REVISION 1

Competition between two redox states in silicate melts: an in-situ simultaneous experiment at the Fe K-edge and Eu L_3-edge.

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ABSTRACT

The understanding of redox equilibria, as well as, the knowledge of the elemental distribution in magmatic melts are of fundamental importance in order to constrain the genesis of magmas. In particular, the partitioning of trace elements (e.g. Eu) has demonstrated to be an useful tool for estimating the redox conditions in Earth and Planetary materials. However, for a more complete comprehension of Eu in silicate melts, still lacking are the information regarding the effects of temperature (T), redox conditions, compositions and the possible interference of other multivalent elements. Here we show new data on the oxidation states of two commonly coexistent multivalent elements (Eu and Fe) in melts, acquired by "in-situ" dispersive-X ray Absorption Spectroscopy experiments at high temperatures and at different oxygen fugacity conditions. This work, for the first time, shows the possibility to monitor in real-time the behaviour and valence variations of two elements under varying environmental conditions (like T and redox state).

INTRODUCTION

Rare earth element (REE) patterns of igneous rocks provide useful information on the conditions and processes during magma formation (e.g., Schnetzler and Philpotts 1970; Henderson 1984; Blundy and Wood 2003). Among the 15 REE, europium is the only one stable as divalent and many authors in the past decades have used Eu valence as a quantitative oxybarometer in magmatic systems (e.g., Philpotts 1970; Drake 1975; McKay 1989;

Wadhwa, 2001; Karner et al. 2010). The distribution and behavior of multivalent elements (Fe, Cr, V, Eu) reflects the prevailing redox conditions of their environment (Shearer et al. 2006), and their oxidation states will influence the mineral crystallization and the element partitioning in a variety of geochemical systems. Thus, a complete understanding of transition and RE elements is important for the geochemical and petrological interpretations of magmatic processes and partition properties between melt and crystals in many planetary materials. To do so, it is necessary to determine the ratios of oxidation states by means of a quantitative knowledge of the effects of composition, T, and redox environment (fO_2).

In previous studies (Cicconi et al. 2009, 2012) it was experimentally demonstrated that Eu behavior in silicate glasses is primarily controlled by the bulk composition and then by temperature and redox conditions of the melt. In particular, Fe has been shown to affect Eu oxidation states (Cicconi et al. 2012). Since Fe is the most abundant transition element, and its redox state affects also the physical properties of magma, we dedicated our attention to the interaction between Eu and Fe. Schreiber (1977) suggested that the higher reduction potential of the Fe^{3+}-Fe^{2+} redox couple in silicate melts, in comparison with the reduction potential of Eu^{3+}-Eu^{2+}, implies that Fe^{3+} could oxidize all the Eu^{2+} present. This interaction in silicate glasses was also described for Fe and Ce (Schreiber et al. 1980).

In order to experimentally visualize the Eu kinetic reduction and therefore to understand how Fe influences Eu-bearing melts, we have carried out a direct determination of Eu and Fe valence states by dispersive-X-ray Absorption Spectroscopy (XAS).

SAMPLES AND ANALYTICAL TECHNIQUES

The sample investigated has an Fe-rich (~ 14wt%) basaltic composition (FeBas). The starting material has been prepared from dried oxides and carbonates in stoichiometric proportions. The mixture has been homogenized in an agate mortar and melted to obtain a glass (T=1400°C), which was then finely ground and doped with 5wt% Eu_2O_3. The resulting glass

