1   REVISION 1

2   American Mineralogist Manuscript 6268

3

4   A Mössbauer-based XANES calibration for hydrous basalt glasses reveals

5   radiation-induced oxidation of Fe

6   ELIZABETH COTTRELL[1,*], ANTONIO LANZIROTTI[2], BJORN MYSEN[3], SUZANNE BIRNER[1,4],

7   KATHERINE A. KELLEY[5], ROMAN BOTCHARNIKOV[6,7], FREDRICK A. DAVIS[1,8], MATTHEW

8   NEWVILLE[2]

9   [1]NMNH, Smithsonian Inst., Washington, DC 20560 USA

10   (*correspondence: cottrelle@si.edu)

11   [2]University of Chicago, Chicago, IL 60637 USA

12   [3]Geophys. Lab., Carnegie Inst. Washington, DC 20015 USA

13   [4]Dept. Geol. Sci., Stanford Univ., Stanford, CA 94305 USA

14   [5]GSO, Univ. of Rhode Island, Narragansett, RI 20882 USA

15   [6]Inst. Mineralogie, Leibniz Univ. Hannover, D-30167 GE

16   [7]Inst. Geowiss., Gutenberg Univ. Mainz, D-55128 GE

17
18   [8]DEES, Univ. of Minnesota Duluth, Duluth, MN 55812 USA

19

20   **ABSTRACT**

21   Oxygen fugacity (fO$_2$) exerts first-order control on the geochemical evolution of

22   planetary interiors, crusts, and hydrospheres, and the Fe^{3+}/ΣFe ratios of silicate glasses

23   provide a useful proxy for fO$_2$. Fe K-edge micro X-ray Absorption Near-Edge Structure

24   (XANES) spectroscopy allows researchers to micro-analytically determine the Fe^{3+}/ΣFe

1

25   ratios of silicate glasses with high precision. In this study we characterize hydrous and

26   anhydrous basalt glass standards with Mössbauer and XANES spectroscopy and show

27   that synchrotron radiation causes progressive changes to the XANES spectra of hydrous

28   glasses as a function of radiation dose (here defined as total photons delivered per square

29   micron), water concentration, and initial $Fe^{3+}/\Sigma Fe$ ratio.

30

31   We report experiments from 8 different radiation dose conditions and show that Fe in

32   hydrous silicate glasses can undergo rapid oxidation upon exposure to radiation. The rate

33   and degree of oxidation correlates with radiation dose and the product of water

34   concentration and ferrous/ferric iron oxide ratio on a molar basis

35   ($\Phi=XHO_{1.5}*XFeO/XFeO_{1.5}$). For example, a basalt glass with 4.9 wt.% dissolved H_2O

36   and $Fe^{3+}/\Sigma Fe = 0.19$ from its Mössbauer spectrum may appear to have a $Fe^{3+}/\Sigma Fe \geq 0.35$

37   when analysed over several minutes at a nominal flux density of $\sim 2 \times 10^9$ photons/sec/μm^2.

38   This radiation-induced increase in $Fe^{3+}/\Sigma Fe$ ratio would lead to an overestimation of fO_2

39   by ~ 2 orders of magnitude, with dramatic consequences for the interpretation of

40   geological processes.

41

42   The sample area exposed to radiation shows measureable hydrogen loss, consistent with

43   radiation-induced breaking of O—H bonds, associated H migration and loss, and

44   oxidation of Fe^{2+}. This mechanism is consistent with the observation that anhydrous

45   glasses show no damage under any beam conditions. Cryogenic cooling does not

46   mitigate, but rather accelerates, iron oxidation. The effects of beam damage appear to

47   persist indefinitely.

2

48

49   We detect beam damage at the lowest photon flux densities tested (3×10^6

50   photons/sec/μm^2); however, at flux densities $\leq 6 \times 10^7$ photons/sec/μm^2, the hydrous glass

51   calibration curve defined by the centroid (derived from XANES spectra) and $Fe^{3+}/\Sigma Fe$

52   ratios (derived from Mössbauer spectra), is indistinguishable from the anhydrous

53   calibration curve within the accuracy achievable with Mössbauer spectroscopy. Thus,

54   published $Fe^{3+}/\Sigma Fe$ ratios from hydrous glasses measured at low photon flux densities are

55   likely to be accurate within measurement uncertainty with respect to what would have

56   been measured by Mössbauer spectroscopy.

57

58   These new results demonstrate that to obtain accurate $Fe^{3+}/\Sigma Fe$ ratios from hydrous,

59   mafic, silicate glasses, it is first necessary to carefully monitor changes in the XANES

60   spectra as a function of incident dose (e.g., fixed-energy scan). Defocusing and

61   attenuating the beam may prevent significant oxidation of Fe in mafic water-bearing

62   glasses.

63

64   **INTRODUCTION**

65   The $Fe^{3+}/\Sigma Fe$ ratio of silicate glass may serve as a direct proxy for the oxygen fugacity

66   (fO_2) of an igneous system and exerts control on phase equilibria, physical properties, and

67   the valence state of other heterovalent elements in solution (e.g. Carmichael, 1991; Kress

68   and Carmichael, 1991; Sack et al., 1980). The use of Fe-K-edge XANES to obtain

69     $Fe^{3+}/\Sigma Fe$ ratios of hydrous silicate glasses has proliferated in recent years owing to the

70   outstanding precision achievable and micron-scale spatial resolution afforded (e.g.

71   Botcharnikov et al., 2005; Brounce et al., 2014a; Cottrell and Kelley, 2011; Gaetani et al.,

72   2012; Helz et al., 2017; Kelley and Cottrell, 2009; Kelley and Cottrell, 2012; Le Voyer et

73   al., 2015; Matjuschkin et al., 2015; Moor et al., 2013; Moussallam et al., 2014; Shorttle et

74   al., 2015; Stamper et al., 2014; Wilke et al., 2006). Most Fe-XANES calibration studies

75   have focused on anhydrous glasses, in large part because fO_2 can be easily controlled in

76   1-atmopshere gas-mixing furnaces (Berry et al., 2003; Cottrell et al., 2009; Dyar et al.,

77   2016; Fiege et al., 2017; Wilke et al., 2001; Wilke et al., 2005; Zhang et al., submitted;

78   Zhang et al., 2016). Given the recent surge in Fe-XANES-based research, however, it is

79   important to understand and quantify how dissolved water and radiation-induced

80   chemical reactions may modify the spectral features used to determine $Fe^{3+}/\Sigma Fe$ ratios.

81

82   Fe-XANES pre-edge features are sensitive to the coordination environment and oxidation

83   state of Fe (e.g. Henderson et al., 2014 and references therein). The potential effects of

84   water dissolved in silicate glass on the structural environment of Fe are therefore of great

85   interest to practitioners of XANES. In their Mössbauer studies on glasses, Wilke et al.

86   (2002, 2006) observed differences in the hyperfine fields and coordination environments

87   between hydrous and anhydrous glasses, but postulated that the differences emerged

88   during quench. Wilke and co-workers concluded that there is no detectable influence of

89   water on the local structural environment of Fe in melts. The effect of dissolved water on

90   the oxidation state of Fe in melts has been the subject of more study and debate, but

91   XANES and wet-chemical studies of mafic glasses synthesized at fixed fO_2 have shown

92   water to have no effect on $Fe^{3+}/\Sigma Fe$ ratios (Botcharnikov et al., 2005; Gaillard et al.,

93   2001; Moore et al., 1995). Given that Fe coordination affects pre-edge intensities, but not

4

94   the pre-edge centroids most commonly employed to extract $Fe^{3+}/\Sigma Fe$ ratios (Bajt et al.,

95   1994; Cottrell et al., 2009; Wilke et al., 2005), and the difficulty of independently varying

96   fO_2 and fH_2O in experimental systems, relatively little effort has been applied to

97   calibrating hydrous glasses for XANES determinations of $Fe^{3+}/\Sigma Fe$ ratios.

98

99   Electron and X-ray beam interactions with materials can shift the oxidation state of

100   various elements in biological, amorphous, and crystalline materials (e.g. Corbett et al.,

101   2007; Eeckhout et al., 2005; Shimizugawa et al., 2001; Gonçalves Ferreira et al., 2013).

102   For example, sulfur dissolved in silicate glass may become oxidized or reduced upon

103   exposure to electron and X-ray beams (Klimm et al., 2012; Rowe et al., 2007; Wilke et

104   al., 2008). Relatively little work has been done to investigate the potential effects of

105   radiation on Fe speciation in silicate glasses. Wilke et al. (2005) and Cottrell et al. (2009)

106   assessed, but saw no evidence for, radiation-induced beam damage in XANES spectra of

107   anhydrous basalt glasses collected at bending magnet sources. Shorttle et al. (2015)

108   assessed beam damage in glasses with <1 wt.% water, and observed an increase in the

109   intensity of the second pre-edge multiplet with time (radiation dose) using an

110   unattenuated undulator-source that was "barely above instrument stability" (i.e. was

111   within the noise). The study of Moussallam et al. (2016) was not able to detect beam

112   damage by analyzing successive XANES spectra collected at a single spot on glasses

113   with <1 wt.% water at an attenuated undulator-source. However, as new radiation sources

114   come online that can deliver higher flux densities to a sample, and studies of hydrous

115   silicate glass proliferate, we find it prudent to examine the potential for radiation to

116   induce beam damage.

117

118   **SAMPLES AND METHODS**

119   *Samples.* We examine 27 glasses of basaltic composition in this study: 13 anhydrous

120   basalt glasses from the study of (Cottrell et al., 2009), which are available to the

121   community upon request to Smithsonian's National Rock Collection, and 14 hydrous

122   glasses (0.72 to 4.82 wt.% dissolved total H_2O) from the study of (Botcharnikov et al.,

123   2005). For this study, all analyses were performed on double-side polished glass wafers

124   of approximately 50-100μm in thickness. Details of the experimental methods and

125   complete sample characterizations can be found in Cottrell et al. (2009), Cottrell and

126   Kelley (2011) (including wet-chemical analyses), and Botcharnikov et al. (2005).

127

128   *Analytical Methods.*

129   *Mössbauer Spectroscopy.* Cottrell et al. (2009) and Botcharnikov et al. (2005) report

130     $Fe^{3+}/\Sigma Fe$ ratios for each glass based on room temperature Mössbauer spectroscopy,

131   without correction for recoilless fraction. We re-report their results in Table 1, along with

132   new fits to the hydrous B glasses discussed below. Method details for previously reported

133   fits can be found in Cottrell et al. (2009) and Botcharnikov et al. (2005). Cottrell et al.

134   (2009) applied the distribution fitting method of Alberto et al. (1996), which adopts a

135   two-dimensional (2D) Gaussian probability distribution function for the isomer shift and

136   quadrupole splitting. This routine minimizes the error (reduced χ^2 values) between the

137   data and the absorption envelope that arises from the contribution of paramagnetic

138   quadrupole doublets. The area of the fitted ferric doublet relative to the entire absorption

139   envelope provides the $Fe^{3+}/\Sigma Fe$ ratio. Using the software package RECOIL (Lagarec and

140   Rancourt, 1998), Botcharnikov et al. (2005) applied an extended Voigt-based fitting

141   (xVBF) method that also assumes a two-dimensional Gaussian distribution of hyperfine

142   parameters for ferric and ferrous iron (Lagarec and Rancourt, 1997). The relative area

143   ratios provide the $Fe^{3+}/\Sigma Fe$ ratios, and the uncertainties estimated by Botcharnikov et al.

144   (2005) that we re-report in Table 1 reflect counting statistics, variation in the results from

145   the application of multiple fitting models, and the possible effect of neglecting the

146   recoilless fraction.

147

148   To isolate the effects of beam damage, deconvolution of the Mössbauer spectra for

149   hydrous and anhydrous glasses must be consistent. Both xVBF and Alberto et al. (1996)

150   methods fit multiple distributions (based on a Gaussian distribution of Lorentzian line

151   shapes). The site distributions derive from maxima in the probability functions that

152   describe the ferrous and ferric hyperfine field distributions (Mysen et al., 2006, and

153   references therein). Zhang et al. (submitted) show that both approaches yield consistent

154    $Fe^{3+}/\Sigma Fe$ ratios for the AII and LW glasses. To test for systematic bias between the

155   Cottrell et al. (2009) and Botcharnikov et al. (2005) approaches, we obtained the raw

156   spectra of Botcharnikov et al. (2005), collected at Bayerisches Geoinstitute, University of

157   Bayreuth, and refit 14 of them using the same methods used by Cottrell et al. (2009). This

158   ensures that our analysis of oxidative beam damage from synchrotron radiation will not

159   be affected by inter-laboratory bias in the Mössbauer fitting protocols.

