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Structural role of molybdenum in nuclear glasses: an EXAFS study

G. Calas [a,*], M. Le Grand [a,b], L. Galoisy [a], D. Ghaleb [b]

[a] *Laboratoire de Minéralogie-Cristallographie, UMR CNRS 7590, Universités Paris 6 et 7, IPGP,*
case 115, 4 place Jussieu, 75252 Paris cedex 05, France
[b] *DEN/DIEC/SESC/LECLT CEA-Valrho-Marcoule, B.P. 171, 30207 Bagnols-sur-Cèze, France*

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Abstract

The Mo environment has been investigated in inactive nuclear glasses using extended X-ray absorption spectroscopy (XAS). Mo is present in a tetrahedron coordinated to oxygen in the form of molybdate groups $[MoO_4]^{2-}$ (d(Mo–O) = 1.78 Å). This surrounding is not affected by the presence of noble metal phases in the nuclear glass. Relying on the XAS results, on the bond-valence model and on molecular dynamics simulations of a simplified borosilicate model glass, we show that these groups are not directly linked to the borosilicate network but rather located within alkali and alkaline-earth rich domains in the glass. This specific location in the glass network is a way to understand the low solubility of Mo in glasses melted under oxidizing conditions. It also explains the possible phase separation of a yellow phase enriched in alkali molybdates in molten nuclear glasses or the nucleation of calcium molybdates during thermal aging of these glasses. Boron coordination changes in the molten and the glassy states may explain the difference in the composition of the crystalline molybdates, as they exert a direct influence on the activity of alkalis in borosilicate glasses and melts.

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1. Introduction

Borosilicate glasses are used to immobilize fission products and transuranic elements coming from the 'light water' high-level nuclear wastes. These glasses contain typically more than 30 elements, among which fission products such as Mo, which is known to be a difficult element to incorporate in nuclear waste glasses. By contrast to most fission products, Mo has a low solubility in borosilicate glasses, typically below 1 wt% of MoO_3 in nuclear glasses under usual elaboration conditions [1]. Above this concentration, it can participate to the formation of a yellow phase in the glass. This complex yellow phase is formed during the melting stage of the process by a phase separation of molten salts from the borosilicate melt and may be responsible for an enhanced corrosion of the glass melter. This phase contains molybdates, such as Cs-molybdate, which may concentrate ^{137}Cs, and chromates, which impart a yellow coloration to the resulting crystalline compounds observed after cooling [2]. On account of the solubility of alkali molybdates in water, this phase separation may decrease the chemical durability of the vitrified nuclear waste material [1,3]. Mo is also known as a nucleating agent and is used in the glass-ceramics industry for its ability to control the phase separation of glasses or as a crystallization catalyst to produce glass-ceramics [4]. However, by contrast to other crystalline phases such as noble metal or spinel precipitates, which have been quantified in nuclear glasses using Rietveld refinements [5], such a phase separation only occurs in the inactive

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[*] Corresponding author. Tel.: +33-1 44 27 68 72; fax: +33-1 44 27 37 85.

E-mail addresses: calas@lmcp.jussieu.fr, georges.calas@lmcp.jussieu.fr (G. Calas).

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French glass (SON 68) when the elaboration conditions are out of the specification domain. In addition, experiments on the long-term thermal stability of nuclear waste glasses show the nucleation of molybdates such as powellite, $CaMoO_4$. The presence of crystalline molybdates may arise from the fact that, under oxidizing conditions, hexavalent Mo is the major oxidation state of molybdenum in silicate and borosilicate glasses [2,3,6], although other oxidation states may be present, such as Mo(III), Mo(IV) and Mo(V), under more reducing conditions [2,3,7]. However, the low solubility of molybdenum in nuclear glasses has not been explained, despite its importance during the encapsulation processing of nuclear waste.