was checked by optical microscope and scanning electron microscopy to ensure homogeneity and the absence of crystalline phases (Cicconi et al. 2012 for details on the syntheses; Tab.1). To carrying out the high-temperature (HT) X-ray Absorption Near-Edge Structure (XANES) experiments, the samples were loaded as μg-powders in the 1-mm hole of the Pt-Ir10 % heating wire of the microfurnace designed following the idea developed by Mysen and Frantz (1992) and previously used for in situ XANES high temperature studies (Neuville et al. 2008; Cochain et al. 2009; Gonçalves Ferreira et al. 2013; see also Neuville et al. 2014 for more details). The XANES spectra have been collected simultaneously at the Eu L_3-edge (6977 eV) and at the Fe K-edge (7112 eV) at ODE beamline (SOLEIL, France). ODE is an energy dispersive beamline with a bent Si(111) polychromator crystal at the focal point of which the sample is placed. The beam size was 30 x 30 μm (FWHM). Due to the fixed energy–position correlation in the diffracted energy band, a complete absorption spectrum was obtained from measurements of the intensity distribution on a position-sensitive detector. The Si(111) bend polychromator provides an energy resolution of ~ 1 eV at 7keV. Because a spectrum is recorded in the order of seconds, this beamline is particularly well suited to investigate fast reduction kinetics processes at HT. The closed microfurnace allows also the use of different gases in order to obtain different redox environments. In these experiments, the first step was to acquire the XAS spectra of the untreated sample (in air, at room temperature). Then, we increased the temperature up to 1500°C and we monitored the changes in both the edges. The final step was to change the gases into the furnace, passing from air to pure Ar, back to air and finally to an Ar/H_2 gas mixture (to simulate a reducing environment). After calibration (by converting pixel position to energy) the spectral background was removed and the signal normalized at the Eu L_3-edge using the Athena software (Ravel and Newville 2005). The Eu threshold energy was taken as the first maximum of the first derivative of the spectra, whereas peak positions were obtained by calculating the second derivative of the spectra. Eu data analysis was carried out by following the procedure described in Cicconi et al (2012). In brief,

the peaks relative to Eu^{2+} and Eu^{3+} can be fitted by a combination of pseudo-Voigt (pV) and arctangent (atg) functions to simulate the XANES spectra (i.e. Takahashi et al. 2005; Cicconi et al. 2012). The pV and atg functions simulate the resonance peak and the absorption edge step, respectively. The Fe pre-edge peak analysis was carried out following the same procedure reported in Wilke et al. (2001) and Giuli et al. (2012) in order to extract information on the Fe oxidation state. The main peak data analysis of the Eu portion of the XANES spectrum was done in the energy range 6950-7020 eV, whereas the pre-edge peak analysis of the Fe edge was done in the energy range 7090-7200 eV.

RESULTS and DISCUSSION

Iron and europium redox reaction in a basaltic melt

The XANES spectrum of the untreated basaltic sample (a glass collected in air and room T) is reported in Figure 1a, along with its first derivative. The spectrum was normalized at the Eu L_3-edge. When both Eu oxidation states are present, the XANES spectrum displays two well-separated peaks related to both Eu^{2+} and Eu^{3+} contributions (Takahashi et al. 2005). A comparison of our XANES peak positions with literature data of Eu and Fe model compounds allows recognition of the presence of both elements prevalently in their trivalent states (Fig. 1a). The main peak data analysis of the Eu portion (6950-7020 eV) and the pre-edge peak analysis of the Fe edge (7090-7200 eV) (see Fig. 1b-c) confirm the prevalence of Eu and Fe oxidized species ($Fe^{3+}/Fe_{tot} = 0.96 \pm 0.05$).

The glass was then melted at 1500°C: the XANES data recorded show no marked differences in the Eu portion and very small changes were detected in the Fe portion (Fig. 2). The calculated Fe^{3+}/Fe_{tot} ratio is 0.85 (±0.05), after 245s at HT in air (inset in Fig. 2). Right after the injection of pure Ar in the furnace it was possible to observe a significant reduction of Fe in the melt (Fig. 2). In fact, through the first derivatives of the signals we observed a shift of the Fe K-edge to lower energies (about 2.5 eV) whereas no significant differences occurred in the Eu spectra (Fig. 2). Thus, just after 50 seconds in pure Ar the Fe^{3+}/Fe_{tot} ratio was

