



The oxidation state of europium in silicate melts as a function of oxygen fugacity, composition and temperature



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ABSTRACT

Europium L_{III} -edge X-ray absorption near edge structure (XANES) spectra were recorded for a series of synthetic glasses and melts equilibrated over a range of oxygen fugacities (fO_2 s, from -14 to $+6$ logarithmic units relative to the quartz–fayalite–magnetite, QFM, buffer) and temperatures (1250–1500 °C). $Eu^{3+}/\Sigma Eu$ (where $\Sigma Eu = Eu^{2+} + Eu^{3+}$) values were determined from the spectra with a precision of ± 0.015 . $Eu^{3+}/\Sigma Eu$ varies systematically with fO_2 from 0 to 1 over the range studied, increases with decreasing melt polymerisation and tempera-

ture, and can be described by the empirical equation: $Eu^{3+}/\Sigma Eu = \frac{1}{1 + 10^{-0.25 \log fO_2 - 6410/T - 14.2\Lambda + 10.1}}$, where Λ is

the optical basicity of the melt and T is the temperature in K. $Eu^{3+}/\Sigma Eu$ in glasses and melts equilibrated at the same conditions are in excellent agreement for Fe-free systems. For Fe-bearing compositions the reaction $Eu^{2+} + Fe^{3+} = Eu^{3+} + Fe^{2+}$ occurs during quenching to a glass and the high temperature value of $Eu^{3+}/\Sigma Eu$ is not preserved on cooling; *in situ* measurements are essential for determining $Eu^{3+}/\Sigma Eu$ in natural melts.

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1. Introduction

Europium is the only rare earth element (REE) that can occur in significant proportions as an oxidation state other than REE^{3+} in natural silicate melts (e.g., Drake, 1975). The oxidation state of Eu is of geochemical interest because Eu^{2+} and Eu^{3+} partition differently (e.g., Drake, 1975) and thus the behaviour of Eu in a magma depends on the oxygen fugacity (fO_2) and the phase(s) crystallising. Chondrite-normalised REE patterns with anomalous Eu concentrations, quantified as $Eu/Eu^* = Eu/\sqrt{[Sm \times Gd]}$, are frequently observed and are attributed to the redox-variability of Eu (e.g., Morris et al., 1974a; Drake, 1975; Hoskin et al., 2000). Experimental studies have calibrated the fO_2 -dependency of Eu partitioning between feldspars and melt and shown $D_{Eu^{2+}}$ (where D_i is the ratio of the weight fraction of i in the crystal to that in the melt) to be an order of magnitude greater than $D_{Eu^{3+}}$ (Aigner-Torres et al., 2007; Drake, 1975; McKay et al., 1994; Wilke and Behrens, 1999). Conversely, Eu^{2+} is far less compatible than REE^{3+} in pyroxenes (McKay et al., 1994; Wadhwa, 2001; see Eby, 1975 for exceptions). The resulting positive or negative Eu anomalies can provide an indication of crystal fractionation (e.g., Brophy and

Basu, 1990; Hoskin et al., 2000). Alternately, these anomalies could be used to estimate the fO_2 at which a sample crystallised. For example, the partitioning of Eu between pyroxene and melt as a function of fO_2 has potential as an oxybarometer, particularly for meteoritic samples (Karner et al., 2010; McKay et al., 1994; Shearer et al., 2006). Anomalous concentrations of Eu are also commonly exhibited by zircon and similarly could record the fO_2 of crystallisation (Burnham and Berry, 2012; Hoskin and Schaltegger, 2003; Trail et al., 2012).

Partitioning between feldspar, or other minerals, and melt allows the oxidation state ratio of Eu in the melt to be estimated, because the observed D_{Eu} can be modelled as an average of D_{Sr} (a proxy for $D_{Eu^{2+}}$) and D_{Gd} or D_{Sm} (a proxy for $D_{Eu^{3+}}$) weighted by the relative proportions of Eu^{2+} and Eu^{3+} in the melt (e.g., McKay et al., 1994). However, such experiments ideally require melts with a compositionally invariant phase on the liquidus and thus cannot fully address the roles of composition and temperature, as neither can be varied freely. Spectroscopic determinations of Eu^{3+}/Eu^{2+} , or $Eu^{3+}/\Sigma Eu$ where $\Sigma Eu = Eu^{2+} + Eu^{3+}$, are not subject to this constraint.