160

161   *X-ray Absorption Near Edge Structure (XANES) Spectroscopy.* Cottrell et al. (2009) and

162   Botcharnikov et al. (2005) report on Fe K-edge XANES spectra collected previously for

163   the glasses used in this study. The former collected spectra at the bending magnet station

164   X26A at the National Synchrotron Light Source (NSLS), Brookhaven National

165   Laboratory, New York, USA, and the latter at the Hamburger

166   Synchrotronstrahulungslabor (HASYLAB), Hamburg, GE. Details about those facilities,

167   collection procedures, and fitting routines can be found in Cottrell et al. (2009) and

168   Botcharnikov et al. (2005).

169

170   For this study, we collected new Fe K-edge XANES spectra on the AII, LW, and B series

171   glasses in fluorescence mode in six synchrotron beam sessions: two on bending magnet

172   station X26A at NSLS in 2015, and four at station 13-ID-E (GSECARS) at the Advanced

173   Photon Source (APS), Argonne National Laboratory, IL, USA, in 2014 - 2016. We

174   applied 8 radiation dose conditions that we detail in Table 2. We cast our results in terms

175   of radiation dose so that the results can be easily generalized to other facilities and

176   beamline configurations. For these experiments it is more convenient and descriptive to

177   represent the mean energy imparted to the sample in terms of flux density, rather than in

178   the more standard SI units of Gray. However, the absorbed dose in Gray (absorption of

179   one joule of radiation energy per kilogram of sample) can be calculated by assuming an

180   average basaltic glass composition and density and the depth at which the incident

181   radiation falls to 1/e within the glass (Henke et al. 1993). For basaltic glass, the flux

182   density is equivalent to ~75-80 times the dose in Grays/sec (Table 2). As we describe

183   below, in all sessions, and at all facilities, we set the area-weighted average energy of the

184   pre-edge peaks (the centroid) equal to 7112.3 for anhydrous glass standard LW_0

185   (Cottrell et al., 2009). LW_0 is analysed frequently throughout all analytical sessions.

8

186   Normalization of all centroids to the energy drift-corrected centroid of LW_0 accounts

187   for within-session instrumental drift in the monochromator energy calibration and for

188   differences in monochromator calibration between facilities and between sessions (Bajt et

189   al., 1994; Cottrell et al., 2009). The empirical drift-corrected precision (1σ) of the area-

190   weighted centroid positions collected over a ten-year period on the AII and LW glasses is

191   0.004±0.009 eV (n for each glass = 30-50) (Zhang et al., submitted).

192

193   We did not correct for over-absorption effects (Manceau et al., 2002). In fluorescence

194   mode XANES, over-absorption can result in a decrease in the amplitude of the absorption

195   peaks in samples where the absorber mass is high. This can result in a relative increase in

196   the pre-edge peak intensities relative to the main absorption edge, but it does not impact

197   the relative intensities of the two pre-edge peak multiplets or their energy positions

198   (Botcharnikov et al., 2005; Cottrell et al., 2009; Zhang et al., 2016). Moreover, while

199   over-absorption can affect pre-edge peak intensities, all glass compositions examined

200   here have sufficiently high total FeO contents (7-12 wt.%) and thicknesses (> 50μm) to

201   be in the infinite thickness regime.

202

203   *X26A, NSLS, Brookhaven National Laboratory, USA.* NSLS (decommissioned in

204   October, 2014) operated at 2.8 GeV and 300 mA. We collected fluorescence spectra on

205   the B series glasses at bending magnet beamline X26A using summed energy dispersive

206   spectra from a 4-element Vortex ME-4 silicon drift diode detector and two single element

207   Vortex-EX detectors (Hitachi) with pulse processing provided by an XMap digital

208   spectrometer system (XIA). The first derivative of Fe K-edge spectra (E_0) collected on

209   zero-valent Fe E_0 is 7112.0 eV. All other methods details are as reported by Cottrell et al.

210   (2009). The incident beam flux at X26A was consistently ~$3x10^9$ photons/sec and the

211   spot size was 9 x 5 microns such that the photon flux density was ~ $6.7x10^7$

212   photons/sec/um^2 (Table 2); after a 15.5 minute collection the absorbed dose per spectrum

213   was ~$6x10^{10}$ photons/um^2.

214

215   *13-ID-E, GSECARS, Advanced Photon Source, Argonne National Laboratory, USA.*

216   Details regarding the beamline configuration for 13-ID-E can be found in Sutton et al.

217   (2017). This undulator-based beam line at APS operates at 7 GeV and 85-101 mA. We

218   collected fluorescence spectra with a Vortex ME4 silicon-drift diode detector array

219   coupled to a high-speed digital spectrometer system (Quantum Xpress3). A cryogenically

220   cooled double-crystal Si (311) monochromator provided the monochromatic radiation.

221   The first derivative of Fe K-edge spectra (E_0) collected on zero-valent Fe E_0 is 7110.75

222   eV. We collected spectra from 7012 to 7102 eV in 2.5 eV steps with 1 sec dwell; from

223   7102 to 7132 eV (pre-edge region) in 0.1 eV steps with 1 sec dwell and from 7132 to

224   7492 eV (XAFS region) in 2.3 angstrom steps with 1 sec dwell. We edge-step normalized

225   the spectra collected at 13-ID-E by the average intensity between 7315 and 7320eV

226   where the spectra were flat.

227

228   The 13-ID-E beamline is capable of delivering and detecting in excess of $1x10^{12}$

229   photons/sec within a focused spot size of 2 x 2 microns at the Fe K-edge, so that focused

230   flux densities of ~$5x10^{11}$ photons/sec/μm^2 are possible – four orders of magnitude higher

231   than what was possible at X26A. We collected the experimental data presented here over

232   a $\sim10^4$ range in flux density to precisely assess the spectral response to absorbed radiation

233   dose. At 13-ID-E we collected spectra using 6 protocols where incident flux density was

234   adjusted, through uspstream aperturing of the X-ray beam; through filtering using varying

235   thicknesses of aluminium foil; and through defocusing of the incident beam on the

236   sample. These conditions are reported in Table 2.

237

238   We also conducted one set of analyses at 13-ID-E under cryogenic conditions, using a

239   customized cryogenic stage described in Tappero et al. (2016, 2017), to investigate the

240   degree to which cryogenic cooling may mitigate the observed iron oxidation. We

241   collected a time series at an energy of 7113.3 eV at both ambient and cryogenic

242   conditions reported in Table 2.

243

244   *Fourier Transform Infrared (FTIR) Spectroscopy*

245   Glass chip B10 (Table 1) was analyzed by FTIR for dissolved total H_2O using a Thermo

246   Nicolet iS50 FTIR bench spectrometer coupled with a Continuum IR microscope with

247   automated mapping capability at the Graduate School of Oceanography, University of

248   Rhode Island. We mapped an area on a chip of B10 that had been purposely exposed to

249   high photon flux at beamline 13-ID-E. The map was collected using transmission FTIR

250   with a 20 x 20 μm square aperture and no overlap between pixels. Each spectrum was

251   collected over 1200-6000 cm^{-1} wavenumbers using 256 scans at 1 cm^{-1} resolution.

252   Individual transmission spectra were reduced for H_2O^{Total} after fitting the spectral

253   background with a spline function and calculating the net intensity of the absorbance

254   band at 3500 cm^{-1}. The H_2O^{Total} concentration was then calculated using the Beer-

11

255   Lambert law, a calculated density of 2.90 g/cm^3, thickness of 49±1 μm, and the molar

256   absorption coefficient ε^{3530}=63 , which is assumed constant within the compositional

257   range of basalts (Dixon et al., 1995).

258

259   **RESULTS**

260   *Mössbauer Spectra*

261   Mössbauer-derived Fe^{3+}/ΣFe ratios are not very sensitive to fitting philosophy or method,

262   but in this study we re-fit the B glass spectra acquired by Botcharnikov et al. (2005) to

263   eliminate any potential bias between the disparate fitting routines of Cottrell et al. (2009)

264   and Botcharnikov et al. (2005). In addition, our new fits allow us to report hyperfine

265   parameters for these glasses that may aid in understanding the structural environment of

266   Fe in hydrous and anhydrous glasses. We provide the Mössbauer spectra from

267   Botcharnikov et al. (2005) and our fits from this study (both raw data and plots) in the

268   Supplementary Material.

269

270   Two quadrupole doublets, one ferric with a low IS of 0.4 to 0.6 mm/s (relative to Fe

271   metal) and low QS of 0.8 to 1.1 mm/s, and one ferrous with a high isomer shift of 0.8 to

272   1.0 mm/s and quadrupole splitting of 1.9 to 2.2 mm/s, describe the Mössbauer spectra of

273   the B glasses (Table 1, and Figures S1, S2). The Botcharnikov et al. (2005) study did not

274   report hyperfine parameters, but the hyperfine parameters derived from the glass spectra

275   in this study are similar to those reported previously in the literature for silicate glasses

276   (Alberto et al., 1996; Jayasuriya et al., 2004; Mysen et al., 1985a; Zhang et al., 2016).

277   Ferrous iron IS and QS in the hydrous B glasses are within error of those for the

12

278   anhydrous glasses for all but the most highly oxidized glasses, for which the quadrupole

279   splitting in the hydrous glasses is higher. The QS for ferric iron is smaller in hydrous

280   glasses than in anhydrous glasses by approximately 0.25 to 0.45 mm/s. The IS of ferric

281   iron is slightly higher in the hydrous glasses than in the anhydrous glasses, and decreases

282   with increasing $Fe^{3+}/\Sigma Fe$ ratio, as expected (Mysen and Richet, 2005; Mysen and Virgo,

283   1989; Mysen et al., 2006). While many factors influence the coordination of ferric iron in

284   silicate glasses (Mysen and Richet, 2005), the greater ferric IS observed in the hydrous

285   glasses suggests that the O—Fe^{3+} bong length is longer, and weaker (e.g.Johnson et al.,

286   1999), and that ferric iron is in higher average coordination (greater domination of $^{VI}Fe^{3+}$)

287   in the hydrous B glasses than in the anhydrous AII and LW glasses. Higher coordination

288   of ferric iron in the hydrous glasses is consistent with results from (Wilke et al., 2002;

289   Wilke et al., 2006), and is corroborated by XANES spectra, as we discuss below.

290

291   The $Fe^{3+}/\Sigma Fe$ ratios in the B glasses, as determined by the new fits reported here, range

292   from 0.12 to 0.56, compared to 0.10 to 0.60 for those same glasses reported in

293   Botcharnikov et al. (2005). The $Fe^{3+}/\Sigma Fe$ ratios of all B glasses with nominal $Fe^{3+}/\Sigma Fe$

294   <0.50 agreed within 1σ (2.7% absolute) with the values reported by Botcharnikov et al.

295   (2005). The three glasses with $Fe^{3+}/\Sigma Fe$ ratios > 0.50 agreed within 2σ of the

296   uncertainties on the fits (4.4% absolute). These fits are within the commonly accepted

297   uncertainty of the technique, which ranges from ±1 to 6% in absolute $Fe^{3+}/\Sigma Fe$ ratio

298   (Dyar et al., 1987; Mysen et al., 1985a; Mysen et al., 1985b). $Fe^{3+}/\Sigma Fe$ ratios from the

299   Botcharnikov et al. (2005) study correlate very well with ratios obtained in this study (R^2

300   > 0.99, m = 0.9, b = 1.87). Consistent with the results of Cottrell et al. (2009), Zhang et

13

301   al. (2015), and Zhang et al. (submitted), inclusion of a second doublet in the present study

302   did not reduce the χ^2 of the fits.

303

304   *XANES*

305   *Bending Magnet Beamlines, X26A NSLS.*

306   Full XANES spectra of hydrous B and anhydrous AII and LW glasses collected at

307   bending magnet beamline X26A are shown in Figure 1. We provide spectra for AII and

308   LW anhydrous glasses for a 2014 NSLS session for reference (there is no substantive

309   change since their initial publication in Cottrell et al., 2009). As demonstrated by

310   Botcharnikov et al. (2005) for previous XANES analyses of the B glasses, the energy of

311   the main absorption edge, the ratio of pre-edge peak intensities, and the area-weighted

312   average energy of the pre-edge peaks (the centroid) in the XANES spectra shift smoothly

313   as a function of $Fe^{3+}/\Sigma Fe$ ratio (e.g., Berry et al., 2003; Botcharnikov et al., 2005; Cottrell

314   et al., 2009; Wilke et al., 2005). The shift in centroid energy provides a precise proxy for

315   $Fe^{3+}/\Sigma Fe$ ratio in basaltic glasses, especially for $Fe^{3+}/\Sigma Fe$ ratios below 0.50 (Henderson et

316   al., 2014). We report the centroids and pre-edge peak intensities for all glasses in Table 3.

317   We provide all fitting parameters in Table S2. Consistent with the results of Cottrell et al.

318   (2009), centroids obtained from spatially independent spectra are precise to $\leq \pm 0.01$ eV.

319

320   For anhydrous LW and AII glasses and hydrous B glasses, we plot the $Fe^{3+}/\Sigma Fe$ ratios

321   derived from Mössbauer fits determined by Botcharnikov et al. (2005) and this study

322   against the $Fe^{3+}/\Sigma Fe$ ratios derived from XANES at low flux using the anhydrous

323   calibration curve of Cottrell et al. (2009). Regardless of which set of Mössbauer values

14

324   are used, the $Fe^{3+}/\Sigma Fe$ ratios of the hydrous glasses fall within 1σ of a 1:1 relationship

325   (Figure 2a).