129 estimated to be already 0.30 (±0.05) demonstrating a strong Fe reduction. However, this
130 process was completely reversible as soon as Ar was removed, bringing the Fe ratio back to
131 higher values ((Fe^{3+}/Fe_{tot} = 0.80 ±0.05). In these conditions, the complete absence of Eu^{2+} and
132 the significant presence of Fe^{2+} could be described by the redox reaction:
133 $Eu^{2+} + Fe^{3+} \Leftrightarrow Eu^{3+} + Fe^{2+}$ (Schreiber 1977). Thus, Fe^{3+} easily oxidized all the Eu^{2+} present.
134 The third step of the experiment consisted of the injection of a gas mixture of Ar/H_2 to
135 simulate a strong reducing environment. The material melted at 1500°C was re-equilibrated in
136 air (time 0 in Fig. 3) and as soon as we injected Ar/H_2 in the furnace box, Fe was completely
137 reduced, whereas Eu started to transform into its reduced form, but much slower than Fe. In
138 fact, it took more than 5 minutes for Eu to reach the almost pure divalent state (337s in Fig.
139 3). Figure 3 also shows the spectra acquired just before (time 0) and right after the injection of
140 Ar/H_2 (37s) and the reverse process: from Ar/H_2 atmosphere (337s) to air (after 34 s).
141 Interestingly it was observed that, in the reverse process (thus, passing from the reducing
142 environment Ar/H_2 to air), it took less than a minute for Eu to transform completely into its
143 oxidized form (about 34 seconds, Fig. 3). The experiment was done twice in order to ensure
144 the reliability of the fast oxidation. From each Eu spectrum the Eu^{3+}/Eu_{tot} ratio was
145 determined (± 0.06; see Fig. 4). The time dependence of the Eu redox ratio in this basaltic
146 glass is reported in Figure 4 and its evolution with time at a given temperature can be
147 described by the expression that was used by Magnien et al. (2006) to study the evolution of
148 Fe^{3+}/Fe_{tot}:
149 $$(F_t - F_{eq}) = (F_0 - F_{eq}) \exp^{(-t/\tau)}, \qquad \text{(Eq. 1)}$$
150 where F_t is the redox ratio at time t, F_0 the initial ratio, F_{eq} the equilibrium value and τ a
151 characteristic time determined from a least-squares fit of Eq. (1) to the experimental redox
152 data. During the experiment, the Eu^{3+}/Eu_{tot} ratio varied from 1.00 to 0.07 (± 0.06) with a well-
153 defined trend (black circles in Fig. 4). Remarkably, it took 34s for the Eu^{3+}/Eu_{tot} ratio to return
154 to the value obtained in the oxidizing process (i.e. by removing the Ar/H_2 gas mixture; empty

155 circle in Fig. 4). On the contrary, the kinetic of the Fe reduction during these experiments was
156 extremely fast (66 s) and the spectra could not be recorded rapidly enough to show the
157 variations of the edge/pre-edge as a function of valence changes and time. Moreover it must
158 be noted that, at such reducing conditions, Fe strongly interacts with the Pt wire, and since
159 there is a complete solid solution between Pt and Fe, iron is not present in the sample
160 anymore, but it concentrates in the Pt wire, making the Fe edge undetectable after 200 s.

161 **IMPLICATIONS**

162 "In-situ" XAS studies can improve our understanding of the behavior of trace and transition
163 elements in melts/glasses, enhancing understanding of the experimental factors that influence
164 redox ratios. Oxidation-reduction equilibria involving e.g. Fe and Eu are very important in
165 studies of magmatic samples. In particular, since Eu anomalies in terrestrial and
166 extraterrestrial materials are largely used to determine the prevailing redox conditions, there is
167 need to fully understand the factors that influence Eu behavior in multicomponent systems,
168 such as bulk composition, temperature, and presence of other multivalent elements. Such
169 studies have been surprisingly rare for a geochemically important element such as Eu.
170 Our in-situ data on Eu are consistent with those obtained from the quenched glasses (Cicconi
171 et al. 2012). In fact, both in-situ and ex-situ data on Fe-bearing melts show that, in air and
172 under slightly reducing conditions, Eu is only present in its oxidized form. On the contrary,
173 some differences were observed for Fe. The fast reduction observed with in-situ XAS data
174 collection and the comparison with data obtained from the quenched glass, show a quench
175 effect that cannot be neglected in future studies.
176 This work, for the first time, shows the possibility to monitor in real-time the valence changes
177 of two elements in silicate glasses/melts, at different temperatures and/or redox environments.
178 We observed experimentally that there is strong competition between the two redox couples
179 investigated: Fe^{3+} could easily oxidize all the Eu^{2+} present, and consequently, in order to use
180 Eu as a quantitative oxybarometer, this mutual interaction must be taken into account.

