Simulation of alteration gel formation on simplified glasses by the geochemical model kindis.

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Within the framework of European program GLASTAB, an experimental study of alteration in aqueous phase of two simplified glasses, similar to R7T7 glass, was undertaken in parallel to an attempt of modelling the processes observed. Two glasses (Si-Al-B-Na and Si-Al-B-Na-Ca-Zr) were placed at 90°C in pure water with two different S/V ratios (1 and 80 cm^{-1}) for lengths of time spreading out between 30 and 180 days. The solutions obtained were then analyzed as well as the alteration gels forms observed on glass surfaces. The processes of glass alteration under these experimental conditions were modelled using the geochemical code KINDIS. The formation of the alteration gel was represented in KINDIS by the way of precipitation of a an ideal solid solution. The cases of oxides, hydroxides and metasilicate as end members was tested. In all the cases, the considered solid solution always contains a siliceous end-member SiO_2. This end-member may consists of amorphous silica, chalcedony or quartz. It is to note that the choice of the end-members of the selected solid solution is essential during simulation. Indeed the relative thermodynamic stability of these end-members influences directly the composition of formed gel and thus the composition of the simulated solution. The results obtained show a good agreement between the experimental and modelled silicon contents in solution, whatever the S/V ratio.

Introduction

The question of the long-term storage of nuclear waste has greatly stimulated the study of glass weathering. The researches moved first toward the study of glasses considered as natural analogues of nuclear glasses (basalt glasses essentially)[12345]. In the same time, the study of dissolution mechanism of the R7T7 borosilicate (SON68) glass, used as the French confinement matrix for the light water reactor (LWR) nuclear waste, developed[167].

The dissolution process of these glasses is very similar and can be decomposed into three successive phases. First, an ion exchange process which leads to the release of alkali metal and alkaline earth cations and to the formation of a leached and hydrated layer. Simultaneously the glass network hydrolyzes. Then, secondary alteration products (amorphous gel and mineral phases) form[12788910111213].

These studies led to the necessity of using mathematical model for simulating long-term glass alteration. The development of geochemical models helped widely the simulation of the alteration products formation during glass dissolution. Applied to basaltic and nuclear glasses, these models (EQ3/6, GLASSOL, KINDIS…) allow to simulate the sequence of precipitation of minerals[214151617]. But, they do not consider the formation of the amorphous alteration gel.

The aim of this study is to simulate the dissolution of glass with the geochemical model KINDIS by taking into account the incidence of the formation of the alteration gel by precipitation of a solid solution on the chemical composition of the solution.

Experimental procedure

Two simplified glasses (details of glass making are reported in Jégou[18] and their chemical composition in Table 1) having a chemical composition corresponding to the elemental molar ratios of the French SON68 nuclear glass were altered in static conditions, in pure water at 90°C (± 1°C) during 30, 60, 90, 120, 150 and 180 days. Two sets of experiments were carried out with two Surface area of glass/Volume of solution (S/V) ratios: 1 cm^{-1} and 80 cm^{-1}.

Boron and silicon concentrations in solution were analysed by Colorimetry (Technicon Autoanalyser II). Al, Na, Ca and Zr were analysed by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES, Jobin-Yvon JY 124). The glass samples were observed by Analytical Scanning Electron Microscopy (ASEM, JEOL JSM 804 link with an EDS detector Tracor TN 5500).

Experimental results

The pH values of the glass 1 leachates at 1 and 80 cm^{-1} stabilised after 60 days around 9, probably due to the buffer effect of boron. These final values were a little higher in the case of experiments at S/V = 80 cm^{-1} as it was often reported. These differences could be likely to be due to high ion exchange in the case of high S/V ratio. Concentrations of B and Na increased regularly in solution. Si and Al concentrations presented similar behaviours according to the S/V ratio: they increased and then stabilized after 90 days for S/V ratio of 1 cm^{-1} and after 60 days for S/V = 80 cm^{-1}. The normalized mass loss of glasses elements were plotted on Fig. 1-a and 1-b. B was released preferentially. Si and Al had a congruent release at 1 cm^{-1}, but at 80 cm^{-1}, Si was preferentially leached from the glass.

The pH of the glass 2 leachates at 1 and 80 cm^{-1} had the same evolution as for the glass 1. Concentrations of B, Na and Ca increased regularly in solution for S/V = 80 cm^{-1} and remained constant after 60 days for S/V = 1 cm^{-1}. Si and Al concentrations remained constant after 30 days, whatever the S/V ratio values. Zr concentrations remained globally constant at 80 cm^{-1} and varied highly at 1 cm^{-1}. The normalized mass losses of glass 2 elements were plotted on Fig. 1-c and 1-d. Elements behaviours were very different according to the S/V ratio. B was preferentially released at 80 cm^{-1} and dissolved congruently with Na at 1 cm^{-1}. Al, Ca and Zr were little liberated.