In this paper, we present new data on the environment of molybdenum in inactive nuclear borosilicate glasses, using Mo–K edge extended X-ray absorption fine structure spectroscopy (EXAFS). These data indicate molybdenum to occur in a hexavalent oxidation state, with the formation of regular molybdate tetrahedra. The absence of connectivity between molybdate groups $(MoO_4)^{2-}$ and the polymerized borosilicate sublattice is explained by the location of Mo in regions enriched in alkali and alkaline-earth cations. This structural position explains the possible phase separation of alkali molybdate-bearing yellow phases in molten nuclear glasses or the nucleation of calcium molybdate in these heated glasses, if the process is made under atmospheric conditions [3]. We also show that the composition of crystalline molybdates directly arises from structural modifications which occur either in the molten or the glassy state, as a result of the heterogeneous glass structure.

2. Experimental procedure

Inactive glasses representative of the French light water nuclear glass were studied. Due to the possible influence of Pd and RuO_2 precipitates on the glass structure, a glass without Pd and RuO_2 (GL-0) was compared to glasses with 1.5 and 3 wt% Pd + RuO_2, labeled GL-1.5 and GL-3, respectively [3,9]. GL-1.5 has the chemical composition of the inactive reference French light water nuclear glass (SON 68). The compositions of the studied glasses are given in Table 1. The glasses were elaborated at the PEV technological inactive facility of the Valrho-Marcoule CEA Center (France), by mixing a calcined solution of inactive elements simulating the calcined high activity solutions with a glass frit and melting the mixture in a stainless steel vessel at 1100–1150 °C. About 400 kg of melt was poured into a stainless steel canister [10]. The examination of glass samples with transmission electronic microscopy has shown the absence of heterogeneities larger than 2 nm.

Table 1
Composition of the investigated glasses (in wt%)

	GL-0	GL-1.5	GL-3
SiO_2	45.29	45.23	44.78
Al_2O_3	4.93	4.87	4.81
B_2O_3	13.94	13.92	13.8
Na_2O	9.93	9.78	9.58
CaO	4.02	4.01	3.98
ZnO	2.49	2.49	2.46
Li_2O	1.97	1.96	1.95
Fe_2O_3	2.98	2.89	2.79
P_2O_5	0.29	0.28	0.27
NiO	0.72	0.42	0.4
Cr_2O_3	0.52	0.5	0.49
ZrO_2	2.69	2.63	2.56
RuO_2		0.85	1.75
Cs_2O	1.32	1.28	1.24
SrO	0.34	0.33	0.32
MoO_3	1.74	1.68	1.63
MnO_2	0.74	0.36	0.35
TeO_2	0.23	0.2	0.19
BaO	0.62	0.61	0.58
La_2O_3	1.99	1.98	1.91
Ce_2O_3	0.96	0.95	0.92
Pr_2O_3	0.53	0.54	0.52
Nd_2O_3	1.63	1.59	1.53
Pd	0	0.52	1.07
K_2O	0.13	0.13	0.12
Total	100.00	100.00	100.00

Mo–K edge EXAFS spectra were recorded in transmission mode, at room temperature, on beam line D44 of the LURE- DCI storage ring (Orsay, France), using a double crystal Si(3 1 1) monochromator. The DCI storage ring was operating at 1.85 GeV, with a 300 mA positron current. EXAFS spectra were recorded between 19 900 and 20 800 eV with a 1 eV energy step and an accumulation time of 1 s/step. For each glass, four spectra were averaged to improve the signal-to-noise ratio. The thicknesses of the polished glass slabs were adjusted to optimize the signal to noise ratio above the absorption threshold and to keep a reasonable absorption contrast at the absorption edge (about 0.3). Energy calibration was checked frequently by reference to metallic Mo foil and is accurate within 0.2 eV.

EXAFS data reduction was achieved using a least-square procedure described in a previous paper [11]. Theoretical phase-shift and amplitude functions containing a full curved wave correction were used to fit glass spectra together with FEFF-6 derived functions [12]. The EXAFS signals were Fourier transformed between 3.45 and 13.1 Å^{-1} to obtain the pair distribution functions relative to Mo. For each atomic shell, the extracted parameters were the interatomic distances (R), the Debye Waller factor (σ) and the number of neighbors (N). Uncertainties were estimated to be ±0.01 Å and 0.5 atom.