Furthermore, it is generally believed that mutual redox interactions take place during the quench process (i.e. Schreiber et al. 1980; Paul 1990), as a result of differences in the change in free energy among the different multivalent elements (Russell 1989; Bingham et al. 2014). Instead, in this study, we verified experimentally that electron transfer occurs also in the melt state, and not just during the quench.

Finally, the procedures adopted for this experiment could be used to study many other redox-couples, involving other transition elements, and could be of interest for a range of applications other than the Geosciences, such as in the glass industry for technologically relevant materials, or interactions in glasses for nuclear waste confinement (such as the redox-couple Ce-Cr).

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269 **Table 1 –** Chemical composition of the Fe-basalt glass (wt%)

	wt%
SiO_2	47.20
Al_2O_3	9.74
FeO	14.10
CaO	3.85
MgO	5.36
K_2O	4.47
Na_2O	2.96
TiO_2	7.63
Eu_2O_3	4.91
tot	100.22

270

271

Figure captions

Figure 1: a) XANES spectrum of the untreated sample (collected in air and room T) normalized at the Eu-L_3 edge, along with the first derivative. The threshold energies (taken as the first maximum of the first derivative) show the dominant presence of trivalent species. b-c) The main peak data analysis of the Eu portion (6950-7020 eV) (b) and the pre-edge peak analysis at the Fe K-edge (7090-7200 eV) (c) are shown. Black circles indicate the experimental signals, the solid lines the theoretical signals, and the dotted lines the different components used for the fitting.

Figure 2: Comparison of the XANES spectra, normalized at the Eu-L_3-edge: collected for the untreated sample (glass) and for the melt after 30s and 245s at 1500°C (HT-air) in air and for the melt after 50s from the injection of pure Ar (HT-Ar). The inset shows the changes occurring in the first derivative of the signals.

Figure 3: Comparison of the XANES spectra, normalized at the Eu-L_3-edge, collected at 1500°C in air (HT air) and after the injection of Ar/H_2 into the furnace box. The spectra acquired just before (time 0) and right after the injection of Ar/H_2 (after 33s) and also the reverse process: from Ar/H_2 atmosphere (337s) to air (after 34 s) are shown. The inset shows the first derivative of the signals acquired from time 0 till 66s.

Figure 4: Time dependence of the Eu redox ratio of the basaltic sample at time 0 (air, HT) and after the injection of Ar/H_2 gases (full symbols). The evolution of the europium redox ratio is very fast and was calculated by using the Magnien et al (2006) expression. The empty circle represents the reverse process: from Ar/H_2 atmosphere (337s) to air (time 371s).

(a)

Fe K-edge

Eu L_{III}-edge

Normalized Absorption (arb. units)

Energy (eV)

(b)

Eu L_{III}-edge

Eu XANES
invtan
pV
sum

Normalised Absorption (arb. units)

Energy (eV)

