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Investigation of local environment around rare earths (La and Eu) by fluorescence line narrowing during borosilicate glass alteration

Estelle Molières [a], Gérard Panczer [b], Yannick Guyot [b], Patrick Jollivet [a], Odile Majérus [c], Patrick Aschehoug [c], Philippe Barboux [c], Stéphane Gin [a], Frédéric Angeli [a,*]

[a] CEA – DEN-DTCD-LCV-SECM Laboratoire d'études du Comportement à Long Terme, 30207 Bagnols-sur-Cèze, France
[b] Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex, France
[c] Laboratoire de Chimie de la Matière Condensée de Paris, UMR-CNRS 7574, École Nationale Supérieure de Chimie de Paris (ENSCP Chimie-ParisTech), 11 rue Pierre et Marie Curie, 75231 Paris, France

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ABSTRACT

The local environment of europium in soda-lime borosilicate glasses with a range of La_2O_3 content was probed by continuous luminescence and Fluorescence Line Narrowing (FLN) to investigate the local environment of rare earth elements in pristine and leached glass. After aqueous leaching at 90 °C at pH 7 and 9.5, rare earths were fully retained and homogeneously distributed in the amorphous alteration layer (commonly called gel). Two separate silicate environments were observed in pristine and leached glasses regardless of the lanthanum content and the leaching conditions. A borate environment surrounding europium was not observed in pristine and leached glasses. During glass alteration, OH groups were located around the europium environment, which became more organized (higher symmetry) in the first coordination shell.

1. Introduction

In recent years, rare earth-doped glasses have been extensively investigated because of their wide range of applications. They are used in optical devices such as lasers, fiber amplifiers, and waveguides [1]. Depending on the nature and concentration of the rare earth elements, the optical properties may be dramatically modified [2]. For example, clustering may be very detrimental for these applications [3]. In France, high-level nuclear wastes are vitrified in borosilicate glass matrices. These wastes include fission products (FP) and minor actinides, which may be simulated by rare earth (RE) surrogates [4]. In the case of glass storage in geological disposal conditions, groundwater is expected to interact with the glassy matrices. During alteration, some soluble elements such as lithium, sodium or boron may be released from the matrices and others retained by an altered layer formed by silicon recondensation [5,6].

The incorporation limit of rare earth ions in glass depends largely on the glass composition and structure. In silica glass, the low solubility of rare earths strongly favors clustering. Their incorporation may be enhanced by adding Al_2O_3 or Na_2O [7]. Recent molecular dynamics simulations have shown that sodium creates openings in the silica network and favors the incorporation of rare earths in an area rich in non-bridging oxygen (NBO) [8]. In the same way, depending on its concentration, aluminum oxide breaks up rare earths clusters by forming bonds with aluminum or silicon (RE–O–Si/Al) instead of RE–O–RE bonds, indicating the incorporation of RE–O coordination polyhedra in the aluminosilicate network [7,9]. Adding RE in borate glasses is trickier: only glass compositions close to Ln_2O_3–$3B_2O_3$ (Ln = La, Pr, Nd, and Sm) can be vitrified [11]. In this case, rare earths are mainly found in metaborate phases: the chains are composed of BO_3 and BO_4 units in a 2:1 ratio and are interconnected by rare earth ions, themselves approximately coordinated by 10 oxygen atoms [10–13]. In borosilicate glasses, the rare earth environment may be strongly modified depending on the Na_2O/B_2O_3 and SiO_2/B_2O_3 ratios from which borosilicate network may be homogeneously distributed or phase separated [14–17].

Previous studies have shown that the rare earths and minor actinides were fully retained in the alteration layer formed during glass leaching [18]. This retention is related to the alteration conditions (static or dynamic, solution pH) and glass composition: rare earths may be retained homogeneously or precipitated at the surface of the altered layer [18–22]. As a consequence, the local environment of rare earths is affected by leaching.

Rare earth environments have been probed by several complementary techniques such as X-ray absorption spectroscopy (EXAFS) [7,23,24], neutron diffraction [25,26] or fluorescence

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[*] Corresponding author. Tel.: +33 466791876.
E-mail address: frederic.angeli@cea.fr (F. Angeli).

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[27–31]. EXAFS provides information such as the coordination number and bond lengths with the first and second neighbors. Neodymium is surrounded by seven or eight oxygen atoms in silica and sodium-silicate glasses, respectively [7]. The rare earth environment in complex borosilicate glasses of nuclear interest involving nine oxides was also probed by EXAFS before and after leaching. It was shown that local environment of Ce, La or Nd was mainly silicate in pristine glasses. After leaching under dynamic conditions, the local environment of rare earth was slightly modified. Hydroxycarbonate, oxyhydroxide and silicate environments could coexist depending on the rare earth element [32,33]. The europium environment was also probed by luminescence. The europium(III) ion is often used as structural probe in luminescence because of its unique energy level structure and the singlet-to-singlet nature of the $^5D_0 \rightarrow ^7F_0$ transition [34]. While EXAFS cannot discriminate between neighbors with close atomic numbers, europium luminescence can, especially when neighbors induce distinct crystal fields parameters on the RE center. Luminescence is also more sensitive to the number of distinct sites (which may be not resolved by EXAFS) and to the site symmetry.