3. Results and discussion

3.1. EXAFS data

For the three studied samples, the EXAFS $\chi(k)$ signals present the same shape, intensity and frequency within the experimental uncertainty (Fig. 1). This shows that the presence of noble metals, that otherwise modifies the medium-range organization around Si in these glasses [8], has no significant effect on the Mo environment. We will thus concentrate on the GL-1.5 sample (SON 68), which will be representative of the three studied glasses. The EXAFS signal (Fig. 1) consists of a unique damped sine function and the intensity of the oscillations decreases monotonically with increasing k values. It corresponds to a single contribution of the nearest neighbors. The Fourier transform of the EXAFS signal, which represents the Mo-centered partial radial distribution function, shows only one peak (Fig. 2). This peak corresponds to the first oxygen neighbors, defining the site occupied by Mo in the glass. Beyond this peak, no significant contribution can be found (Fig. 2). These data show that molybdenum does not have the same structural behavior as other nuclear glass components: e.g., zinc and zirconium always appear connected to the borosilicate framework with a significant contribution of Si second neighbors to the EXAFS spectra.

EXAFS analysis of the first coordination shell indicates that Mo is 4-coordinated to oxygen, with a mean Mo–O distance of 1.78 ± 0.01 Å (Table 2), which corresponds to the characteristic Mo–O distance encountered in $[MoO_4]^{2-}$ molybdate groups, in which Mo is hexavalent and tetrahedrally coordinated [13]. This confirms the prevailing hexavalent oxidation state of Mo in these inactive borosilicate glasses melted in air, in agreement with previous works on silicate glasses [2,3]. The stability of the Mo–O distance is observed from the crystal chemistry of molybdate groups in crystalline molybdates, such as $CaMoO_4$, Cs_2MoO_4, Na_2MoO_4 etc., in which the nature of the associated cation does not have a significant influence on the length of Mo–O bonds [6]. The low values of σ (Table 2) in the three glasses show that the tetrahedral sites occupied by molybdenum in these glasses do not suffer a significant distortion, a general property observed in crystalline molybdates [13].

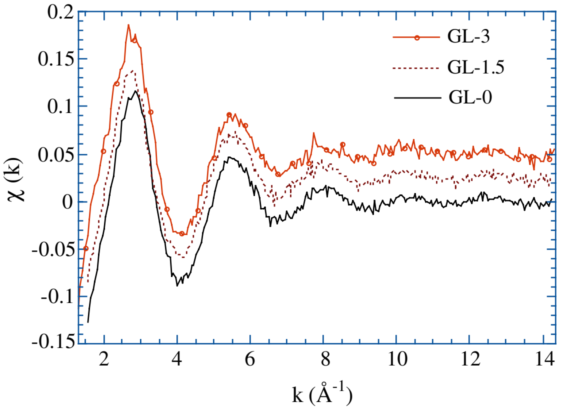

Fig. 1. EXAFS spectra of the three investigated glasses. The three EXAFS functions exhibit similar period and amplitude.

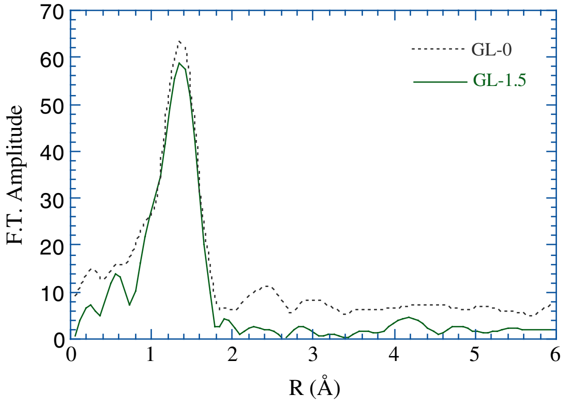

Fig. 2. Fourier transform of the EXAFS spectra of the GL-1.5 and GL-0 glass samples. The main peak corresponds to the Mo–O interactions and is not modified by the presence of noble metal phases in the nuclear glass. The additional small features do not have any structural significance as they represent artifacts due to the Fourier transform procedure.