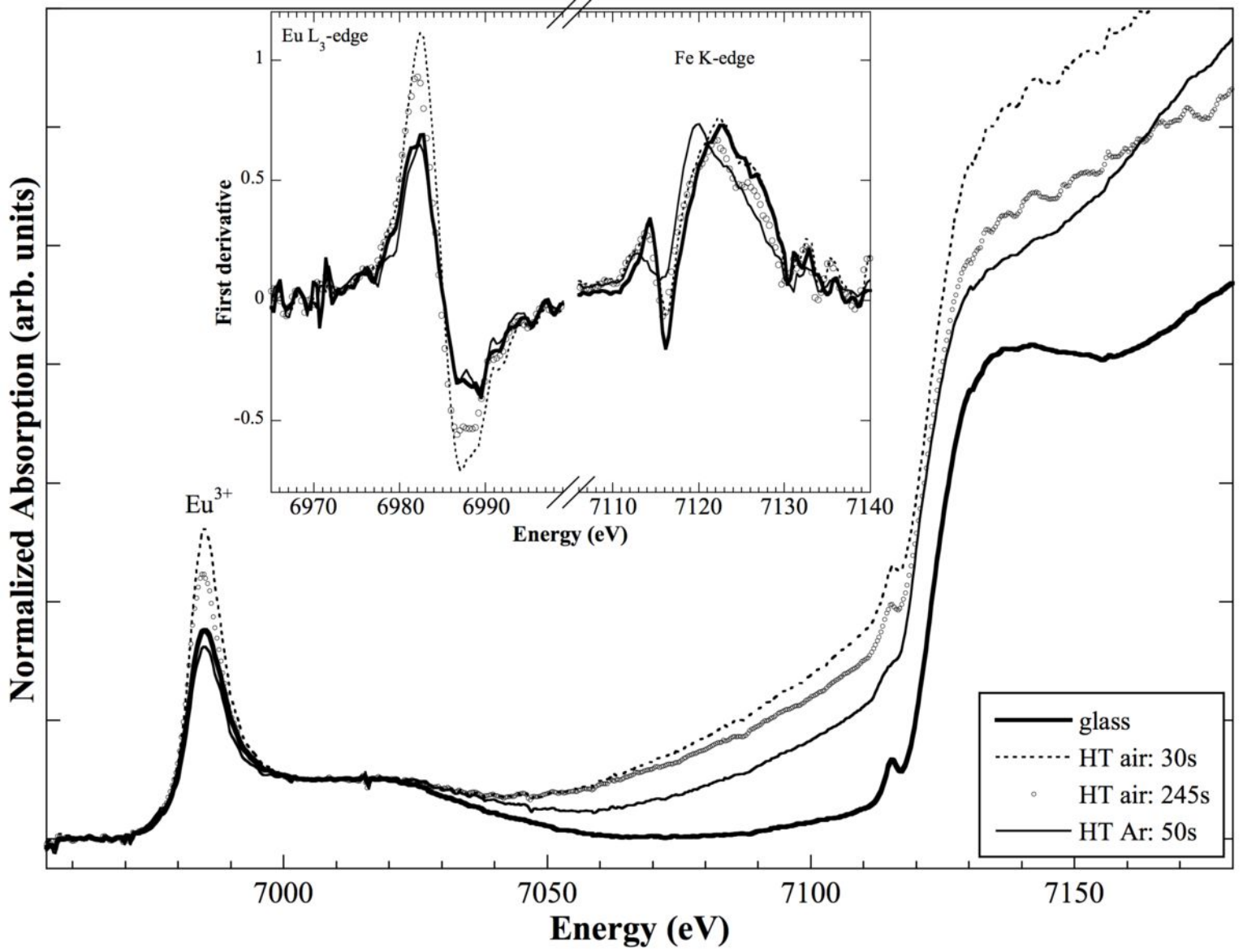
(c)