326

327   *Undulator-based Beamlines, 13-ID-E, APS.*

328   Full XANES spectra of AII, LW, and B glasses collected at insertion device beamline 13-

329   ID-E (GSECARS) are shown in Figure 1 and we provide fitting parameters in Table S2.

330

331   *Condition XANES$_1$, Anhydrous Glasses.* We report centroids (area weighted average

332   energy of the two pre-edge multiplets) under "nominal" operating conditions at 13-ID-E,

333   our condition "XANES$_1$," for each glass in Table 3.

334

335   Under normal high flux operating conditions at station 13-1D-E, we recover the $Fe^{3+}/\Sigma Fe$

336   ratios of anhydrous glasses when we use the calibration of Cottrell et al. (2009), which

337   was developed at low flux. Anhydrous glass $Fe^{3+}/\Sigma Fe$ ratios derived from XANES at

338   high flux fall within 1σ of a 1:1 relationship with the Mossbauer-derived values (Figure

339   2b). Supplemental Figure S3a and Table 3 show that high flux centroids are on average

340   within $\pm 0.008eV$ (within 1σ) of low flux centroids. One might conclude from this that the

341   centroid, as a spectral feature, is a robust proxy for assessment of the $Fe^{3+}/\Sigma Fe$ ratio for

342   anhydrous glasses. We emphasize again, however, the importance of normalizing to a

343   standard. While the centroids at the two facilities are reproducible, the individual spectral

344   features are not. Differences in modelled spectral features (Figures S3b,c,d), and the raw

345   spectra (Figure S4), reflect the smaller vertical emittance of the 13-ID-E undulator

346   electron beam compared to the X26A bending magnet source, and the optical

347   configuration at each beamline. That we reproduce the centroids of anhydrous glasses

348   across facilities to approximately ± 0.01 eV is a non-trivial result. Fiege et al. (2017) state

349   that the "overall uncertainty" in the centroid is an order of magnitude higher (± 0.1 eV).

350   We attribute the high precision we achieve primarily to ensuring that we account for

351   instrumental drift within and between analytical sessions by shifting the energy of all

352   centroids such that the centroid of LW_0 ≡ 7112.3 eV. The key result is that the

353   anhydrous glass centroids remain stable within uncertainty at all beam conditions and

354   across all facilities.

355

356   *Condition XANES$_1$, Hydrous Glasses.* At a given $Fe^{3+}/\Sigma Fe$ ratio, the centroids of hydrous

357   B glasses are variably shifted to higher values at 13-ID-E under nominal operating

358   conditions (XANES$_1$), in stark contrast to the highly reproducible anhydrous glasses

359   (Table 3). For some hydrous glasses (e.g., B20), we derive the same centroid within

360   0.003eV (within 1σ) between facilities, but for others (e.g., B11) we derive a centroid up

361   to 0.25eV higher (25σ higher) under high flux conditions than low flux conditions

362   (Figure S4). This manifests as XANES-derived $Fe^{3+}/\Sigma Fe$ ratios that are up to 1.7 times

363   higher than those derived from Mössbauer spectroscopy (Figure 2b).

364

365   *Intensity of 2nd Multiplet with Time.* To better evaluate how the Fe XANES spectra of

366   these glasses evolve with accumulated radiation dose, we conducted experiments to

367   monitor changes in the intensity of the second pre-edge multiplet at 7113.3 eV (attributed

368   to Fe^{3+}) as a function of time and flux density (i.e. dose). Glass B11 was used for this

369   experiment; it is the most hydrous in the suite under study, with 4.82 wt.% total dissolved

16

370   water. This glass is relatively reduced relative to other hydrous glasses tested, with a

371    $Fe^{3+}/\Sigma Fe = 0.19$.

372

373   Figure 3 plots the peak amplitude of the second pre-edge multiplet peak of hydrous glass

374   B11 with time, measured at high flux density and low flux density under both ambient

375   and cryogenically cooled conditions. We first consider data collected at ambient

376   temperature. Peak amplitude increases with time under high and low flux conditions, with

377   a rapid increase observed within the first 100 seconds of high flux irradiation. The higher

378   photon flux density generated by the focused beam causes a greater increase in the

379   amplitude of the second pre-edge multiplet at all time points. However, when the change

380   in amplitude is measured relative to the dose delivered, the amplitude of the second

381   multiplet (extent of damage) increases at approximately the same rate in high and low

382   flux density conditions. This evidences the dose-dependence of the spectral change.

383   While low flux beam damage does not affect the centroid of these hydrous glasses within

384   the measurement error of our calibration (Figures 2, S5), these data show that damage

385   occurs in hydrous glasses even at low flux density.

386

387   We then explored the degree to which cryogenic cooling impacts spectral evolution with

388   time. Studies over a broad range of incident beam energies show that cryo-cooling of

389   biological samples significantly reduces damage due to mass (water) loss during

390   exposure to ionizing radiation (e.g. Dubochet et al., 1988; Steinbrecht and Zierold, 2012).

391   Cryo-cooling may also potentially reduce the rate of beam-induced changes in metal

392   valence state in some materials (Corbett et al., 2007; Grabolle et al., 2006), although the

17

393   degree to which this mitigates the effects is debated (Beetz and Jacobsen, 2003; Meents

394   et al., 2010). We repeated the time series experiments described previously on sample

395   B11, with the glass held at -195°C. The measurements show the surprising result that at

396   cryogenic temperatures, under both high and low flux density conditions, the relative rate

397   of Fe oxidation increases. Beam damage is worse at cryogenic temperatures.

398

399   It is also instructive to see that spectral changes plateau under all conditions studied

400   within 3-16 minutes. It takes anywhere from approximately 4 to 30 minutes to collect an

401   entire quality XANES spectrum on glass with FeO concentrations between 5 and 10 wt.%

402   (e.g. Cottrell and Kelley, 2011; Shorttle et al., 2015). Therefore, successive XANES

403   spectra, collected at a single sample position, may not show any measurable change if

404   damage begins to plateau before acquisition of the first spectrum is finished.

405

406   *Conditions XANES$_{3, 4}$. Successive Analysis at one position.* Using glass B11 again, we

407   show in Figure 4a and Table S3 how the centroids of successive analyses on the same

408   spot in glass B11 increase if we employ condition XANES$_4$, a very low flux achieved by

409   attenuating and defocusing the beam to 50x50μm. The centroid increases approximately

410   logarithmically in energy for each successive spectrum. Contrast this with successive

411   spots at the same incident flux, but with the beam focused to 2x2μm (XANES$_3$), in which

412   case the total number of photons delivered to a given area (photons/μm^2) is higher after

413   one spectral acquisition than after successive analyses under condition XANES$_4$. The

414   centroid is commensurately higher, and plateaus after one acquisition. Consistent with

415   Cottrell et al., 2009, we observe no change in the centroid or pre-edge peak intensities

18

416   with successive analyses on anhydrous glass AII_0. Figure 4b reveals how the integrated

417   intensity (area) of the Gaussian extracted for the first multiplet (I_{Fe2+}) decreases while the

418   integrated intensity of the second multiplet (I_{Fe3+}) increases. Evolution of the spectra in

419   this manner is consistent with oxidation of Fe^{2+} to Fe^{3+}.

420

421   Observations of the raw spectra (Figure 5) confirm the spectral evolution seen in the

422   modelled parameters. Raw spectra collected sequentially at a given position on sample

423   B11, under condition $XANES_4$, show decreases in the intensity of the first pre-edge

424   multiplet and increases in intensity of the second pre-edge multiplet. In addition, we see

425   the main absorption edge move to higher energy as radiation dose accumulates. Spectral

426   changes are consistent with an increase in the average oxidation state of Fe with

427   increasing radiation dose.

428

429   *Beam Damage Persists Indefinitely*

430   To assess the longevity of beam damage, we mapped glass B11 approximately one year

431   after a session in which we investigated beam damage. In figure 6, image brightness

432   scales with the ratio between the Fe $K\alpha$ fluorescence peak amplitude at 7113.2 eV, the

433   energy maximum for the Fe^{3+} pre-edge multiplet peak, and at 7111.6 eV, the energy

434   maximum for the Fe^{2+} pre-edge multiplet peak. In the false-color inset, the bright white

435   areas correspond to previously analysed spots. From this map it is evident that areas

436   exposed to high radiation dose retain higher Fe^{3+}/Fe^{2+} ratios than adjacent areas that were

437   not exposed to the X-ray beam at least one year after exposure. Beam damage persists

438   indefinitely.

19

439

Coordination of Fe in Hydrous and Anhydrous Glasses

440

441 Figure 7 compares the summed integrated pre-edge intensities ($I_{Fe2+} + I_{Fe3+}$) of hydrous

442 and anhydrous glasses as a function of their centroids – what Wilke et al. (2001) coined a

443 "variogram." A negative non-linear correlation between coordination and oxidation state

444 is inferred for glasses as well as minerals with mixed geometries (e.g. Jackson et al.,

445 2005; Wilke et al., 2001). Because I_{Fe2+} and I_{Fe3+} are extremely sensitive to detector dead

446 time, edge-step normalization procedure, self-absorption etc., they are generally not

447 comparable between facilities and are even difficult to compare between analytical

448 sessions at the same facility (Cottrell et al., 2009). We only compare spectra acquired at

449 APS in Figure 7; these have been collected and processed under conditions as uniform as

450 can be practically achieved.

451

452 All glasses display typical pre-edge intensities indicative of 5-fold or mixed 4-fold and 6-

453 fold coordination (Wilke et al., 2001; Wilke et al., 2005). We see that hydrous glasses fall

454 along the same trend of increasing integrated pre-edge intensity with centroid energy

455 under both the high flux density condition XANES$_3$ and the low flux density condition

456 XANES$_4$. Covariation in the oxidation state and coordination of Fe in these glasses is

457 consistent with a shift in Fe coordination upon exposure to radiation only in proportion to

458 the shift in Fe oxidation state. This analysis therefore also points to actual oxidation of

459 Fe^{2+} to Fe^{3+} in the hydrous glasses.

460

461 The variogram also corroborates the site geometry analysis of the Mössbauer spectra,

20

462   which revealed higher Fe^{3+} isomer shift (and smaller quadrupole splitting) in hydrous B

463   glasses relative to anhydrous glasses (Figure S1), consistent with longer, weaker, O—

464   Fe^{3+} bonds, and Fe^{3+} in higher coordination in the hydrous glasses than the anhydrous AII

465   and LW glasses. In Figure 7, anhydrous glasses display higher integrated intensities

466   (lower average coordination) than hydrous glasses at any given centroid energy,

467   consistent with longer and weaker O—Fe^{3+} bonds in the hydrous glasses. Correcting for

468   over-absorption does not change this relationship.

469

470   **DISCUSSION**

471   *Beam Damage Mechanism*

472   The *1s* absorption edge and pre-edge peaks in *3d* transition metals, like Fe, are due to

473   electron transitions from *1s* to *3d* states (e.g. Henderson et al., 2014). Quadrupole (*1s3d*)

474   and dipole (*1s* to the *4p* character of the *3d* band) transitions are possible in silicate

475   glasses, owing to iron's mixed coordination. In XANES spectra, Fe^{2+} exhibits 2 or 3 pre-

476   edge peaks, and Fe^{3+} exhibits 1 or 2 pre-edge peaks, depending on coordination (Westre

477   et al., 1997). I_{Fe2+} and I_{Fe3+} increase as coordination number decreases (i.e. with higher

478   extents of *3d + 4p* mixing) because of the added dipole contribution (Penner-Hahn, 2005;

479   Roe et al., 1984; Westre et al., 1997). The relative integrated intensities and energies of

480   the pre-edge peaks therefore depend on the metal site geometry: the relative proportions

481   of Fe^{2+} and Fe^{3+} and their coordination as tetrahedral (4-fold) or octahedral (6-fold)

482   (Henderson et al., 2014; Wilke et al., 2001). Thus, it is necessary to evaluate the degree

483   to which the observed beam-induced changes in the XANES spectra reflect changes in

484   effective Fe valence as compared to coordination, particularly since in glasses these

21

485   effects are coupled.

486

487   We considered the possibility that exposure to radiation in hydrous glasses, but not

488   anhydrous glasses, might increase *3d-4p* hybridization of Fe^{3+} centers. For example,

489   Fe^{3+}—OH^- bonds could respond differently to radiation than Fe^{3+}—O bonds. Augmented

490   hybridization of Fe^{3+} centers in hydrous glasses would increase the dipole contribution to

491   the second multiplet, increase its integrated intensity, and increase the centroid, without

492   any change in the actual average oxidation state of Fe. Yet, several lines of evidence

493   argue against this possibility. First, upon exposure to a high photon flux density, the

494   XANES spectra of the hydrous glasses show that the Fe^{3+} multiplet integrated intensity

495   increases and the Fe^{2+} multiplet intensity concomitantly decreases (Figure 4). Moreover,

496   the white line shifts to progressively higher energy as well (Figure 5).   These three

497   spectral changes together are much more consistent with oxidation of Fe^{2+} to Fe^{3+} than an

498   increase in *3d-4p* hybridization, as the latter would result in neither a decrease in the

499   intensity of the first multiplet, nor a shift in the main edge.