Table 2
EXAFS parameters

Sample	R (Å)	σ (Å)	N
GL-0	1.78(1)	0.04(1)	4.2(3)
GL-1.5	1.78(1)	0.04(1)	4.1(3)
GL-3	1.77(1)	0.06(1)	4.0(3)

R: Mo–O distance (Å), σ: Debye Waller factor (Å), N: number of neighbors.

3.2. Use of the bond valence model

The bond valence model may explain the absence of contribution from the borosilicate framework. Indeed, EXAFS spectroscopy usually allows detecting the contribution of next-nearest neighbors around cations in oxide glasses. For instance, the presence of Zr–Si and Zn–Si correlations in the EXAFS spectra of the inactive French nuclear glass (SON 68) together with the bond valence model has been used to explain the structural role of these elements in nuclear glasses [8,14]. As only the coordination shell is detected by Mo–K edge EXAFS in inactive nuclear borosilicate glasses, $[MoO_4]^{2-}$ tetrahedra are not linked to the polymerized [Si, Al, B]O_4 or BO_3 part of the glassy network. The absence of Mo–(Si, Al, B) contributions on the Mo–K edge EXAFS spectra is confirmed by the bond valence model [15]. According to this model, the sum of the bond valences relative to an oxygen must be close to the theoretical value of 2.0 valence units (2.0 ± 0.1 v.u.). The valence of the M–O bond, S, is calculated using the relationship:

$$S = e^{(R_0-R)/0.37},$$

where R is the M–O distance and R_0 is the bond valence parameter for M, tabulated in reference for most cations in different valence states [15].

The Mo–O bond valence derived from the EXAFS-determined Mo–O distance, is 1.45 v.u., a value which is close to the theoretical value for Mo in molybdate groups (1.5 v.u.). An important overbonding of the oxygen atoms would thus result from a bonding with Si, Al, or B (Table 3). This explains why molybdate groups are not associated to the borosilicate network. Charge compensation of the $[MoO_4]^{2-}$ groups may be achieved by alkalis, alkaline-earths or lanthanide cations, and it may be suspected that the composition of the crystalline molybdates will reflect the associations existing in the nuclear glasses/melts. This may explain why more than 60 wt% of the crystalline phases constituting the yellow phase are Na-bearing molybdates, when this yellow phase appears as the reference elaboration conditions of the inactive SON 68 glass are modified [16]. However, the different composition of crystalline molybdates formed after phase separation or glass nucleation point out the need to discuss more in detail the structure of nuclear glasses.

3.3. Simplified structural model of the reference inactive French nuclear glass (SON 68)

The structural model represented on Fig. 3 is a qualitative description of the Mo environment in the glass, derived from molecular dynamics (MD) simulations of a five oxide glass (SiO_2–$B_2O_3Al_2O_3$–Na_2O–CaO). Simulation conditions and computed structural parameters have been described in detail elsewhere [8]. This simplified glass has been chosen as representative of the inactive reference French nuclear glass. Some Na^+ and Ca^{2+} ions, whose positions were calculated for the five oxide glass, have been replaced by other alkalis or alkaline earths, which are present in the reference inactive French nuclear glass, so as to respect the relative concentration of these cations in the glass. As these elements play a similar role, is indeed expected that these cations occur in the same glass regions. MD calculations suggest that this glass has an heterogeneous structure at the nanometer scale, with some domains enriched in alkalis and alkaline earth cations coexisting with SiO_4 tetrahedra-based polymerized domains [8]. These simulations are consistent with the modified random network