^{151}Eu (47.8% natural abundance) Mössbauer spectroscopy has been used to determine $Eu^{3+}/\Sigma Eu$ in silicate glasses (Nemov et al., 2007; Virgo et al., 1981), though the limited applications and the long spectral acquisition times (several days) have probably hampered greater uptake of this technique. $Eu^{3+}/\Sigma Eu$ can also be determined by electron paramagnetic resonance (EPR) spectroscopy (Eu^{2+} is EPR active), however, the

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Table 1

Glass compositions (wt.% oxide) determined by EPMA, and melt parameterisations Λ (optical basicity, Duffy, 1993; Leboutellier and Courtine, 1998) and nbo/t (Mills, 1993). Sample nomenclature follows Berry et al. (2006) with the addition of the Zr-glass; errors are 1 standard deviation.

	SiO ₂	Al ₂ O ₃	FeO ^a	MgO	CaO	Eu ₂ O ₃	ZrO ₂	Total	Λ	nbo/t
AD	51.21(39)	15.41(16)	–	10.41(12)	23.90(17)	0.61(5)	–	101.5(5)	0.604(4)	0.924(10)
AD + fo	48.62(15)	13.18(9)	–	16.49(5)	20.77(5)	0.49(2)	–	99.5(2)	0.610(2)	1.218(5)
AD + wo	49.95(10)	9.58(3)	–	6.55(3)	33.35(10)	0.63(2)	–	100.1(1)	0.625(1)	1.301(4)
AD + en	52.85(19)	10.85(3)	–	18.81(6)	17.17(7)	0.52(1)	–	100.2(2)	0.598(2)	1.220(5)
AD + qz	63.21(15)	11.11(5)	–	7.79(3)	17.18(6)	0.53(2)	–	99.8(2)	0.568(1)	0.615(3)
MORB	52.88(16)	12.32(6)	9.84(6)	7.85(3)	16.04(4)	0.53(2)	–	99.5(2)	0.597(2)	0.886(3)
CAS-4 ^b	66.78(54)	19.98(25)	–	–	10.40(9)	0.55(2)	–	97.8(6)	0.536(4)	–0.014(4)
MAS-1 ^b	60.30(39)	18.23(27)	–	20.04(15)	0.07(1)	0.65(2)	–	99.5(5)	0.551(3)	0.470(7)
Longhi1 ^b	63.48(22)	7.20(5)	–	13.19(7)	16.12(9)	0.50(2)	–	100.6(3)	0.573(2)	0.909(5)
Longhi2 ^b	50.41(33)	13.52(14)	–	5.25(5)	31.39(9)	0.56(1)	–	101.2(4)	0.617(3)	1.010(7)
Longhi5 ^b	68.20(16)	16.64(9)	–	8.71(4)	5.52(4)	0.65(2)	–	99.8(2)	0.537(1)	0.207(2)
Osborn4 ^b	46.05(28)	14.49(9)	–	10.47(7)	29.52(12)	0.61(1)	–	101.2(3)	0.627(3)	1.226(8)
Zr-glass	52.23(25)	12.79(12)	–	8.94(7)	19.50(11)	0.51(2)	6.34(8)	100.3(3)	0.589(3)	0.839(6) ^c

– below detection limits or not analysed.

^a All Fe expressed as FeO and treated as such for calculation of Λ and nbo/t .

^b Compositions contain 0.1(1) wt.% Na₂O.

^c Zr treated as a network modifier (Cormier et al., 2015). nbo/t was calculated for Zr as a network former in Burnham and Berry (2014), but this would not have affected the results of that study.

method is restricted to Fe-free compositions since the resonances of other paramagnetic ions will overlap with the Eu signal (Morris et al., 1974a, 1974b; Schreiber, 1977).