500

501   Because no measurable change in the XANES spectra is observed as a function of dose in

502   spectra collected from anhydrous glasses (e.g. Figures 2, 4), we hypothesize that the

503   changes we observe in the spectra of hydrous B glasses with exposure to ionizing

504   radiation relates to their dissolved water contents. Here we use $Fe^{3+}/\Sigma Fe_{Möss}$ −

505    $Fe^{3+}/\Sigma Fe_{XANES}$ as a proxy for beam-induced Fe oxidation, where Mössbauer spectra

506   establish the "true" $Fe^{3+}/\Sigma Fe$ ratio, and the XANES centroid the "apparent" $Fe^{3+}/\Sigma Fe$

507   ratio (Table 3). Indeed, when we compare glass B8 to B16, glasses of similar $Fe^{3+}/\Sigma Fe$

22

508   ratio, we see that the centroid of glass B16, with > 3.6 times more dissolved water, is

509   overestimated by ~70%, whereas the centroid of glass B8 is overestimated by ~27%

510   when exposed to the same radiation dose. Figure 8a shows, however, that total dissolved

511   H_2O in the glasses does not correlate with beam-induced Fe oxidation. For example, the

512   anhydrous XANES calibration of Cottrell et al. (2009) predicts the $Fe^{3+}/\Sigma Fe$ ratio of

513   hydrous glass B17, with 4.67 wt.% total water, within error of its "true" value, while the

514   centroid of B11, with nearly indistinguishable dissolved water content, is overestimated

515   by >70% (Figure 4, 11). The latter overestimation of $Fe^{3+}/\Sigma Fe$ ratio leads to

516   overestimation of f_{O2} by two orders of magnitude.

517

518   Following this, it is also clear that when the initial oxidation state of Fe is high, the

519   spectral response to radiation (beam damage) is lessened (Figure 8b). Upon exposure to

520   the same high photon dose (condition $XANES_1$), the $Fe^{3+}/\Sigma Fe$ ratios of hydrous glasses

521   with lower $Fe^{3+}/\Sigma Fe$ ratios are greatly overestimated in comparison to glasses with higher

522   $Fe^{3+}/\sum Fe$ ratios, which appear to be well predicted by the Mössbauer calibration (R^2

523   linear correlation = 0.53; R^2 exponential correlation = 0.72, Figure 8b).

524

525   All the evidence suggests to us that the mechanism of Fe oxidation involves breaking of

526   O—H bonds by incident ionizing radiation, loss of hydrogen, and concomitant oxidation

527   of Fe^{2+} to Fe^{3+}. One possible reaction, analogous to that proposed for radiation-induced

528   oxidation of S dissolved in hydrous silicate glasses by Klimm et al. (2012) is:

$$H_2O + 2Fe^{2+}O \rightarrow H_2^{\uparrow}{}_{(gas?)} + Fe_2^{3+}O_3$$
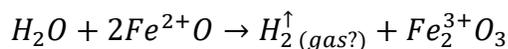
529   The loss of hydrogen gas is consistent with the longevity of the beam damage, as

23

530   discussed above and shown in Figure 6. This mechanism is also consistent with the

531   observed dependence on both the initial $Fe^{3+}/\Sigma Fe$ ratio and the dissolved water content of

532   the hydrous glass.

533

534   The hypothesized mechanism suggests that a fruitful metric for predicting the

535   susceptibility of hydrous glass to beam damage is the molar ratio of dissolved total water

536   to the ferric/ferrous ratio as determined by Mössbauer spectroscopy

537   ($\Phi=XHO_{1.5}*XFeO/XFeO_{1.5}$ ratio) (Table 1). We find that beam damage susceptibility,

538   Φ, correlates strongly with the extent to which high photon flux $XANES_1$ overestimates

539   the $Fe^{3+}/\Sigma Fe$ ratio ($R^2 = 0.92$, n=14, $b \equiv 0$ because anhydrous glasses show no damage)

540   (Figure 8c).

541

542   Inspection of the raw spectra of the B glasses under conditions $XANES_3$ and $XANES_4$

543   confirms that spectral changes increase as a function of dose and increasing Φ, with

544   anhydrous glasses showing no spectral change (Figure 9). Visual inspection also verifies

545   that the spectral features all evolve in a manner consistent with oxidation of ferrous iron

546   to ferric iron: I_{Fe2+} falls; I_{Fe3+} grows; and the K edge shifts to higher energy. Spectral

547   changes increase in proportion to Φ. We provide the raw spectra for Figure 9 in Table S4.

548

549   We tested this hypothesis by subjecting glass B10 to a 25 μm beam of high photon flux

550   of $\sim 1\times 10^{12}$ photons/sec for $\sim$ 12 minutes (Figure 10). We subsequently mapped the area

551   surrounding this spot on the sample via Fourier Transform Infrared spectroscopy (FTIR).

552   The FTIR data show that the area of the glass adjacent to the exposed spot (e.g., pixel 1,

24

553   Figure 10) also has significantly lower dissolved H_2O than areas of the glass distant from

554   exposure (e.g., pixel 2, Figure 10). We reduced individual FTIR spectra from pixels 1 and

555   2 by fitting the background of the total H_2O absorption band at 3500 cm^{-1} with a spline

556   function that was then subtracted from the spectra before measuring the band height. This

557   analysis shows that pixel 2, away from the potential damage zone, has a total dissolved

558   H_2O content of 2.43 wt.%, which is identical to the reported H_2O content for this glass by

559   Botcharnikov et al. (2005). The dissolved H_2O content of pixel 1, however, is 900 ppm

560   lower (2.34 wt.%). Pixel 1 is not coincident with the location of the XANES beam at the

561   sample surface. Rather, the incident X-ray beam intersects the sample surface at a 45°

562   angle relative to the FTIR incident beam, which is normal to the sample surface. The high

563   flux X-ray beam travelled through the sample, from right to left in Figure 10, at 45°

564   angle, and thus interacted with the glass chip to the left of the beam cross-hair location.

565   We conclude from this assessment that exposure of this sample to a high-flux XANES

566   beam caused both oxidation of Fe and loss of H_2O from the glass, which supports the

567   proposed mechanism of Fe oxidation via hydrogen loss. We note that only a few percent

568   of the Fe fluorescence we measure comes from the sample surface. The geometrical

569   considerations we present above and the magnitude of the spectral changes and water loss

570   we observe require chemical changes to the bulk affected volume. Damage cannot be

571   limited to the sample surface.

572

573   Cryo-cooling has been shown to mitigate beam damage (e.g. Steinbrecht and Zierold,

574   2012; Corbett et al., 2007). Our finding that cryo-cooling exacerbated Fe^{2+} oxidation in

575   hydrous glass is an important and counterintuitive observation. We have shown that

25

576   hydrogen concentrations in the glass are lower in areas that have experienced oxidizing

577   beam damage, consistent with radiation-induced breaking of O—H bonds, and

578   preferential diffusion of hydrogen, relative to oxygen, away from the area. Because it is

579   the relative diffusivity of hydrogen and oxygen that matters, and diffusivity depends

580   strongly on temperature, we speculate that oxygen is able to diffuse farther from the

581   analysed spot in the room temperature case than the cryo-cooled case (whereas hydrogen

582   is always able to diffuse away). This may be why cryo-cooling is counterproductive

583   when attempting to mitigate radiation-induced oxidation of Fe in hydrous silicate glass.

584   Indeed, Gonçalves Ferreira et al. (2013) found that heating soda-lime glasses to 500°C

585   actually mitigated radiation-induced *reduction* of iron, emphasizing that the effect of

586   temperature on beam damage will depend on the nature and mechanism of beam damage

587   and is difficult to predict a priori.

588

589   **IMPLICATIONS**

590   *Prior XANES studies of hydrous glasses*

591   We have shown that synchrotron radiation causes progressive changes to the XANES

592   spectra of hydrous glasses, but not anhydrous glasses, as a function of radiation dose.

593   Spectral changes are consistent with preferential migration of hydrogen relative to

594   oxygen, and oxidation of iron, in the analysis spot. Our study reveals that oxidative beam

595   damage occurs in hydrous glasses even at the lowest flux densities achieved, but that

596   damage is not detectable outside of the error of anhydrous calibrations with exposure to

597   radiation doses typically found at bending magnet sources. Conversely, it would be

598   prudent to re-evaluate results from studies carried out on hydrous glasses at undulator

26

599   beam lines using a focused spot.

600

601   Mafic glasses may be synthesized experimentally with a wide range of Φ

602   ($XHO_{1.5}$*$XFeO$/$XFeO_{1.5}$) that may readily exceed those investigated in this study. Most

603   naturally occurring basaltic glasses, however, will have $0 < \Phi < 1$. For example, basaltic

604   glass inclusions in volcanic rocks from subduction zones have Φ ranging from ~0.34 to

605   ~1; natural basaltic glasses from sea floor volcanoes erupting in back arc basins have

606   ratios ranging from ~0.2 to ~0.6; and mid-ocean ridge basalts have ratios between ~0.05

607   to ~0.28 (ranges estimated from data in Brounce et al. 2014b; Cottrell and Kelley, 2011;

608   Kelley and Cottrell, 2012; Zhang et al., submitted). Based on the work presented here, all

609   submarine basalts and undegassed melt inclusions would suffer significant beam damage

610   under nominal acquisition conditions (i.e. a focused beam) at unattenuated undulator

611   beam lines. We have also shown, however, that a radiation dose of $\leq 6 \times 10^{7}$

612   photons/sec/μm^{2} mitigates (but does not prevent) beam damage on hydrous glasses with

613   Φ up to ~1.

614

615   We hypothesize that previous studies conducted at undulator beam lines have not

616   detected beam damage in hydrous glasses because, under nominal operating conditions,

617   radiation damage is maximum or "complete" after acquisition of a single spectrum (~600

618   seconds for spectra acquired under condition $XANES_1$). Collection of multiple spectra at

619   a single position on the glass under condition $XANES_1$ will therefore return the same

620   centroid because damage is complete ("saturated") before the pre-edge is scanned the

621   first time (e.g. Moussallam et al., 2016; Moussallam et al., 2014). For materials with

27

622   relatively low Φ, it may be sufficient at an undulator source to attenuate the beam to

623   prevent beam damage from exceeding detection limits (e.g. Shorttle et al., 2015). We

624   have shown here, however, that even at the lowest fluxes achievable at 13-ID-E,

625   attenuation is insufficient to prevent beam damage; the beam must also be defocused.

626

627   *Recommended analytical protocols for acquisition of Fe-XANES spectra on hydrous*

628   *glasses*

629   Synchrotron radiation causes progressive changes to the XANES spectra of hydrous

630   glasses as a function of radiation dose and Φ. Dose is a function of photon flux, beam

631   diameter, and exposure time, and can/should be calculated and reported for any

632   synchrotron experiment. Attenuating the beam, defocusing the spot, or both, may

633   mitigate beam damage. Using a cryostat is unlikely to mitigate beam damage; it may

634   even exacerbate damage. This study suggests that a radiation dose of $\leq 6 \times 10^7$

635   photons/sec/μm^2 will allow the centroids of most terrestrial basalts to lie within analytical

636   error of anhydrous calibration curves. We emphasize that beam damage must be assessed

637   at each beamline and for the specific materials under analysis in a given study.

638

639   **ACKNOWLEDGEMENTS**

645 from Smithsonian's Scholarly Studies program. FD also acknowledges support from a

646 National Museum of Natural History Peter Buck Fellowship. We are grateful for support

647 for X26A from Department of Energy (DOE) GeoSciences DE-FG02-92ER14244. The

648 DOE Office of Science supported use of the NSLS under Contract No. DE-AC02-

649 98CH10886. We acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is

650 supported by the National Science Foundation - Earth Sciences (EAR-1128799), and the

651 Department of Energy, Geosciences (DE-FG02-94ER14466). This research used

652 resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of

653 Science User Facility operated for the DOE Office of Science by Argonne National

654 Laboratory under Contract No. DE-AC02-06CH11357. We thank editorial handling by

655 Sasa Bajt and Keith Putirka as well as two anonymous reviewers for constructive

656 comments that improved the submission.

657

658

REFERENCES

Alberto, H.V., Pinto da Cunha, J.L., Mysen, B.O., Gil, J.M., and Ayres de Campos, N. (1996) Analysis of Mossbauer spectra of silicate glasses using a two-dimensional Gaussian distribution of hyperfine parameters. Journal of Non-Crystalline Solids, 194, 48-57.

Arlot, S. and Celisse, A. (2010) A survey of cross-validation procedures for model 655 selection. Statist. Surv. 4, 40-79.

Bajt, S., Sutton, S.R., and Delaney, J.S. (1994) X-Ray Microprobe Analysis of Iron Oxidation-States in Silicates and Oxides Using X-Ray-Absorption near-Edge Structure (Xanes). Geochimica Et Cosmochimica Acta, 58(23), 5209-5214.

Beetz, T., and Jacobsen, C. (2003) Soft X-ray radiation-damage studies in PMMA using a cryo-STXM. Journal of Synchrotron Radiation, 10(3), 280-283.

