



Impact of iron and magnesium on glass alteration: Characterization of the secondary phases and determination of their solubility constants



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ABSTRACT

In this study, the effects of iron and magnesium on International Simple Glass (ISG) alteration were studied throughout 511 days of aqueous leaching experiments. The aim was to determine by thorough characterization, the nature of the alteration products that control glass alteration. Iron and magnesium were added separately or together in solution as FeCl₂ and MgCl₂ salts, with monthly additions to compensate for their consumption. The alteration degree was determined by leachate analyses (ICP-AES) and the alteration products composition, morphology and microstructure were characterized (SEM, TEM-EDX and XRD).

The results indicated that magnesium and iron increase glass alteration, forming tri-octahedral smectites with the same (Fe + Mg)/Si ratio. With iron, two kinds of silicates precipitate with the same composition but with a different morphology, whereas with magnesium alone, a single Mg-silicate forms. Moreover, it was found that the glass alteration rate drops when the pH stabilizes at a minimum value of 7.8 for Mg-silicates and 6.2 for Fe-silicates. At this point the secondary silicates stop precipitating. This result was confirmed by geochemical simulation and the solubility product of these silicates was estimated considering the presence or absence of aluminum in their structure.

Finally, a two-step process was proposed to explain the location of the secondary phase precipitation: firstly in solution and at the solution/gel interface, and secondly in a highly porous upper zone of the gel.

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1. Introduction

Glass alteration is driven by several processes involving several stages (Frugier et al., 2008). During the first stage, water penetration through the glass leads to network hydration and interdiffusion, inducing ion exchange between protons from the solution and alkalis from the glass. Concomitantly, hydrolysis of the glass covalent bonds occurs at a maximum rate. The glass surface thus consists of a layer of hydrated glass (Geneste et al., 2006; Rébiscoul et al., 2007) whose thickness depends on the rates of the water penetration and of the glass network hydrolysis. The first stage is followed by a rate drop due to two processes: (i) a decrease in network hydrolysis due to the increase in solution of silicon and aluminum concentrations as they are released from the glass, and

(ii) the formation of a gel layer at the hydrated glass/solution interface by the recondensation of several dissolved elements released from the glass (Si, Al, etc.). Depending on its composition and its porosity, this hydrated nanoporous material has protective properties influencing the transport of the elements coming from the glass (Cailleteau et al., 2008; Gin et al., 2013b, 2015a; Rébiscoul et al., 2005). Finally, in the third stage, the alteration rate is controlled by the reactive diffusion of species from the glass and the solution through the hydrated glass and the gel, and also by the precipitation of secondary phases. During their formation, these secondary phases consume elements from the solution and from the gel, particularly silicon and aluminum, leading to a decrease in the gel protective properties (Aréna et al., 2016; Crovisier et al., 2003; Frugier et al., 2008). In special conditions, with high pH

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(>10.7 measured at 20 °C) or high temperatures (>90 °C), zeolites and Hydrated-Calcium-Silicates can precipitate, triggering a sudden resumption of glass alteration (Fournier et al., 2014).

Numerous studies conducted on glass alteration over the last 50 years have indicated that the chemical elements present either in the glass or in its environment can impact the glass alteration stages described above (Aréna et al., 2016; Burger et al., 2013; Chave et al., 2011; Curti et al., 2006; Debure et al., 2012a, b; Dillmann et al., 2016; Fleury et al., 2013; Mercado-Depierre et al., 2013; Michelin et al., 2013b; Rebiscoul et al., 2015; Thien et al., 2012). For nuclear glasses that are intended for disposal in a deep geological repository, the groundwater composition may influence glass alteration. Groundwater is expected to be charged with both magnesium, from the clay host rock, and iron generated by the corrosion of the metallic materials involved in the multi-barrier repository concept (ANDRA, 2006).

The effects of iron and magnesium on glass alteration have already been studied separately or together, but in complex media. Magnesium usually participates in the formation of secondary phases, leading to an increase in glass alteration (Abdelouas et al., 1997; Curti et al., 2006; Debure et al., 2012a, b; Fleury et al., 2013; Grambow and Muller, 1990; Maeda et al., 2011; Strachan, 1983; Thien et al., 2010a, 2012). Former studies indicate the precipitation of trioctahedral smectites such as hectorite and saponite (Curti et al., 2006; Debure et al., 2016; Thien et al., 2010b). Using geochemical modeling, Debure et al. determined thermodynamic constants consistent with those available for magnesium and sodium saponites in the existing thermodynamic databases (Debure et al., 2016). However, depending on the glass composition and the alteration conditions, magnesium can also be integrated into the gel (Barkatt et al., 1989; Feng, 1994; Grambow and Strachan, 1984; Thien et al., 2012) making it more protective. In this case, it has the same effect that calcium whose behavior has been precisely studied by several authors (Chave et al., 2011; Mercado-Depierre et al., 2013). When a glass with a lack of charge compensating elements is altered in a solution containing both magnesium and calcium, calcium is preferentially integrated into the gel (Debure et al., 2012b).