The direct observation of the surface of altered glasses by ASEM showed the presence of an alteration layer, whatever the glass or the S/V ratio. This layer seemed to be formed to the detriment of glass but without total dissolution of this last since the initial surface was preserved and traces of polishing were perfectly observed, even after 180 days.

Discussion and conclusion

Silicon content in solution has been widely considered as the main factor influencing the dissolution rate of nuclear glasses in solution. When considering the affinity of the glass dissolution reaction, silicon concentration in solution is determined by the amount of dissolved glass and by the formation of silicated secondary products, having reached their solubility limit. The thermodynamic stability of these products may thus have a great influence on silicon concentration in solution.

In order to measure the incidence of the thermodynamic stability of siliceous secondary products, three different siliceous end-members constituting the solid solution representing the alteration gel have been tested. On Fig. 2-a and -b, were plotted the three simulated curves corresponding to the three tested siliceous end-members: amorphous silica (the less thermodynamically stable), quartz (the most stable) and chalcedony (of medium stability), for both glasses considered. The other end-members are constituted by $Al(OH)_3$, NaOH, $Ca(OH)_2$ or $Zr(OH)_4$. Very similar curves (not shown) were obtained by using other end-members (metasilicates and oxides).The experimental values were represented by empty marks. On this Fig. 2, the reaction progress corresponds to boron concentration in solution, since it increases with the alteration time without being reincorporated in secondary products.

The simulated curves render the thermodynamic stability of the siliceous pole since more the end-member is stable, more the gel is stable and lower is the silicon content in solution. The relative stability of the end-members is amorphous silica > chalcedony > quartz and thus the silicon concentration in solution follows the same order, whatever the glass dissolution simulated.

For the glass 1 (Fig. 2-a), the best agreement was obtained for quartz and chalcedony at 1 cm^{-1}. At 80 cm^{-1}, the experimental values are slightly higher than those simulated by chalcedony as end-member. Concerning the glass 2 (Fig. 2-b), most of experimental values were located just above the simulated curve by chalcedony.

For the simplest glass, silicon concentration in solution stabilized close to the curve simulated with quartz when the S/V ratio is small whereas, at high S/V ratio, it stabilized above chalcedony curve. The alteration of the glass 2, which has a more complex composition, led to silicon concentration close to but slightly higher than the one obtained with chalcedony simulation, whatever the S/V ratio.

On Fig. 2 were also reported simulated curves obtained when no solid solution can form and which thus correspond only to the increase of silicon concentration in solution due to glass dissolution. When the glass dissolves without the formation of minerals or gel, silicon concentration in solution increases sharply and the difference in concentration, corresponding to simulation with and without alteration gel formation, can exceed one order of magnitude, especially at high S/V ratio. Therefore, these curves indicate the fundamental incidence of the gel formation on the evolution of silicon concentration in solution.

These results illustrate the complexity of phenomena[19], which can take place when the S/V ratio varies (glass 1) but they also show that it is clearly possible to reproduce with a good agreement the experimental silicon concentrations by using a solid solution model to simulate the gel formation. Beside, this gel is simulated by a solid solution using only thermodynamic data coming from literature (i. e. not fitted). Furthermore, it is fundamental to note that the agreement between experiments and simulation justify the description of the alteration gel in simulation by considering a total dissolution process followed by an in-situ precipitation of the gel at equilibrium with the solution.

	B_2O_3	Al_2O_3	SiO_2	Na_2O	CaO	ZrO_2
Glass 1	18.90	6.61	61.22	13.27	-	-
Glass 2	17.34	6.06	56.18	12.17	4.98	3.28

TABLE 1: Theoretical composition of the two studied glasses in % weight oxides.