Berry, A.J., O'Neill, H.S.C., Jayasuriya, K.D., Campbell, S.J., and Foran, G.J. (2003) XANES calibrations for the oxidation state of iron in a silicate glass. American Mineralogist, 88(7), 967-977.

Botcharnikov, R.E., Koepke, J., Holtz, F., McCammon, C., and Wilke, M. (2005) The effect of water activity on the oxidation and structural state of Fe in a ferro-basaltic melt. Geochimica Et Cosmochimica Acta, 69(21), 5071-5085.

Brounce, M., Kelley, K., and Cottrell, E. (2014a) Variations in $Fe3+/\sum Fe$ of Mariana arc basalts and mantle wedge fO2. Journal of Petrology, 55(12), 2513-2536.

Brounce, M., Kelley, K.A., and Cottrell, E. (2014b) The $Fe3+/\Sigma Fe$ variations in Mariana Arc basalts and primary fO2 of the mantle wedge. Journal of Petrology, 55(12), 2513-2536.

Carmichael, I.S.E. (1991) The Redox States of Basic and Silicic Magmas - a Reflection of Their Source Regions. Contributions to Mineralogy and Petrology, 106(2), 129-141.

Corbett, M.C., Latimer, M.J., Poulos, T.L., Sevrioukova, I.F., Hodgson, K.O., and Hedman, B. (2007) Photoreduction of the active site of the metalloprotein putidaredoxin by synchrotron radiation. Acta Crystallographica Section D: Biological Crystallography, 63(9), 951-960.

Cottrell, E., and Kelley, K.A. (2011) The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. Earth and Planetary Science Letters, 305(3-4), 270-282.

Cottrell, E., Kelley, K.A., Lanzirotti, A., and Fischer, R.A. (2009) High-precision determination of iron oxidation state in silicate glasses using XANES. Chemical Geology, 268(3-4), 167-179.

Dixon, J.E., Stolper, E.M., and Holloway, J.R. (1995) An experimental study of water and carbon dioxide solubilities in mid ocean ridge basaltic liquids .1. Calibration and solubility models. Journal of Petrology, 36(6), 1607-1631.

Dubochet, J., Adrian, M., Chang, J.-J., Homo, J.-C., Lepault, J., McDowall, A.W., and Schultz, P. (1988) Cryo-electron microscopy of vitrified specimens. Quarterly reviews of biophysics, 21(2), 129-228.

Dyar, M.D., Breves, E.A., Gunter, M.E., Lanzirotti, A., Tucker, J.M., Carey, C., Peel, S.E., Brown, E.B., Oberti, R., and Lerotic, M. (2016) Use of multivariate analysis for synchrotron micro-XANES analysis of iron valence state in amphiboles. American Mineralogist, 101(5), 1171-1189.

Dyar, M.D., Naney, M.T., and Swanson, S.E. (1987) Effects of Quench Methods on Fe3+/Fe2+ Ratios - a Mossbauer and Wet-Chemical Study. American Mineralogist, 72(7-8), 792-800.

Eeckhout, S.G., Neisius, T., and Castañeda, C. (2005) Oxidation effects in beryl induced by synchrotron radiation. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 229(1), 73-77.

Fiege, A., Ruprecht, P., Simon, A.C., Bell, A.S., Göttlicher, J., Newville, M., Lanzirotti, T., and Moore, G. (2017) Calibration of Fe XANES for high-precision determination of Fe oxidation state in glasses: Comparison of new and existing results obtained at different synchrotron radiation sources. American Mineralogist, 102(2), 369-380.

Frost, B.R. (1991) Introduction to oxygen fugacity and its petrologic importance. In D.H. Lindsley, Ed. Oxide minerals: Petrologic and magnetic significance, 25, p. 1-9. BookCrafters Inc., Chelsea, MI.

Gaetani, G.A., O'Leary, J.A., Shimizu, N., Bucholz, C.E., and Newville, M. (2012) Rapid reequilibration of H2O and oxygen fugacity in olivine-hosted melt inclusions. Geology, 40(10), 915-918.

30

710   Gaillard, F., Scaillet, B., Pichavant, M., and Beny, J.L. (2001) The effect of water and fO(2) on the ferric-
711   ferrous ratio of silicic melts. Chemical Geology, 174(1-3), 255-273.
712   Grabolle, M., Haumann, M., Müller, C., Liebisch, P., and Dau, H. (2006) Rapid loss of structural motifs in
713   the manganese complex of oxygenic photosynthesis by X-ray irradiation at 10–300 K. Journal of
714   Biological Chemistry, 281(8), 4580-4588.
715   Gonçalves Ferreira, P., de Ligny, D., Lazzari, O., Jean, A., Cintora Gonzalez, O., and Neuville, D.R. (2013)
716   Photoreduction of iron by a synchrotron X-ray beam in low iron content soda-lime silicate glasses.
717   Chemical Geology, 346, 106-112.
718   Helz, R., Cottrell, E., Brounce, M., and Kelley, K. (2017) Olivine-melt relationships and syneruptive redox
719   variations in the 1959 eruption of Kīlauea Volcano as revealed by XANES. Journal of
720   Volcanology and Geothermal Research, 333, 1-14.
721   Henderson, G.S., de Groot, F.M.F., and Moulton, B.J.A. (2014) X-ray Absorption Near-Edge Structure
722   (XANES) Spectroscopy. Reviews in Mineralogy and Geochemistry, 78(1), 75-138.
723   B.L. Henke, E.M. Gullikson, and J.C. Davis. (1993) X-ray interactions: photoabsorption, scattering,
724   transmission, and reflection at E=50-30000 eV, Z=1-92. Atomic Data and Nuclear Data Tables
725   Vol. 54 (no.2), 181-342.
726   Jackson, W.E., F., F., Yeager, M., Mabrouk, P.A., Rossano, S., Waychunas, G.A., Solomon, E.I., and
727   Brown, G.E. (2005) Multi-spectroscopic study of Fe(II) in silicate glasses: Implications for the
728   coordination environment of Fe(II) in silicate melts. Geochimica Et Cosmochimica Acta, 69,
729   4315.
730   Jayasuriya, K.D., O'Neill, H.S., Berry, A.J., and Campbell, S.J. (2004) A Mossbauer study of the oxidation
731   state of Fe in silicate melts. American Mineralogist, 89(11-12), 1597-1609.
732   Johnson, J., Johnson, C., Holland, D., Mekki, A., Appleyard, P., and Thomas, M. (1999) Transition metal
733   ions in ternary sodium silicate glasses: a Mössbauer and neutron study. Journal of non-crystalline
734   solids, 246(1), 104-114.
735   Kelley, K.A., and Cottrell, E. (2009) Water and the Oxidation State of Subduction Zone Magmas. Science,
736   325(5940), 605-607.
737   -. (2012) The influence of magmatic differentiation on the oxidation state of Fe in a basaltic arc magma.
738   Earth and Planetary Science Letters, 329, 109-121.
739   Klimm, K., Kohn, S.C., O'Dell, L.A., Botcharnikov, R.E., and Smith, M.E. (2012) The dissolution
740   mechanism of sulphur in hydrous silicate melts. I: Assessment of analytical techniques in
741   determining the sulphur speciation in iron-free to iron-poor glasses. Chemical Geology, 322-323,
742   237-249.
743   Kress, V.C., and Carmichael, I.S.E. (1991) The compressibility of silicate liquids containing Fe2O3 and the
744   effect of composition, temperature, oxygen fugacity and pressure on their redox states.
745   Contributions to Mineralogy and Petrology, 108, 82-92.
746   Lagarec, K., and Rancourt, D.G. (1998) RECOIL, Mössbauer spectral analysis software for windows
747   (version 1.0). Department of Physics, University of Ottawa, Canada.
748   Lagarec, K., and Rancourt, D. (1997) Extended Voigt-based analytic lineshape method for determining N-
749   dimensional correlated hyperfine parameter distributions in Mössbauer spectroscopy. Nuclear
750   Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and
751   Atoms, 129(2), 266-280.
752   Le Voyer, M., Cottrell, E., Kelley, K.A., Brounce, M., and Hauri, E.H. (2015) The effect of primary versus
753   secondary processes on the volatile content of MORB glasses: An example from the equatorial
754   Mid- Atlantic Ridge (5° N–3° S). Journal of Geophysical Research: Solid Earth, 120(1), 125-144.
755   Matjuschkin, V., Brooker, R.A., Tattitch, B., Blundy, J.D., and Stamper, C.C. (2015) Control and
756   monitoring of oxygen fugacity in piston cylinder experiments. Contributions to Mineralogy and
757   Petrology, 169(1), 1-16.
758   Meents, A., Gutmann, S., Wagner, A., and Schulze-Briese, C. (2010) Origin and temperature dependence
759   of radiation damage in biological samples at cryogenic temperatures. Proceedings of the National
760   Academy of Sciences, 107(3), 1094-1099.
761   Moor, J., Fischer, T., Sharp, Z., King, P., Wilke, M., Botcharnikov, R., Cottrell, E., Zelenski, M., Marty,
762   B., and Klimm, K. (2013) Sulfur degassing at Erta Ale (Ethiopia) and Masaya (Nicaragua)

763   volcanoes: Implications for degassing processes and oxygen fugacities of basaltic systems.
764   Geochemistry, Geophysics, Geosystems, 14(10), 4076-4108.

765 Moore, G., Righter, K., and Carmichael, I.S.E. (1995) The Effect of Dissolved Water on the Oxidation-
766   State of Iron in Natural Silicate Liquids. Contributions to Mineralogy and Petrology, 120(2), 170-
767   179.

768 Moussallam, Y., Edmonds, M., Scaillet, B., Peters, N., Gennaro, E., Sides, I., and Oppenheimer, C. (2016)
769   The impact of degassing on the oxidation state of basaltic magmas: A case study of Kīlauea
770   volcano. Earth and Planetary Science Letters, 450, 317-325.

771 Moussallam, Y., Oppenheimer, C., Scaillet, B., Gaillard, F., Kyle, P., Peters, N., Hartley, M., Berlo, K., and
772   Donovan, A. (2014) Tracking the changing oxidation state of Erebus magmas, from mantle to
773   surface, driven by magma ascent and degassing. Earth and Planetary Science Letters, 393, 200-
774   209.

775 Mysen, B.O., Carmichael, I.S.E., and Virgo, D. (1985a) A Comparison of Iron Redox Ratios in Silicate-
776   Glasses Determined by Wet-Chemical and Fe-57 Mossbauer Resonant Absorption Methods.
777   Contributions to Mineralogy and Petrology, 90(2-3), 101-106.

778 Mysen, B.O., and Richet, P. (2005) Silicate Glasses and Melts - Properties and Structure. 548 p. Elsevier,
779   New York.

780 Mysen, B.O., and Virgo, D. (1989) Redox equilibria, structure, and properties of Fe-bearing
781   aluminosilicate melts: Relationships between temperature, composition, and oxyen fugacity in the
782   system Na2O-Al2O3-SiO2-FeO. American Mineralogist, 74, 58-76.

783 Mysen, B.O., Virgo, D., Neumann, E.R., and Seifert, F.A. (1985b) Redox Equilibria and the Structural
784   States of Ferric and Ferrous Iron in Melts in the System Cao-Mgo-Al2o3-Sio2-Fe-O -
785   Relationships between Redox Equilibria, Melt Structure and Liquidus Phase-Equilibria. American
786   Mineralogist, 70(3-4), 317-331.

787 Penner-Hahn, J.E. (2005) X-ray Absorption Spectroscopy.

788 Roe, A., Schneider, D., Mayer, R., Pyrz, J., Widom, J., and Que Jr, L. (1984) X-ray absorption
789   spectroscopy of iron-tyrosinate proteins. Journal of the American Chemical Society, 106(6), 1676-
790   1681.

791 Rowe, M.C., Kent, A.J.R., and Nielsen, R.L. (2007) Determination of sulfur speciation and oxidation state
792   of olivine hosted melt inclusions. Chemical Geology, 236(3-4), 303-322.

793 Sack, R.O., Carmichael, I.S.E., Rivers, M., and Ghiorso, M.S. (1980) Ferric-Ferrous Equilibria in Natural
794   Silicate Liquids at 1bar. Contributions to Mineralogy and Petrology, 75(4), 369-376.

795 Shimizugawa, J., Umesaki, M., Hanada, M., Sakai, M., and Qiu, M. (2001) X-ray induced reduction of rare
796   earth ion doped in Na2O-Al2O3-B2O3 glasses. Journal of synchrotron radiation, 8(2), 797-799.

797 Shorttle, O., Moussallam, Y., Hartley, M.E., Maclennan, J., Edmonds, M., and Murton, B.J. (2015) Fe-
798   XANES analyses of Reykjanes Ridge basalts: Implications for oceanic crust's role in the solid
799   Earth oxygen cycle. Earth and Planetary Science Letters, 427, 272-285.

800 Stamper, C., Melekhova, E., Blundy, J., Arculus, R., Humphreys, M., and Brooker, R. (2014) Oxidised
801   phase relations of a primitive basalt from Grenada, Lesser Antilles. Contributions to Mineralogy
802   and Petrology, 167(1), 954.