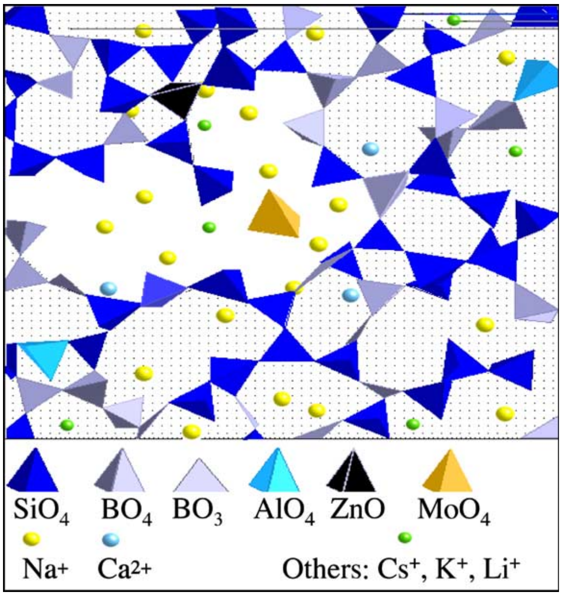

Fig. 3. Simplified representation of the local structure of a borosilicate glass. The initial model was derived from molecular dynamics calculations on a simplified Na–Ca alumino-borosilicate glass taken as a model for the French nuclear reference glass. The other elements have been located in the glass structure in order to obey the bond valence model.

Table 3
M–O bond valences, S, at 298 K, for some selected elements

Elements	S (v.u.)	Elements	S (v.u.)	Elements	S (v.u.)
Mo	1.45	Na	0.21	Ca	0.35
Si	1.01	Cs	0.16	Ba	0.27
Al	0.77	Rb	0.15	Sr	0.26
B(CN = 3)	0.77	K	0.14	La	0.39
B(CN = 4)	1.00	Li	0.27	Nd	0.26

and stereochemically defined models of the glass structure [17] as well as with a convergent set of experimental and numerical data, indicating an extensive medium range ordering in silicate glasses [18]. Molybdate groups are set within the regions enriched in alkalis and alkaline earths, and are not directly linked to the borosilicate matrix. As discussed above, a direct (Mo–O–(Si, B, Al)) linkage would result in a significant over-bonding of the oxygen atoms surrounding Mo.

3.4. Structural origin of the formation of molybdate phases

The preferential linkage of molybdenum to alkalis and alkaline earths, derived from EXAFS data and bond valence model in the three glasses investigated, sheds light on the behavior of Mo in nuclear glasses. The low solubility of Mo in nuclear glasses may be explained by a high activity coefficient due to its occurrence in cationic domains. Molybdenum affects the properties of nuclear waste glasses under oxidizing conditions, with the formation of crystalline molybdates. Two different stages are important in the process, which result in phases with different compositions.

First, in the molten stage, a phase separation of molybdate-bearing molten salts, associated to chromates, has been observed in various compositions at temperatures between 900 and 1000 °C, when the technological separation conditions are modified for. The cooling process will result in the crystallization of alkali molybdates, such as a Na- and Li–Na molybdates, with only minor $CaMoO_4$ [16]. The presence of these phases may affect the long-term thermal stability of nuclear waste glasses. The preferential location of molybdate groups within cationic domains explains the role of molybdenum during the phase separation in the molten stage. High temperature conditions favor atomic motions and hinder the nucleation and further growth of molybdate phases. Mo is indeed expected to diffuse through the glass within these cationic domains [19].

Second, in the glass, crystalline molybdates form after appropriate thermal treatments above the glass transition temperature ($T_g = 510 \pm 5$ °C in the composition selected in this study). For instance, a thermal treatment between 630 and 880 °C favors the formation of $CaMoO_4$ [20]. The proportion of this phase does not exceed 1.5 wt%, i.e. remains lower than the $CaO + MoO_3$ sum, showing that some molybdenum remains in the glass structure. With increasing crystallization temperature, the proportion of $CaMoO_4$ decreases, until it eventually disappears, an indication of the modification of Ca-molybdate activity with temperature. Our data show that the nucleating role of Mo in alkali or alkaline earth silicate glasses arises from the presence of the Mo-bearing cationic domains observed in the glass.