In aluminoborosilicate glasses, europium was located in two different sites: silicate and aluminoborate in the pristine glass and silicate and aluminate in the altered glasses [35,36]. An aluminoborate site was suggested, however, due to the superposition of the crystal field parameters of the borate and aluminate environment. Therefore, aluminum was removed from the studied glass compositions. These compositions were chosen to have SiO_2/B_2O_3 and Na_2O/B_2O_3 ratios representative of that found in nuclear waste containment glasses. According to models of the borosilicate glass structure [14–16], the borosilicate glass network is homogeneous in these compositions. The aim of this study is to determine the environments of rare earths in these simple glasses, and whether or not rare earths have distinct distributions of sites discriminated by the nature of their second neighbors (boron or silicon). These structural features may have consequences on the behavior of rare earths during the glass alteration and generally have interest for the formulation of rare earths bearing borosilicate glasses.

Samples studied in this paper are more complex than crystalline materials generally studied for their fluorescence properties. In this study the challenge will be to use FLN to obtain complementary structural information taking advantage of the optical properties of complex amorphous materials such as borosilicate glasses and their alterated products.

The local environment of europium in borosilicate glass containing various amounts of lanthanum was investigated using europium fluorescence (continuous and Fluorescence Line Narrowing, FLN): $(60-x)SiO_2$–$18B_2O_3$–$18Na_2O$–$4CaO$–$(x-0.15)La_2O_3$–$0.15Eu_2O_3$ (where $x=0$, 2, 4, 8, and 12). Europium was then used to probe the lanthanum local environment, since both rare earths have the same structural behavior. Compositions were chosen to avoid site superimposition as previously observed for aluminate and borate environments [35,36]. Glass samples were leached in water at pH 7 (the pH of a typical clayey groundwater [37]) and at pH 9.5 (representing the equilibrium pH reached during borosilicate glass alteration [38]). Glass leaching was carried out in static mode (without solution renewal). Soluble elements (boron and sodium) were fully released, meaning that glasses were entirely altered. Altered glasses have an unclear structure but RE were fully retained in the gel recondensation layer, allowing their local environment to be examined by fluorescence.

2. Experimental setup

Glasses with molar compositions $(60-x)SiO_2$–$18B_2O_3$–$18Na_2O$–$4CaO$–$(x-0.15)La_2O_3$–$0.15Eu_2O_3$ (where $x=0$, 2, 4, 8, and 12) were synthesized by melting appropriate amounts of analytical grade H_3BO_3, SiO_2, Na_2CO_3, CaO, La_2O_3, and Eu_2O_3. Mixed powders were decarbonated for 1 h at 700 °C and melted for 3 h at 1300 °C. The glasses were quenched and crushed before a second melting for 2 h at 1300 °C to ensure homogeneity. Weight loss indicated that volatility was not significant and the glass compositions were checked by ICP after alkaline fusion. Glasses are labeled *x*La, where *x* corresponds to the molar percentage of La_2O_3. A soda-lime silicate glass was also synthesized for use as a reference, and a glass with 4 mol% Eu_2O_3 (4 Eu) was also used to check that the La environment can be probed directly with Eu if 4La and 4 Eu exhibit the same behavior. Analyzed compositions of the pristine and altered glasses (or "gel") are shown in Table 1.

Glasses were leached using only the glass powder fraction between 5 and 10 μm; since fluorescence does not only probe the surface, complete glass alteration is necessary (without a pristine glass core) in order to characterize only the gel layer. Leaching was performed at 90 °C in static mode in Teflon® reactors. The glass surface area to solution volume ratio was 1500 m^{-1}. Solutions were prepared from deionized water, then adjusted to pH 7 (buffered with Tris(hydroxymethyl)aminomethane-HNO_3) and to pH 9.5 (KOH). The percentage of alteration was calculated from elemental analysis of the leachates by ICP-AES (boron and sodium were used as tracers of glass alteration). Each experiment was stopped when all boron and/or sodium initially present in the glass sample was dissolved (i.e. after approximately 3 months). In addition, the silicon retention factor (*RF*) in the alteration layer is calculated

$$RF = 1 - \left(\frac{NL_i}{NL_{tracer}}\right) \quad (1)$$

where the element tracer is boron (at pH 9.5) or sodium (at pH 7) and *NL* is the normalized mass loss. The tracer depended on the solution pH because it was observed at pH 7 that sodium is released slightly faster than boron. Normalized mass losses (*NL*) are expressed as

$$NL_i(\mathrm{g\ m^{-2}}) = \frac{[C_i](\mathrm{mg\ L^{-1}})}{x_i \times (S/V)(\mathrm{m^{-1}})} \quad (2)$$

Table 1
Theoretical composition of the pristine glass and gel composition deduced by the leachate analysis (mol%).

Pristine glasses	**0La**	**2La**	**4La**	**8La**	**12La**	**Soda-lime silicate**	**4Eu**
SiO_2	60	58	56	52	48	69.4	56
B_2O_3	18	18	18	18	18	–	18
Na_2O	18	18	18	18	18	22.2	18
CaO	4	4	4	4	4	8.0	4
Eu_2O_3	0.15	0.15	0.15	0.15	0.15	0.4	4
La_2O_3	–	1.85	3.85	7.85	11.85	–	–
Gel pH 7	**0La**	**2La**	**4La**	**8La**			
SiO_2	98.6	88.0	85.8	80.9			
B_2O_3	0.0	0.0	3.5	0.0			
Na_2O	0.0	0.0	0.0	0.0			
CaO	1.0	0.0	0.5	0.0			
Eu_2O_3	0.4	0.9	0.4	0.4			
La_2O_3	–	11.2	9.7	18.7			
Gel pH 9.5	**0La**	**2La**	**4La**	**8La**			
SiO_2	82.2	78.2	77.8	75.1			
B_2O_3	0.0	0.0	0.0	0.0			
Na_2O	4.1	4.9	0.0	1.9			
CaO	12.8	7.9	10.9	4.5			
Eu_2O_3	0.9	0.6	0.4	0.3			
La_2O_3	–	8.4	10.9	18.2			