803 Steinbrecht, R.A., and Zierold, K. (2012) Cryotechniques in biological electron microscopy. Springer
804   Science & Business Media.

805 Sutton, S.R., Lanzirotti, A., Newville, M., Rivers, M.L., Eng, P., and Lefticariu, L. (2017) Spatially
806   Resolved Elemental Analysis, Spectroscopy and Diffraction at the GSECARS Sector at the
807   Advanced Photon Source. Journal of Environment Quality, 0(0), 0.

808 Tappero, R., Smith, R.J., Acerbo, A.S., DiFabio, J., and Miller, L. (2016) Can cryo-cooling mitigate
809   chemical changes for hydrated samples? International Conference on X-ray Microscopy.

810 Tappero, R., Smith, R.J., Acerbo, A.S., Lanzirotti, A., Newville, M., Sutton, S.R., Northrup, P., O'Hara, S.,
811   and Miller, L.M. (2017) A portable cryostage system for X-ray fluorescence microprobes. 14th
812   International Conference on the Biogeochemistry of Trace Elements (ICOBTE).

813 Westre, T.A., Kennepohl, P., DeWitt, J.G., Hedman, B., Hodgson, K.O., and Solomon, E.I. (1997) A
814   Multiplet Analysis of Fe K-Edge 1s-3d Pre-Edge Features of Iron Complexes. Journal of
815   American Chemical Society, 119, 6297-6314.

816   Wilke, M., Behrens, H., Burkhard, D.J.M., and Rossano, S. (2002) The oxidation state of iron in silicic
817   melt at 500 MPa water pressure. Chemical Geology, 189(1-2), 55-67.
818   Wilke, M., Farges, F., Petit, P.-E., Brown, G.E., Jr., and Martin, F. (2001) Oxidation state and coordination
819   of Fe in minerals: An Fe K-XANES spectroscopic study. American Mineralogist, 86(5-6), 714-
820   730.
821   Wilke, M., Jugo, P.J., Klimm, K., Susini, J., Botcharnikov, R., Kohn, S.C., and Janousch, M. (2008) The
822   origin of S4+ detected in silicate glasses by XANES. American Mineralogist, 93(1), 235-240.
823   Wilke, M., Partzsch, G.M., Bernhardt, R., and Lattard, D. (2005) Determination of the iron oxidation state
824   in basaltic glasses using XANES at the K-edge. Chemical Geology, 220(1-2), 143-161.
825   Wilke, M., Schmidt, C., Farges, F., Malavergne, V., Gautron, L., Simionovici, A., Hahn, M., and Petit, P.E.
826   (2006) Structural environment of iron in hydrous aluminosilicate glass and melt-evidence from X-
827   ray absorption spectroscopy. Chemical Geology, 229(1-3), 144-161.
828   Zhang, H.L., Cottrell, E., Hirschmann, M.M., and Kelley, K.A. (submitted) Determination of Fe3+/ΣFe of
829   XANES basaltic glass standards by Mössbauer spectroscopy and its application to the oxidation
830   state of iron in MORB. Chemical Geology.
831   Zhang, H.L., Hirschmann, M.M., Cottrell, E., Newville, M., and Lanzirotti, A. (2016) Structural
832   environment of iron and accurate determination of Fe3+/ΣFe ratios in andesitic glasses by XANES
833   and Mössbauer spectroscopy. Chemical Geology, 428, 48-58.
834   Zhang, H.L., Solheid, P.A., Lange, R.A., von der Handt, A., and Hirschmann, M.M. (2015) Accurate
835   determination of Fe3+/∑Fe of andesitic glass by Mössbauer spectroscopy. American Mineralogist,
836   100(8-9), 1967-1977.

837
838
839

840   **FIGURE CAPTIONS**

841

842   **Figure 1.** XANES spectra for hydrous B glasses and anhydrous LW and AII glasses

843   under three radiation dose conditions. Left hand panels show full spectra; right hand

844   panels magnify the pre-edge region. Spectra are color-coded by relative $Fe^{3+}/\Sigma Fe$ ratio as

845   determined by Mössbauer spectroscopy (black are the most reduced glasses, grading

846   through red and orange to yellow, which are the most oxidized glasses). Note the

847   smooth, monotonic, decrease in the intensity in the first pre-edge multiplet and increase

848   in intensity of the second pre-edge multiplet as a function of $Fe^{3+}/\Sigma Fe$ ratio for the

849   hydrous samples under the bending magnet and low radiation dose conditions, and the

850   anhydrous glasses under all dose conditions. Spectra of hydrous B glasses under the high

851   radiation dose condition do not evolve systematically as a function of $Fe^{3+}/\Sigma Fe$ ratio.

852

853   **Figure 2. (A)** $Fe^{3+}/\Sigma Fe$ ratios determined by Mössbauer spectroscopy versus $Fe^{3+}/\Sigma Fe$

854   ratios determined by XANES at a flux of 10^{6-7} photons/sec/μm^2 using the anhydrous

855   basalt calibration curve of Cottrell et al. (2009). Filled circles: anhydrous basalts, Cottrell

856   et al. (2009). Open squares: hydrous basalts, Botcharnikov et al (2005). Filled squares

857   and filled triangles: hydrous basalts, this study. The anhydrous basalts, on which this

858   calibration is based, fall slightly off the 1:1 line because we have used the average

859   centroid of these glasses collected over a 10 year period (n=30-50 per glass) as reported

860   in Zhang et al. (submitted) to highlight the reproducibility of the measurement. **(B)** The

861   same analysis as in (A), but at a higher flux of 10^{10} photons/sec/μm^2. Vertical 1σ error

862   bars are smaller than the symbol sizes. Horizontal 1σ error bars are the errors on the

863   Mössbauer determinations. Dashed lines show the predictive capability of the model

864   using a leave-one-out cross validation method (Arlot and Celisse, 2010). The root mean

865   square uncertainty for the predicted $Fe^{3+}/\Sigma Fe$ ratios of unknowns determined from the

866   basaltic calibration is $<\pm0.01$ (1σ).

867

868   **Figure 3.** Time-dependence of the intensity of the second pre-edge multiplet ($\Delta FeK\alpha/IO$)

869   during exposure to synchrotron radiation under four beam conditions: high flux density

870   (filled squares) and low flux density (open circles); and at ambient temperature (red) and

871   with the sample cryogenically cooled to -195°C (blue). The intensity of the second pre-

872   edge multiplet is higher (i.e. more radiation-induced oxidative beam damage) when the

873   sample is cryogenically cooled under both beam conditions.

874

875   **Figure 4.** Evolution of spectral features as a function of spectrum number (proxy for

34

876   dose) for spectra acquired in succession in the same position on the sample for hydrous

877   glass B11 and anhydrous glass AII. **(A)** Evolution of centroids under two beam

878   conditions, high radiation dose condition $XANES_3$ ('+' and 'x' symbols) and low

879   radiation dose condition $XANES_4$ (circles and triangles). Centroids of successive spots on

880   anhydrous glass AII show no significant changes under either beam condition.

881   Application of a high radiation dose, typical of focused beams at undulator beamlines,

882   does not result in significant changes to the centroids of successive spectra on the same

883   spot of hydrous glass B11; however, centroids acquired using a high radiation dose are

884   higher than centroids collected on the same sample at low radiation dose. Significant

885   increases in the centroids of successive spots on hydrous glass B11 only become apparent

886   using a low radiation dose. Vertical 1σ error bars are smaller than the symbol sizes.

887   **(B)** Evolution of I_{Fe2+} and I_{Fe3+} with successive spectra taken at the same position under

888   low radiation dose condition $XANES_4$. Vertical 1σ error bars are smaller than the symbol

889   sizes.

890

891   **Figure 5. (A)** Evolution the background-subtracted pre-edge, acquired via successive

892   analyses in the same sample position, as a function of radiation dose, using condition

893    $XANES_4$. As the total dose increases, the intensity of the first pre-edge multiplet

894   decreases while the second increases**. (B)** The main edge moves to progressively higher

895   energy as dose increases.

896

897   **Figure 6.** The grey-scale image is a peak amplitude map collected at ~7113.2 eV (energy

898   of 2nd pre-edge multiplet) of hydrous glass B11. Image color is scaled to maximum

899   intensity, where white is high and black is low. The inset map is a peak amplitude map

900   collected at 7113.2/7111.6eV (peak amplitude of the 2nd pre-edge multiplet divided by

901   the peak amplitude of the 1st pre-edge multiplet). Image color is scaled to maximum peak

902   amplitude, where white is high and red is low. White areas show spots analysed >1 year

903   earlier.

904

905   **Figure 7.** A "variogram" showing the spectral characteristics of centroid versus

906   integrated pre-edge intensity (area) of Fe in end-member structural environments (large

907   empty circles) from Wilke et al., 2001 and glasses from this study. Anhydrous (black

908   circles) and hydrous glass (red and blue squares) spectral characteristics from this study

909   are consistent with iron in five-fold coordination or a mixture of four-fold and six-fold

910   coordination. Under the same radiation dose conditions, anhydrous glasses display higher

911   pre-edge intensities relative to hydrous glasses at a given centroid energy. Hydrous

912   glasses under high radiation dose conditions display higher pre-edge intensities than

913   under low radiation dose conditions; however, increases in pre-edge intensities are

914   proportional to increases in the centroid ($Fe^{3+}/\Sigma Fe$ ratio). Vertical 1σ error bars are

915   smaller than the symbol sizes.

916

917   **Figure 8.** We use $\Phi = Fe^{3+}/\Sigma Fe_{M\ddot{o}ss} - Fe^{3+}/\Sigma Fe_{XANES}$ as a proxy for beam-induced Fe

918   oxidation (where Mössbauer spectra establish the "true" $Fe^{3+}/\Sigma Fe$ ratio, and the XANES

919   centroid the "apparent" $Fe^{3+}/\Sigma Fe$ ratio). The molar concentration of **(A)** dissolved water

920   (single cation basis), $XHO_{1.5}$, **(B)** ferric iron (single cation basis), $XFeO_{1.5}$, and **(C)** the

921   ratio of dissolved water multipled by the ferrous/ferric ratio, $XHO_{1.5}*XFeO/XFeO_{1.5}$,

922   versus $\%Fe^{3+}/\Sigma Fe_{Möss} - Fe^{3+}/\Sigma Fe_{XANES}$. The correlation in **(C)** is forced through the

923   origin, because we observe no oxidative beam damage in anhydrous glasses. 1σ error

924   bars are smaller than the symbol sizes.

925

926   **Figure 9.** Pre-edge spectra of one anhydrous and four hydrous glasses, with varying Φ

927   and under two radiation dose conditions. We display merged, successive spectra,

928   acquired under two different beam conditions: high radiation dose condition $XANES_3$

929   (red) and low radiation dose condition $XANES_4$ (blue). The black line shows the

930   difference between the spectra.

931

932   **Figure 10. (A)** FTIR transmission map of glass B10 surrounding an area purposely

933   exposed with a 2x2μm synchrotron radiation beam at a photon flux of $\sim 1x10^{12}$

934   photons/sec for ~12 minutes. We show the location of the beam at the sample surface, but

935   the beam intersects the sample surface at a 45° angle and travels through the sample from

936   left to right. Color scale shows the intensity of the H_2O_{Total} absorbance band at 3500 cm-1

937   after subtraction of a reference intensity at 2300 cm-1. Each pixel is 20 x 20 μm. FTIR

938   spectra for pixels designated (1) and (2) are discussed in the text.