The chemical difference between the nature of crystalline molybdates, which may form in the molten or glassy stage, and the thermal dependence of $CaMoO_4$ activity in the glass, may be explained by the present results. The preferential location of molybdate groups within cationic domains implies a dependence on the activity of the cations present in these domains. MD simulations of model alumino-borosilicate glasses show the presence of only few non-bridging oxygen (<10%), indicating that most Na atoms charge compensate network-forming Al or B atoms. These calculations have been recently improved by a combination of MD and reverse Monte Carlo calculations based on wide angle X-ray scattering [21]. The calculated glass structure indicates a competition for charge compensation between elements such as B, Al or Zr. For instance, aluminum is preferentially associated to sodium, as octahedral zirconium is preferentially charge compensated by calcium [9]. As a consequence, some boron may occur in triangular coordination in the nuclear glasses investigated, because of the low activity of sodium ions, which are needed for charge compensation of tetrahedral boron. The nature of the cation ensuring the charge compensation of molybdate groups will then depend on the structural role of the other glass components.

Temperature-induced coordination changes of boron will modify the activity of cations, acting either as charge compensator or network modifier. Such a coordination change of boron has been recently evidenced in borosilicate glasses and melts by 11-B NMR data, which show that boron partially changes from tetrahedral to triangular coordination with increasing temperature. We may expect an increase in the activity of network modifying Na cations, according to the reaction

$$\mathrm{Na_{CC}} + \mathrm{BO_4} = \mathrm{BO_3} + \mathrm{O_{NBO}} + \mathrm{Na_{NM}}$$

where $\mathrm{Na_{CC}}$ stands for charge compensating Na, $\mathrm{O_{NBO}}$ for non-bridging oxygen and $\mathrm{Na_{NM}}$ for network modifying Na.

This will explain that, under oxidizing conditions, alkali molybdates will form in the molten stage, as a result of a higher availability of alkali cations in presence of majority 3-coordinated boron. By contrast, the partial transformation of boron from triangular to tetrahedral coordination during the cooling of the glass will increase the proportion of Na cations involved in charge compensation. As a consequence, they will no more charge compensate molybdate groups, by contrast to Ca cations, which will be available for that role, on account of their lower affinity for charge compensation of tetrahedral boron. This may explain the nucleation of $CaMoO_4$ in heated glasses and its further disappearance as the temperature increases to 880 °C, with the subsequent release of Na^+ ions associated to boron coordination change from tetrahedral to triangular coordination with increasing temperature [22]. The actual composition of the crystalline molybdates crystallizing from a borosilicate glass may directly illustrate the heterogeneous structure of the glassy state, and its modification as a function of the glass thermal history.

4. Conclusions

Mo–K edge EXAFS spectroscopy in inactive nuclear glasses indicates that Mo forms $[MoO_4]^{2-}$ tetrahedra, which are not directly connected to the glassy network. A location within alkali- and alkaline earth-rich sublattices of the glass favors the charge compensation of the molybdate groups. This peculiar structural position explains the low Mo-solubility, the separation of Mo-rich phases in the melts and the nucleation of molybdates in nuclear glasses. It is also at the origin of the well-known use of molybdenum as a nucleating agent in silicate or borosilicate glasses. In nuclear glasses, the competition for charge compensating alkalis between B and Mo explains the chemical difference observed between the molybdates formed by phase separation in the melts or by crystallization of heated glasses. The temperature-induced coordination change of B explains the temperature dependence of the activity of Ca-molybdate, a nice illustration of the influence of thermal history on the heterogeneous glass structure. A better understanding of the behavior of molybdenum in nuclear glasses and melts will allow the development of new wasteforms that can incorporate increased amounts of Mo, whilst avoiding yellow phase production.

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