Iron usually increases glass alteration by forming secondary phases and making the gel less protective (de Combarieu et al., 2011; Grambow et al., 1987; Bjorner et al., 1988; Inagaki et al., 1996; Kim et al., 1997; Luo et al., 1995; McVay and Buckwalter, 1983; Shade et al., 1984; Werme et al., 1990). Therefore, iron can also be integrated into the gel pores as amorphous oxyhydroxides or as ferrosilicates (Parruzot, 2014; Pélegrin et al., 2010) (Burger et al., 2013; Dillmann et al., 2016; Michelin et al., 2013a). These precipitations could have two opposite effects: enhancing glass alteration by silicon consumption or slowing it down by porosity clogging.

Despite all of these results, the nature of the secondary phases, their properties and the processes involved in their precipitation have not yet been thoroughly studied, especially to assess the long term behavior of nuclear glasses in geological repositories.

Using an experimental method similar to that already published in Aréna et al. (2016) investigating the effects of zinc, magnesium, nickel and cobalt on glass alteration, this study determined the effects of iron and magnesium on the alteration processes and on the alteration products, when added separately and when combined.

To determine the processes occurring during glass alteration, the solutions were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and the solids were characterized using Scanning and Transmission Electron Microscopy (SEM, TEM), Energy-Dispersive X-ray (EDX) and X-ray Diffraction (XRD).

2. Materials and methods

2.1. Leaching experiments

International Simple Glass (ISG), a six-oxide glass based on the French SON68 inactive reference glass composition and currently used for studies in different countries (Table 1), was chosen for reasons described in detail in Gin et al. (2013a). Firstly, it has the same elemental ratio as the reference glass SON68 and similar dissolution rates at the various stages of alteration. Moreover, its simple composition makes the phenomenology easier to understand. Secondly, even after 14 years of alteration in static conditions (90 °C, free pH, SA/V = 10 m⁻¹) there was no detectable precipitation of secondary silicate phases (Gin et al., 2012). This should therefore mean a better determination of the effects of magnesium and iron.

An ISG glass rod from a 50 kg international batch (Gin et al., 2013a) was ground and sieved to recover the 40–63 µm size grain fraction. Monolithic glass slices were also cut to perform surface analyses. The composition of ISG glass is given in Table 1.

The glass powder was cleaned several times by sedimentation in acetone and ethanol to remove the fine particles remaining on the surface. The specific surface area of the powder was measured by krypton adsorption-desorption according to the Brunauer–Emmett–Teller (BET) model and was 1060 g m⁻² (2.2 times the geometrical surface determined with the average radius of the grains).

Static glass alteration tests were performed in PTFE reactors with a glass surface area to solution volume ratio (S/V) of 20,000 m⁻¹ at 50 °C and free pH for 511 days. Experiments involving iron (F and MF) were conducted in an anoxic environment (nitrogen glove box) and with degassed water (argon bubbling during 2 h). Glass powder was mixed with Teflon chips to disperse the grains and to prevent the formation of a crust made of secondary phases that could have created various different local conditions within the system. Iron and/or magnesium were brought in contact with the glass by monthly additions of chloride salts (Normapure prolabo FeCl₂ and MgCl₂) to the leaching solution. Each month, a total volume of 1.5 mL of solution was sampled to perform analyses and to determine the concentration of iron and/or magnesium left in the leachate. Until day 183, samples were collected twice a month and then only once after day 183, at the end of the month. In order to compensate for the iron and/or magnesium consumption and the evaporation, additions of concentrated (Fe, Mg)Cl₂ solutions and pure water were made once a month, two days after the previous sampling, once analyses were available. In all experiments, the renewal was approximately 15% vol/year.

Mono-elemental experiments were designed to monitor the separate effects of magnesium and iron with a concentration of 1.10⁻² mol.L⁻¹ in solution. This concentration was chosen to be in the same range as that expected for magnesium in groundwater. A multi-elemental experiment was also performed with a concentration of 5.10⁻³ mol.L⁻¹ of magnesium and iron to determine if their effects would be the same when added simultaneously. Thus, the total concentration of Mg + Fe was the same in the multi-elemental experiment as in the mono-elemental runs. The names

Table 1
Composition of the ISG in weight percentage.

Oxide	Na ₂ O	CaO	SiO ₂	B ₂ O ₃	Al ₂ O ₃	ZrO ₂
%wt	12.2	5.0	56.2	17.3	6.0	3.3

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