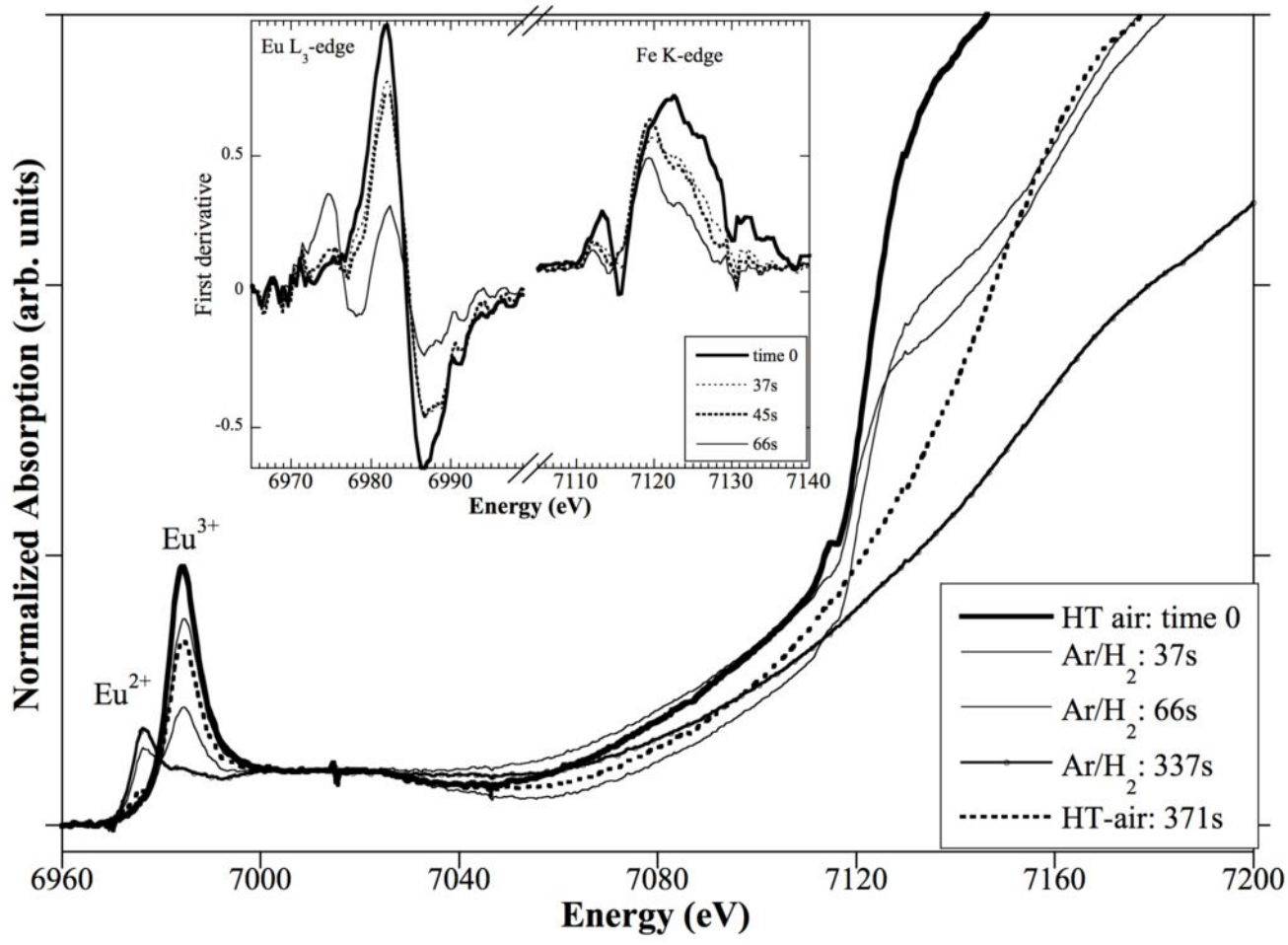
Fe pre-edge

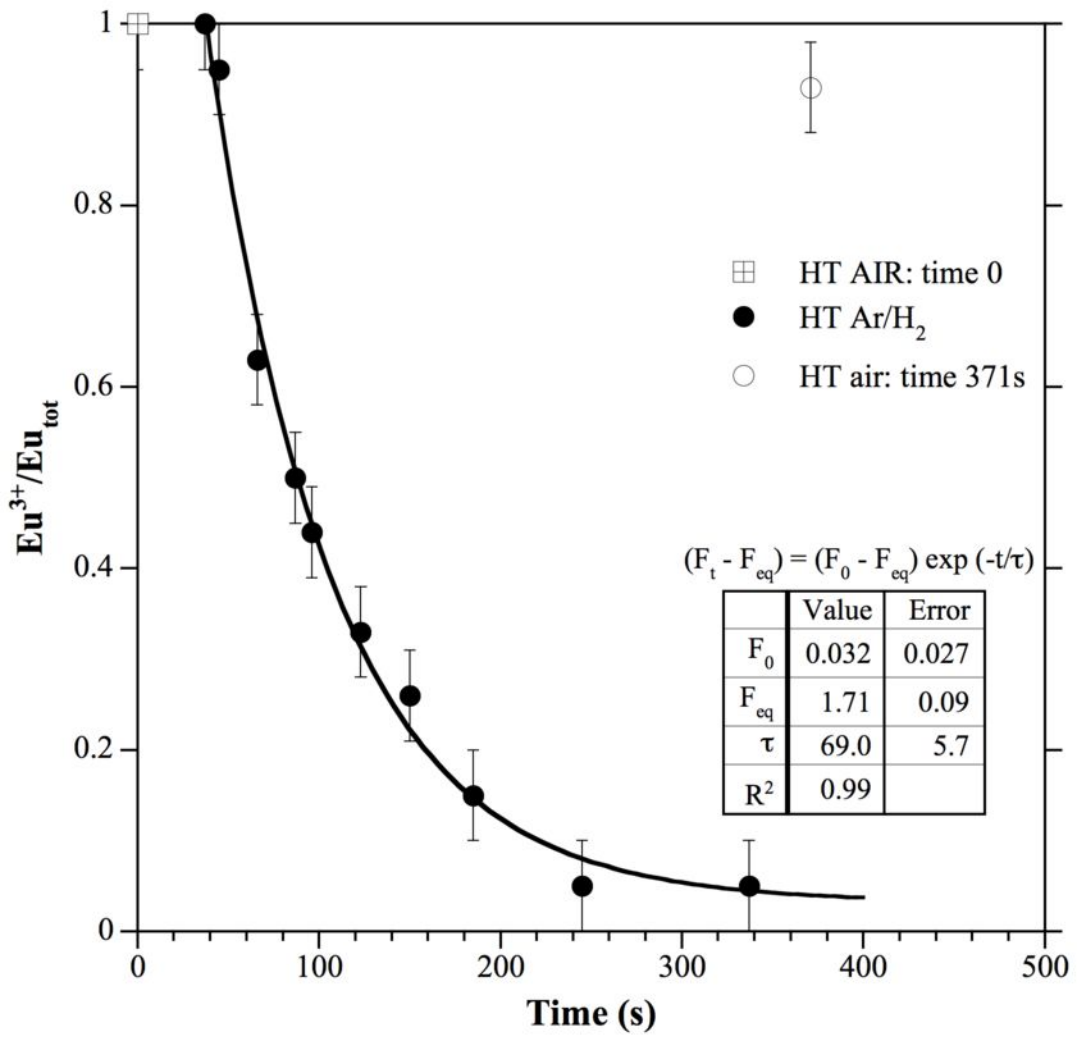
Fe pre-edge
pV1
pV2
sum

Normalised Absorption (arb. units)

Energy (eV)


Normalized Absorption (arb. units)
Energy (eV)
7000
7050
7100
7150
Eu^{3+}
Eu L$_3$-edge
Fe K-edge
First derivative
1
0.5
0
-0.5
6970
6980
6990
7110
7120
7130
7140
Energy (eV)
glass
HT air: 30s
HT air: 245s
HT Ar: 50s


Eu L3-edge
Fe K-edge
First derivative
0.5
0
-0.5
6970
6980
6990
7110
7120
7130
7140
Energy (eV)
time 0
37s
45s
66s
Normalized Absorption (arb. units)
Eu3+
Eu2+
HT air: time 0
Ar/H2 : 37s
Ar/H2 : 66s
Ar/H2 : 337s
HT-air: 371s
6960
7000
7040
7080
7120
7160
7200
Energy (eV)


1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
Time (s)
Eu3+/Eutot
HT AIR: time 0
HT Ar/H2
HT air: time 371s
(Ft - Feq) = (F0 - Feq) exp (-t/τ)
Value
Error
F0
0.032
0.027
Feq
1.71
0.09
τ
69.0
5.7
R2
0.99