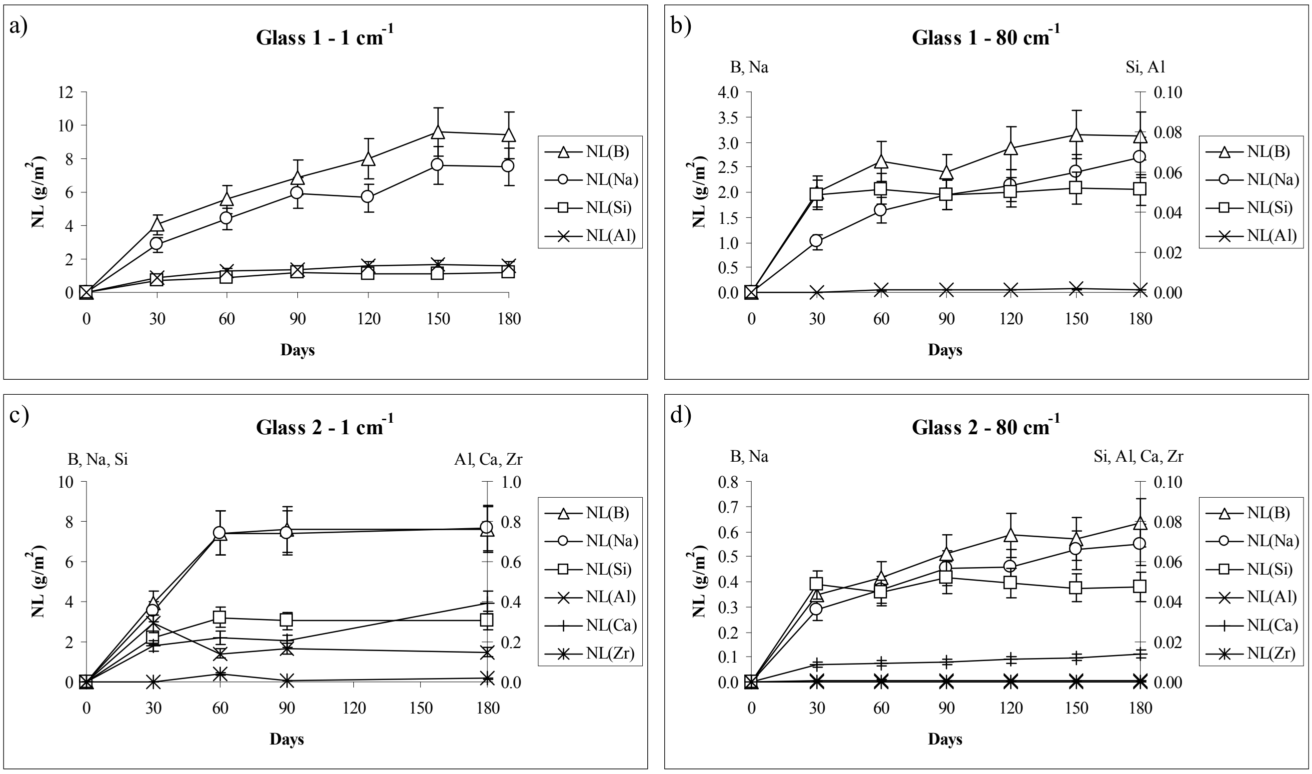

FIG. 1: Normalized mass loss (g/m^2) versus time of elements liberated by glasses alteration in pure water at 90°C (a and b: glass 1, c and d: glass 2) (error: 15%).

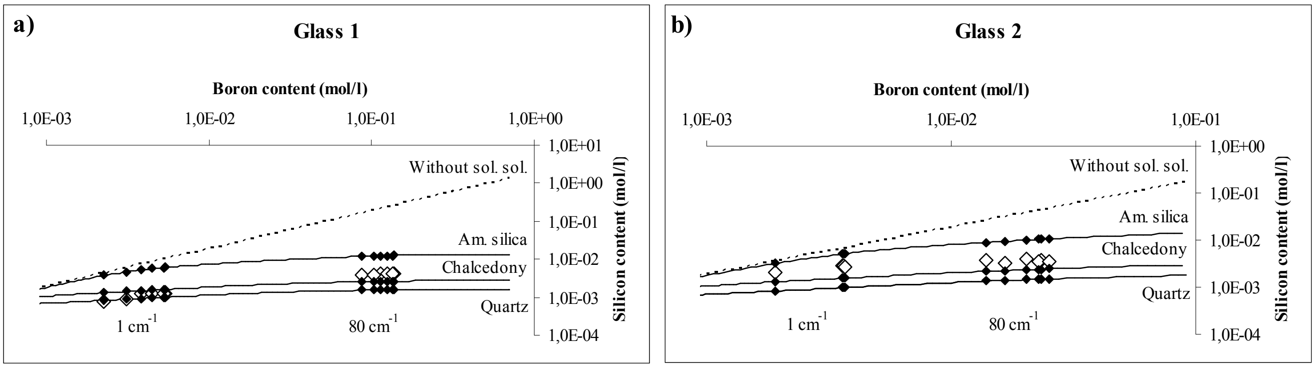

FIG. 2: Silicon content versus boron content in solution (mol/l). Experimental values (empty mark) and simulated values (solid mark) with a solid solution having amorphous silica, chalcedony or quartz as siliceous end-member and hydroxides as other end-members (a): glass 1 and b): glass 2).

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