939

Table 1: Room Temperature
Mössbauer hyperfine parameters, Fe3+/ΣFe ratios, and select compositional parameters

	$Fe^{3+}/\Sigma Fe * 100$						spectral fitting parameters (this study)								B et al., 2005		
Sample	B et al. 2005	1σ	this study	1σ	X^2	Bkgrd.	Fe^{3+} CS	Fe^{3+} δCS	Fe^{3+} QS	Fe^{3+} δQS	Fe^{2+} CS	Fe^{2+} δCS	Fe^{2+} QS	Fe^{2+} δQS	FeO Total Wt.%	H2O Total Wt.%	Φ^
B11	19	2	18.7	1.45	1.0	1024543	0.46	0.19	0.93	0.14	0.95	0.12	1.98	0.44	12.49	4.82	1.05
B16	18	2	16.8	1.23	0.8	1427668	0.53	0.09	0.92	0.39	0.95	0.14	1.97	0.41	12.93	3.02	0.81
B12	11	2	12.3	1.81	1.2	598904	0.52	0.28	1.12	0.01	0.97	0.14	2.00	0.42	12.02	1.9	0.77
B13	10	2	12	1.41	1.0	1988275	0.48	0.34	1.00	0.02	0.94	0.03	1.91	0.48	11.39	1.71	0.72
B10	40	4	36.3	1.61	1.1	680688	0.50	0.02	0.90	0.38	0.91	0.28	2.02	0.12	12.61	2.43	0.24
B6	39	3	36.9	1.72	1.2	644411	0.44	0.02	0.91	0.46	0.96	0.12	1.93	0.38	12.94	2	0.19
B9	29	3	26.7	2.14	1.4	570588	0.55	0.19	0.82	0.00	0.91	0.28	1.99	0.10	12.62	1.14	0.19
B7	23	2	21.1	0.94	0.6	1068960	0.57	0.18	0.87	0.00	0.92	0.28	1.94	0.12	12.91	0.97	0.22
B8	16	2	17.8	1.15	0.8	905216	0.59	0.02	0.92	0.34	0.93	0.28	1.92	0.14	12.67	0.82	0.23
B17	60	2	55.6	2.03	1.4	392639	0.50	0.16	0.88	0.29	0.93	0.29	2.11	0.09	12.65	4.67	0.19
B21	49	2	45.7	1.58	1.1	735417	0.50	0.05	0.90	0.38	0.89	0.31	2.04	0.15	12.34	2.9	0.19
B19	52	2	49.3	1.68	1.1	628828	0.54	0.15	0.82	0.28	0.81	0.28	2.21	0.11	12.91	1.85	0.11
B22	28	2	25.3	0.38	0.3	5545128	0.58	0.20	0.82	0.00	0.89	0.28	1.98	0.11	12.77	0.94	0.17
B20	25	2	24.8	1.00	0.7	2254268	0.58	0.20	0.83	0.00	0.90	0.28	1.98	0.11	12.80	0.72	0.13
			C et al., 2009^v	1σ	X^2	Bkgrd.	Fe^{3+} CS	Fe^{3+} δCS	Fe^{3+} QS	Fe^{3+} δQS	Fe^{2+} CS	Fe^{2+} δCS	Fe^{2+} QS	Fe^{2+} δQS			
AII_0	-	-	14.7	0.38	0.55	5408375	0.44	0.09	1.31	0.47	0.95	0.15	1.88	0.44	-	-	-
AII_05	-	-	19.4	0.63	0.63	7463896	0.50	0.17	1.27	0.46	0.95	0.16	1.88	0.42	-	-	-
AII_-05	-	-	13.8	0.50	0.5	6400103	0.44	0.04	1.30	0.63	0.95	0.18	1.88	0.37	-	-	-
AII_15	-	-	24.7	0.44	0.44	5948886	0.44	0.03	1.26	0.50	0.95	0.17	1.88	0.42	-	-	-
AII_-15	-	-	9.3	0.60	0.6	694310	0.44	0.33	1.29	0.03	0.95	0.14	1.88	0.45	-	-	-
AII_25	-	-	35.6	0.38	0.38	5951129	0.41	0.09	1.27	0.50	0.95	0.18	1.88	0.41	-	-	-
AII_35	-	-	48.4	0.40	0.4	12486195	0.38	0.10	1.25	0.48	0.93	0.17	1.88	0.14	-	-	-
AII_45	-	-	61.1	0.26	0.26	10318722	0.37	0.09	1.26	0.48	0.91	0.18	1.88	0.44	-	-	-
LW_0	-	-	16.2	0.55	0.38	7123408	0.44	0.14	1.23	0.55	0.95	0.16	1.90	0.42	-	-	-
LW_10	-	-	23.5	0.53	0.53	7922396	0.46	0.17	1.22	0.40	0.95	0.15	1.91	0.43	-	-	-
LW_-10	-	-	13.0	0.58	0.58	9201577	0.44	0.10	1.25	0.70	0.95	0.16	1.90	0.42	-	-	-
LW_20	-	-	30.3	0.14	1.4	2072205	0.30	0.12	1.22	0.48	0.86	0.10	1.91	0.47	-	-	-
LW_-20	-	-	8.8	0.53	0.53	6835643	0.44	0.03	1.28	0.03	0.95	0.15	1.90	0.42	-	-	-

^{v} Cottrell et al., 2009. Recommended $Fe^{3+}/\Sigma Fe$ ratios, considering recoiless fraction, can be found in Zhang et al., submitted.
Room Temperature values are used in this work for comparison with Botcharnikov et al., 2005.

940

$^\wedge \Phi = XHO_{0.5}*XFeO/XFeO_{1.5}$ based on Fe3+/ΣFe ratios from this study and H_2O from Botcharnikov et al., 2005.

Table 2: Synchrotron radiation dose conditions					
Flux Condition	spot size (μm)	photon flux (photons/sec)	flux density (photons/sec/μm^2)	Gray/sec**	notes
XANES$_1$	2x2	$5 \times 10^{10-11}$	$1 \times 10^{10-11}$	$9.0 \times 10^{10-11}$	nominal at 13-ID-D
XANES$_3$	2x2	$1.5\text{-}8.6 \times 10^9$	4×10^8 to 2×10^9	$\sim 1.3 \times 10^7$	
XANES$_4$	50x50	$1.5\text{-}8.6 \times 10^9$	8×10^5 to 3×10^6	$\sim 1.3 \times 10^4$	
XANES$_5$	25x25	2×10^9	3×10^6	3.8×10^4	
XANES$_{CRYO-HI}$	38x28	$3\text{-}4 \times 10^7$	$3\text{-}4 \times 10^4$		monochrometer = 7113.3eV
XANES$_{CRYO-LO}$	38x28	$2\text{-}4 \times 10^6$	$2\text{-}4 \times 10^3$		monochrometer = 7113.3eV
X26A	9x5	3×10^9	6×10^7	7.7×10^5	

**Dose in Gray (Joules/kg/sec) is calculated for glass of basaltic composition through 1/e absorption length

941

Table 3: XANES centroids and integrated pre-edge intensities

| | X26A❖ | | | | XANES₁ | | | | XANES₅ | | | | |
| | $5x10^{10}$ photons/um² | | | | $3x10^{15}$ photons/um² | | | | $2x10^{9}$ photons/um² | | | | |
sample	centroid	σ	I1	I2	centroid	σ	I1	I2	centroid	σ	I1	I2	%Δ**
B11	7112.402	0.012	0.06	0.037	7112.654	0.015	0.053	0.066	7112.421	0.003	0.058	0.045	71.9
B16	7112.342	0.008	0.063	0.031	7112.578	0.007	0.057	0.057	7112.362	0.01	0.061	0.04	69.2
B12	7112.226	0.007	0.073	0.026	7112.4	0.016	0.07	0.046	7112.228	0.002	0.074	0.032	66.4
B13	7112.177	0.002	0.077	0.024	7112.328	0.011	0.073	0.038	7112.211	0.015	0.076	0.031	46.0
B10	7112.784	0.01	0.047	0.062	7112.86	0.018	0.045	0.082	7112.773	0.004	0.048	0.074	18.4
B6	7112.733	0.012	0.05	0.06	7112.793	0.017	0.049	0.076	7112.735	0.007	0.052	0.07	6.5
B9	7112.585	0.006	0.06	0.05	7112.633	0.006	0.06	0.066	7112.568	0.011	0.06	0.058	16.5
B7	7112.477	0.007	0.064	0.042	7112.505	0.009	0.066	0.054	7112.468	0.009	0.064	0.05	18.7
B8	7112.413	0.007	0.07	0.04	7112.451	0.026	0.066	0.05	7112.418	0.006	0.067	0.047	27.2
B17	7113.083	0.013	0.03	0.088	7113.108	0.016	0.029	0.106	7113.059	0.001	0.032	0.098	3.8
B21	7112.988	0.006	0.039	0.082	7113.029	0.014	0.039	0.104	7112.957	0.008	0.04	0.088	15.5
B19	7113.01	0.008	0.04	0.083	7112.99	0.011	0.042	0.097	7112.969	0.008	0.042	0.094	2.3
B22	7112.587	0.01	0.062	0.051	7112.613	0.008	0.06	0.064	7112.582	0.01	0.06	0.06	19.1
B20	7112.548	0.002	0.064	0.048	7112.551	0.009	0.064	0.058	7112.538	0.009	0.063	0.057	9.5
	$5x10^{10}$ photons/um²				$4x10^{15}$ photons/um²								
AII0	7112.275	0.01	0.091	0.03	7112.271	0.009	0.079	0.036					
AII05	7112.361	0.011	0.086	0.038	7112.368	0.002	0.08	0.046					
AII-05	7112.219	0.01	0.09	0.029	7112.22	0.004	0.084	0.034					
AII15	7112.52	0.013	0.078	0.047	7112.529	0.002	0.069	0.058					
AII-15	7112.147	0.026	0.093	0.02	7112.134	0.007	0.087	0.025					
AII25	7112.742	0.014	0.068	0.07	7112.76	0.009	0.061	0.079					
AII35	7112.962	0.027	0.055	0.091	7112.974	0.002	0.052	0.106					
AII45	7113.184	0.025	0.046	0.124	7113.186	0.003	0.042	0.14					
LW_0	7112.3	0.01	0.085	0.032	7112.302	0.01	0.079	0.04					
LW10	7112.434	0.013	0.078	0.042	7112.433	0.009	0.07	0.05					
LW-10	7112.154	0.024	0.095	0.023	7112.155	0.004	0.085	0.028					
LW20	7112.608	0.02	0.072	0.058	7112.62	0.002	0.069	0.069					
LW-20	7112.112	0.01	0.097	0.018	7112.128	0.002	0.092	0.027					

❖ centroids are 7-yr avgs (n=30-48) as reported in Zhang et al., submitted

**$Fe^{3+}/\Sigma Fe_{Möss} - Fe^{3+}/\Sigma Fe_{XANES}$

Doses reported in this table are per spectrum (photons/sec/μm2*total collection time)
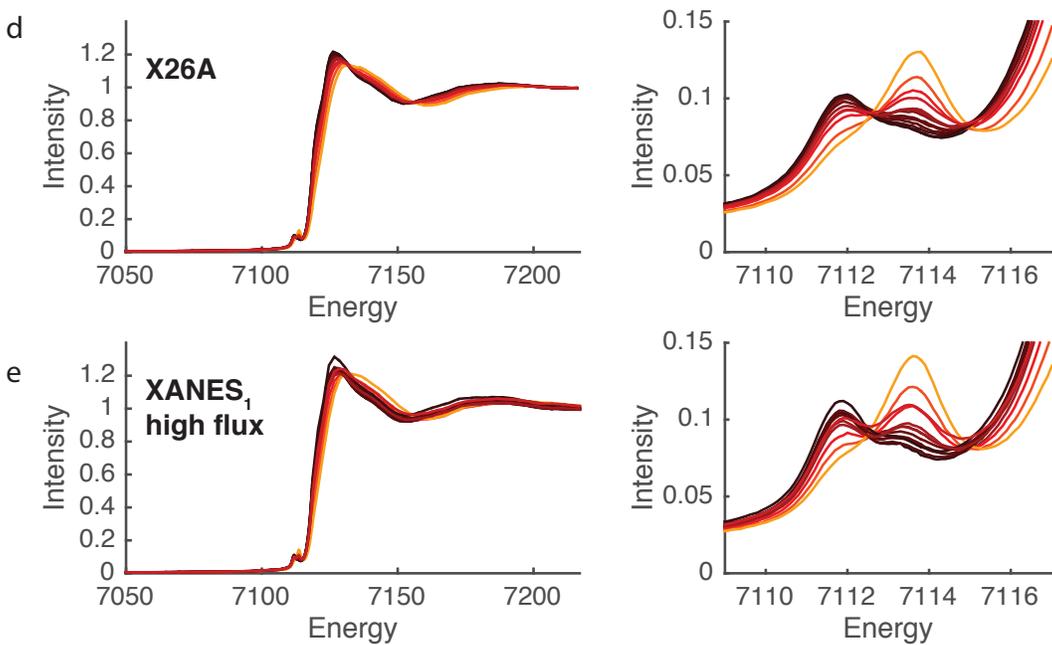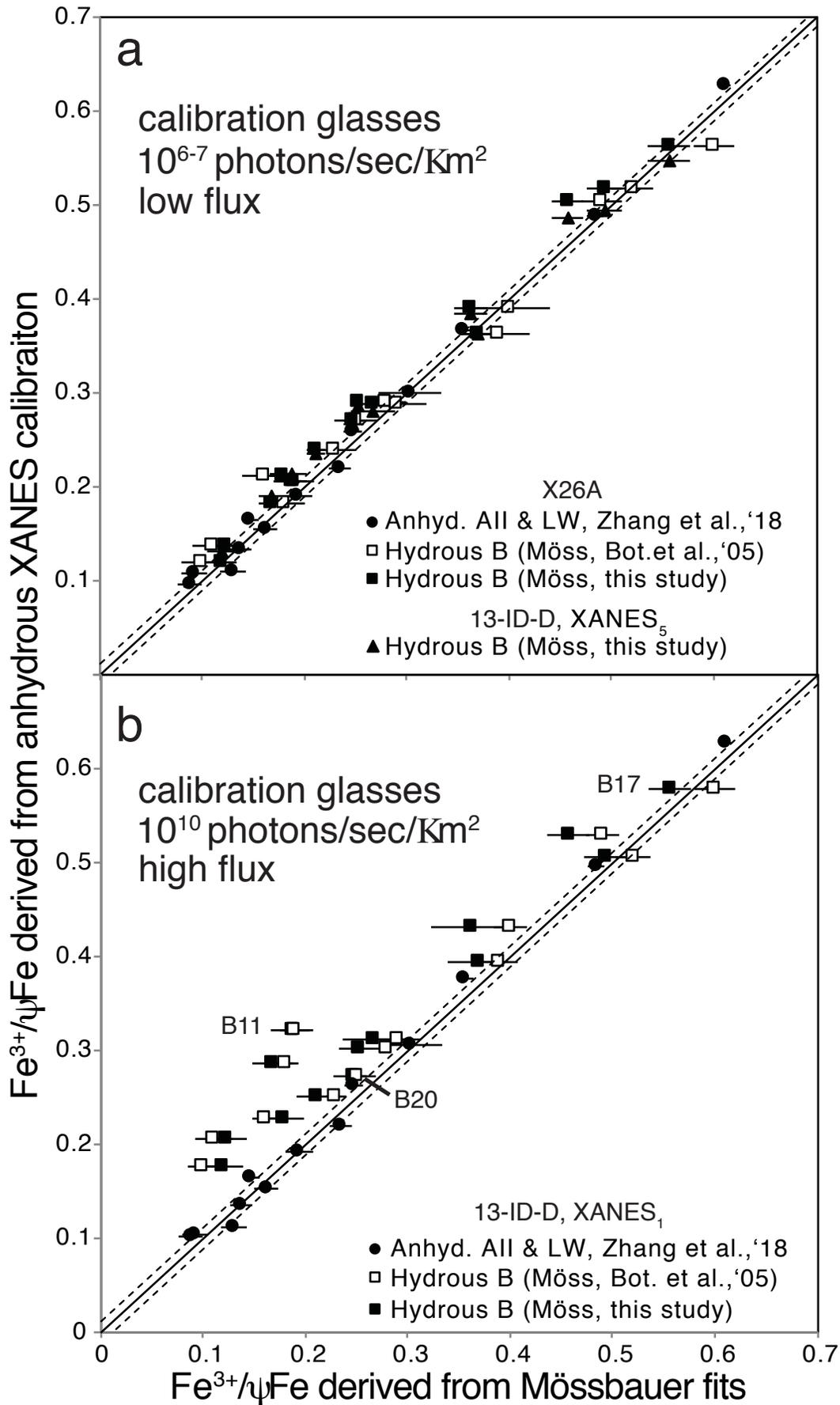
942