Eu *L*_{III}-edge X-ray absorption near edge structure (XANES) spectroscopy has been used to provide information on the oxidation state ratio and coordination environment of Eu in aqueous solutions, silicate melts and minerals (Antonio et al., 1997; Cicconi et al., 2012; Karner et al., 2010; Mayanovic et al., 2007; Rakovan et al., 2001; Shearer et al., 2011). Eu²⁺ spectra are characterised by an intense peak (white line) at ~6974 eV and Eu³⁺ spectra by a white line at ~6982 eV (Rakovan et al., 2001; Shimizugawa et al., 1999; Takahashi et al., 2005). The peaks are assigned to the 2p_{3/2} → 5d transitions of Eu²⁺ and Eu³⁺ (Rakovan et al., 2001; Takahashi et al., 2005). The ~8 eV difference in energy between these features is large compared to the core

hole width of 3.91 eV (Krause and Oliver, 1979), and hence for mixed valence systems the two peaks are well resolved and the relative contributions from each oxidation state can be determined. This resolution makes quantification of redox ratios potentially easier than for many other elements (e.g. Berry and O'Neill, 2004; Sutton et al., 2005). For example, Eu³⁺/ΣEu has been determined with a precision of 0.01 for a sample of apatite containing only 700 ppm Eu (Rakovan et al., 2001). XANES spectroscopy can also be used to determine oxidation state ratios *in situ*; oxidation states present in a melt may not be preserved in a glass, even with rapid quenching, due to electron exchange reactions (Berry et al., 2006). *In situ* experiments on melts have suggested that electron exchange may occur between Eu and Fe (Cicconi et al., 2015).

In order to use Eu anomalies in minerals as an oxybarometer it is necessary to understand the separate effects of *f*O₂, melt composition, and

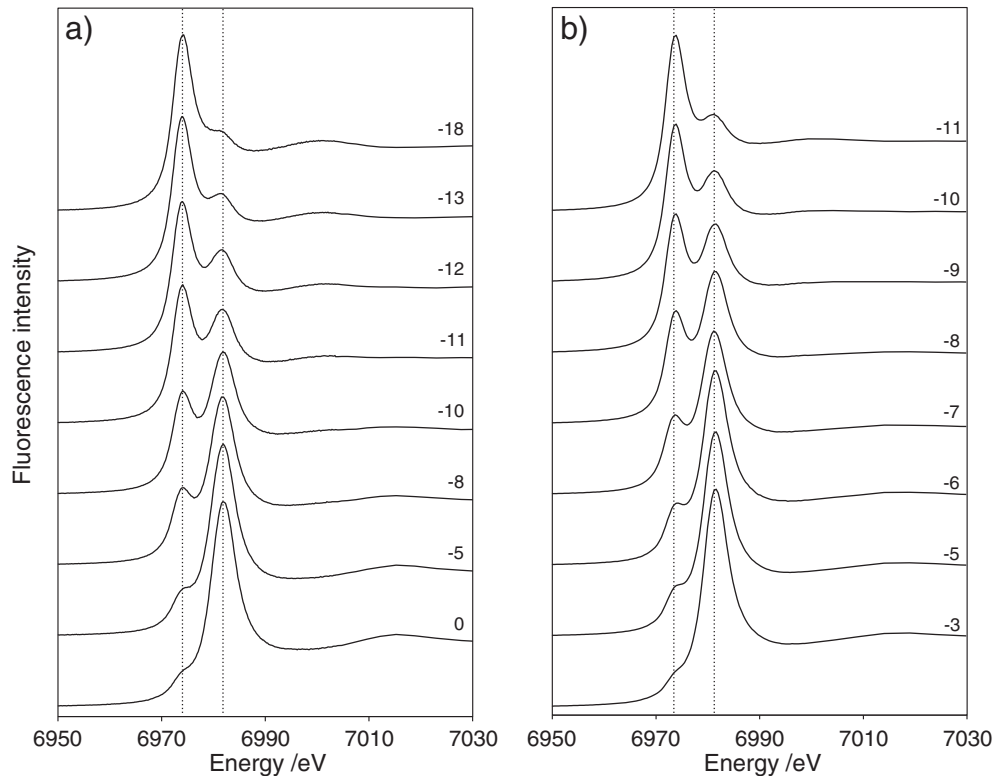


Fig. 1. Eu *L*_{III}-edge XANES spectra of a) AD glasses and b) MORB melt (*in situ*) equilibrated at 1400 °C and the log*f*O₂ values indicated (QFM = –6.3). Spectra are offset for clarity. The dotted lines indicate peaks characteristic of Eu²⁺ (6974.2 eV) and Eu³⁺ (6982.4 eV).

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