIII, US Government Printing Office, 1980, p. 1299.
- [36] J.K. Bohlke, J. Honnorez, B.M. Honnorez-Guerstein, Contrib. Mineral. Petrol. 73 (1980) 341.
- [37] J.K. Bohlke, J. Honnorez, B.M. Honnorez-Guerstein, K. Muehlenbachs, N. Petersen, J. Geophys. Res. 86 (1981) 7935.
- [38] J.K. Bohlke, J.C. Alt, K. Muehlenbachs, Can. J. Earth Sci. 21 (1984) 67.
- [39] Y. Noack, Bull. Minéral. 104 (1981) 36.
- [40] J.C. Alt, J. Honnorez, Contrib. Mineral. Petrol. 87 (1984) 149.
- [41] M.J. Jercinovic, R.C. Ewing, Swedish Nuclear Fuel and Waste Management, JSS Report 88-01, 1987, p. 221.
- [42] I.H. Thorseth, H. Furnes, O. Tumyr, Geochim. Cosmochim. Acta 55 (3) (1991) 731.
- [43] X. Le Gal, Étude de l'altération de verres volcaniques du Vatnajökull (Islande), Mécanismes et bilans à basse température, Thèse de l'Université Louis Pasteur, Strasbourg, 1999, p. 153.
- [44] X. Le Gal, J.-L. Crovisier, F. Gauthier-Lafaye, J. Honnorez, B. Grambow, Comptes Rendus de l'Académie de Sciences Paris – Série IIa: Sciences de la Terre et des Planètes 329 (1999) 175.
- [45] J. Honnorez, La palagonitisation: l'altération sous marine du verre volcanique basique de Palagonia (Sicile), Vulkaninstitut Immanuel Friedlaender, Birkhäuser Verlag Ed., 1972, p. 131.
- [46] J. Honnorez, in: S.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites, Occurrence, Properties, Use, Pergamon, 1978, p. 245.
- [47] M. Fieldes, I. Walker, P.P. Williams, New Zeal. J. Sci. Technol. 38 (1956) 31.
- [48] A. Singer, Clays Clay Minerals 22 (1974) 231.
- [49] S.I. Wada, C. Mizota, Clays Clay Minerals 30 (1982) 315.
- [50] G. Berger, J. Schott, M. Loubet, Earth Planet. Sci. Lett. 84 (1987) 431.
- [51] R.A. Eggleton, J. Keller, N. Jb. Miner. Mh. H. 7 (1982) 321.
- [52] D.H. Matthews, Nature 194 (1962) 368.
- [53] R.Y. Nayudu, Bull. Volcanologique 27 (1964) 391.
- [54] J. Honnorez, La palagonitisation: l'altération sous marine du verre volcanique basique de Palagonia (Sicile), Thèse de Doctorat, Université Libre de Bruxelles, 1967, p. 227.
- [55] K.R. Stockes, Mineral. Mag. 38 (1971) 205.
- [56] K.V. Summers, Amer. Mineral. 61 (1976) 492.
- [57] Y. Noack, Altération sous marine des verres volcaniques basiques, Essai sur la palagonitisation, Thèse Doc. Spéc., Université Louis Pasteur, Strasbourg, 1979, p. 95.
- [58] Y. Noack, J.L. Crovisier, Bull. Minéral. 103 (1980) 523.
- [59] M. Morgenstein, T.J. Riley, Asian Perspect. 17 (1974) 145.
- [60] R.R. Marshall, Geol. Soc. Amer. Bull. (72) (1961) 1493.
- [61] I. Friedman, A.L. Smith, W.D. Long, Geol. Soc. Amer. Bull. 77 (1966) 323.
- [62] E. Bonatti, Bull. Volc. 28 (1965) 257.
- [63] R. Hekinian, M. Hoffert, Mar. Geol. 19 (1975) 91.
- [64] G.P.L. Walker, D.H. Blake, Quat. J. Geol. Soc. Lond. 122 (1966) 45.
- [65] J.G. Moore, Amer. J. Sci. 263 (1965) 40.
- [66] G.D. Nicholls, Min. Mag. 34 (1965) 373.
- [67] A. Miyashiro, F. Shido, M. Ewing, Contrib. Mineral. Petrol. 23 (1969) 38.
- [68] S.P. Jakobsson, Surtsey Prog. Rep. VI (1972) 1.

- [69] S.P. Jakobsson, Bull. Geol. Soc. Denmark 27 (1978) 91.
- [70] J. Trichet, Contribution à l'étude de l'altération expérimentale des verres volcaniques, Thèse Doc. ès Sci., École Normale Supérieure de Paris, 1970, p. 152.
- [71] H. Staudigel, S.R. Hart, Geochim. Cosmochim. Acta 47 (1983) 337.
- [72] J. Honnorez, private communication.
- [73] W.G. Melson, G. Thompson, Geol. Soc. Amer. Bull. 84 (1973) 703.
- [74] G.D. Garlick, J.R. Dymond, Geol. Soc. Amer. Bull. 81 (1970) 2142.
- [75] J.H. Thomassin, P. Baillif, J.C. Touray, Sci. Géol. Bull. 36 (1983) 173.
- [76] J.H. Thomassin, P. Baillif, J.C. Touray, Sci. Géol. Bull. 36 (1983) 165.
- [77] J.H. Thomassin, J.L. Crovisier, J.C. Touray, T. Juteau, F. Boutonnat, Bull. Soc. Géol. France 1 (1985) 217.
- [78] J.H. Thomassin, J.C. Touray, Bull. Minéral. 102 (1979) 594.
- [79] J.H. Thomassin, J.C. Touray, Bull. Minéral. 105 (1982) 312.
- [80] A. Decarreau, Bulletin de la Société Française de Minéralogie et Cristallographie 100 (1977) 289.
- [81] H. Atassi, Étude du mode de dissolution du verre basaltique dans l'eau à 60 °C, Diplôme d'Études Approfondies, École Nationale Supérieure de Chimie de Mulhouse., 1986, p. 29.
- [82] J.L. Crovisier, H. Atassi, V. Daux, J. Honnorez, J.C. Petit, J.P. Eberhart, M.R.S. Conference Proceedings, Scientific Basis for Nuclear Waste Management XII, 1988, p. 41.
- [83] S.R. Gislason, H.P. Eugster, Geochim. Cosmochim. Acta 51 (10) (1987) 2827.
- [84] C. Guy, Mécanismes de dissolution des solides dans les solutions hydrothermales déduits du comportement de verres basaltiques et de calcites déformées, Thèse de Doctorat de l'Université Paul Sabatier, Toulouse, 1989, p. 188.
- [85] C. Guy, J. Schott, Chem. Geol. 78 (1989) 181.
- [86] G. Berger, C. Claparols, C. Guy, V. Daux, Geochim. Cosmochim. Acta 58 (22) (1994).
- [87] B. Grambow, M.J. Jercinovic, R.C. Ewing, C.D. Byers, Materials Research Society Conference Proceedings, Scientific Basis for Nuclear Waste Management, IX, vol. 50, 1985, p. 263.
- [88] V. Daux, C. Guy, T. Advocat, J.-L. Crovisier, P. Stille, Chem. Geol. 142 (1997) 109.
- [89] B. Grambow, Mater. Res. Soc. Symp. Proc. 44 (1985) 15.
- [90] V. Blet, D. Rudloff, P. Berne, P. Jollivet, D.A. Schweich, Chem. Eng. Sci. 57 (2002) 3427.
- [91] N. Valle, Traçage isotopique (^{29}Si et ^{18}O) des mécanismes de l'altération du verre de confinement des déchets nucléaires SON68», Thèse de Doctorat, Université de Nancy, 2000, p. 260.
- [92] C.D. Byers, R.C. Ewing, M.J. Jercinovic, Adv. Ceram. 20 (1987) 733.
- [93] M.J. Jercinovic, K. Keil, M.R. Smith, R.A. Schmitt, Geochim. Cosmochim. Acta 54 (1990) 2679.
- [94] H. Furnes, Chem. Geol. 22 (1978) 249.
- [95] S.P. Jakobsson, J.G. Moore, Geol. Soc. Amer. Bull. 97 (1986) 648.
- [96] P. Jollivet, Y. Minet, M. Nicolas, Domaine de validité de la modélisation de l'altération du verre R7T7. Université d'été CEA Valrho, Le verre, recherche scientifique pour un confinement de haute performance, Méjannes Le Clap, 1997, p. 336.
- [97] P. Jollivet, M. Nicolas, E. Vernaz, Nucl. Technol. 123 (1998) 37.
- [98] J.L. Crovisier, J. Honnorez, B. Fritz, J.C. Petit, Appl. Geochem. Supplement 1 (1992) 55.
- [99] P. VanIseghem, B. Grambow, Materials Research Society Conference Proceedings, Scientific Basis for Nuclear Waste Management XI, 1988.
- [100] D. Strachan, J. Nucl. Mater. 298 (2001) 69.