943
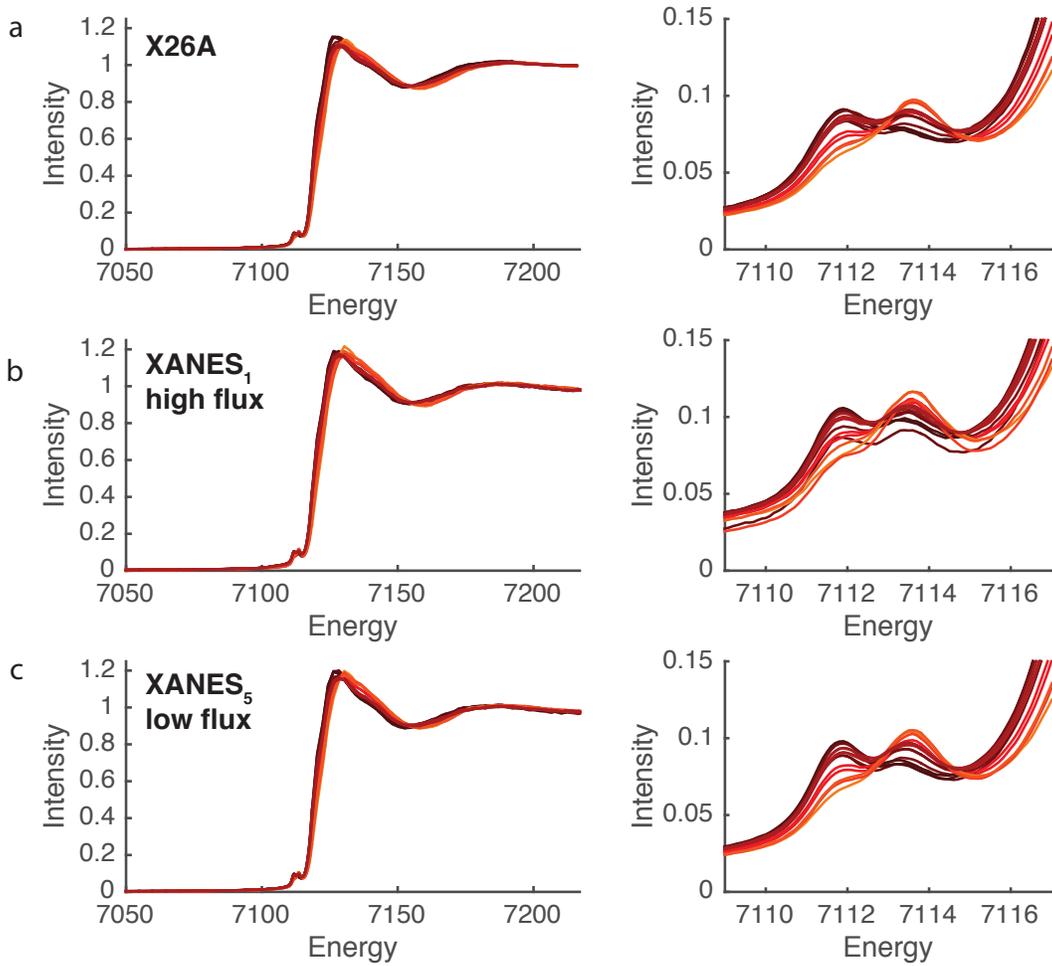
Hydrous B Glasses

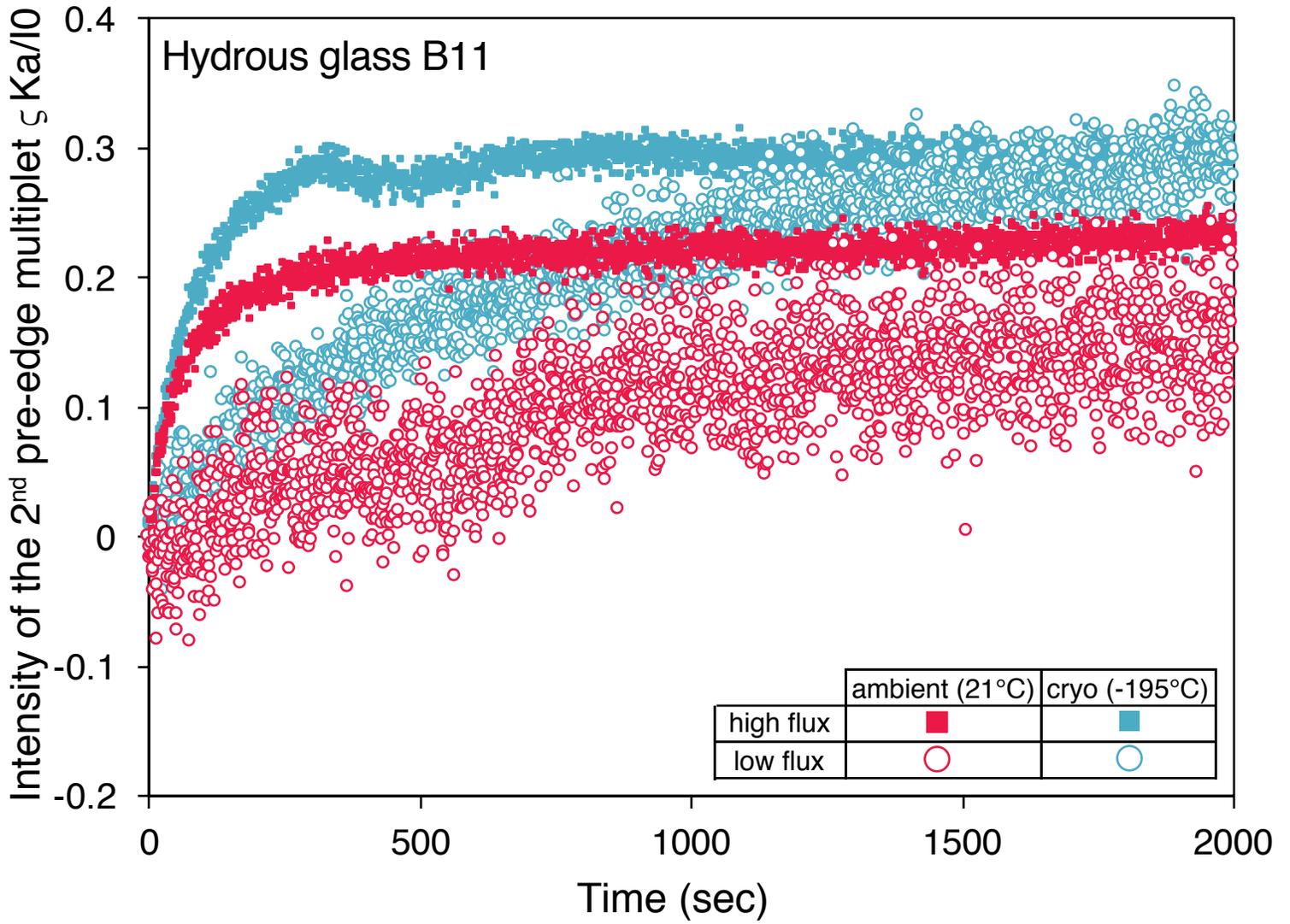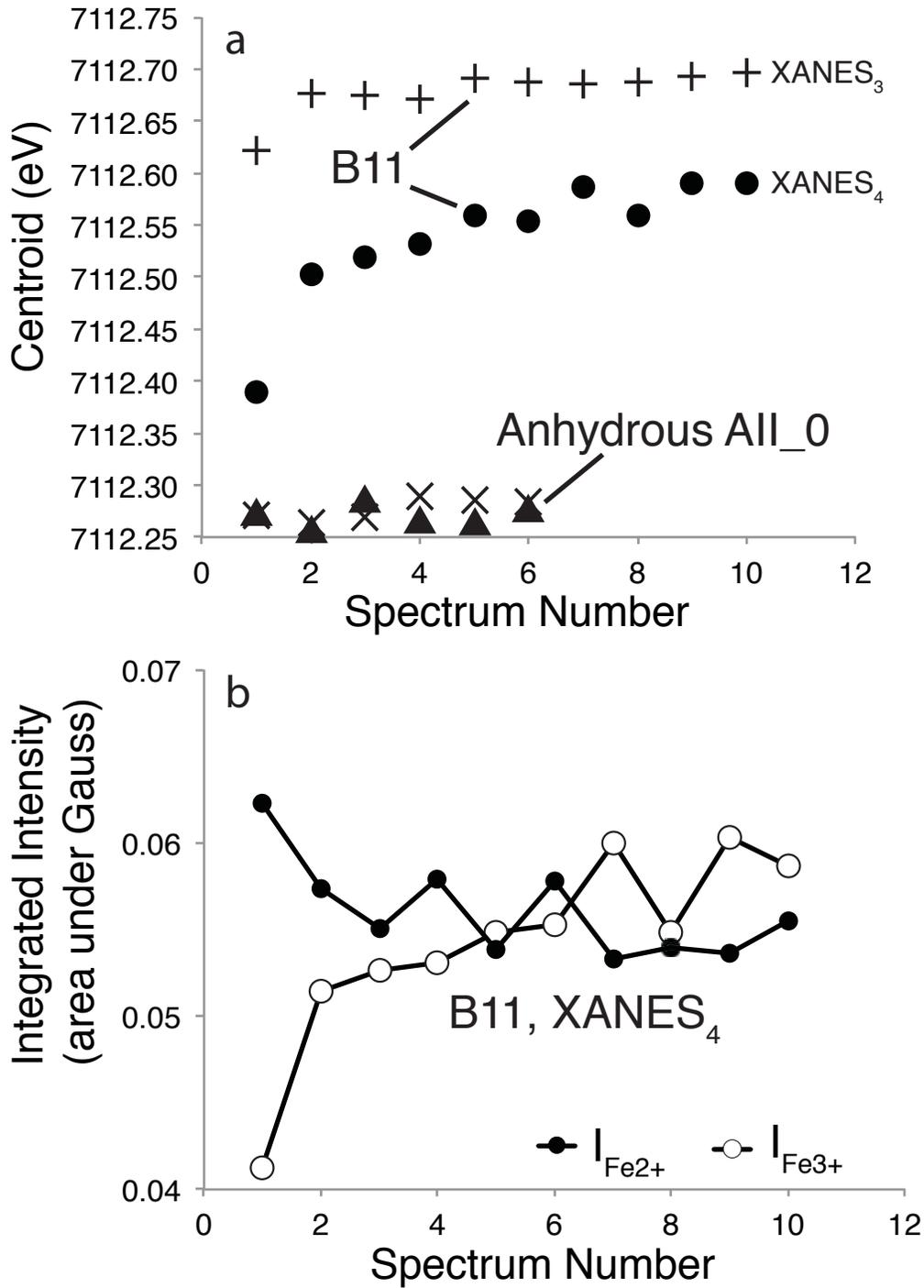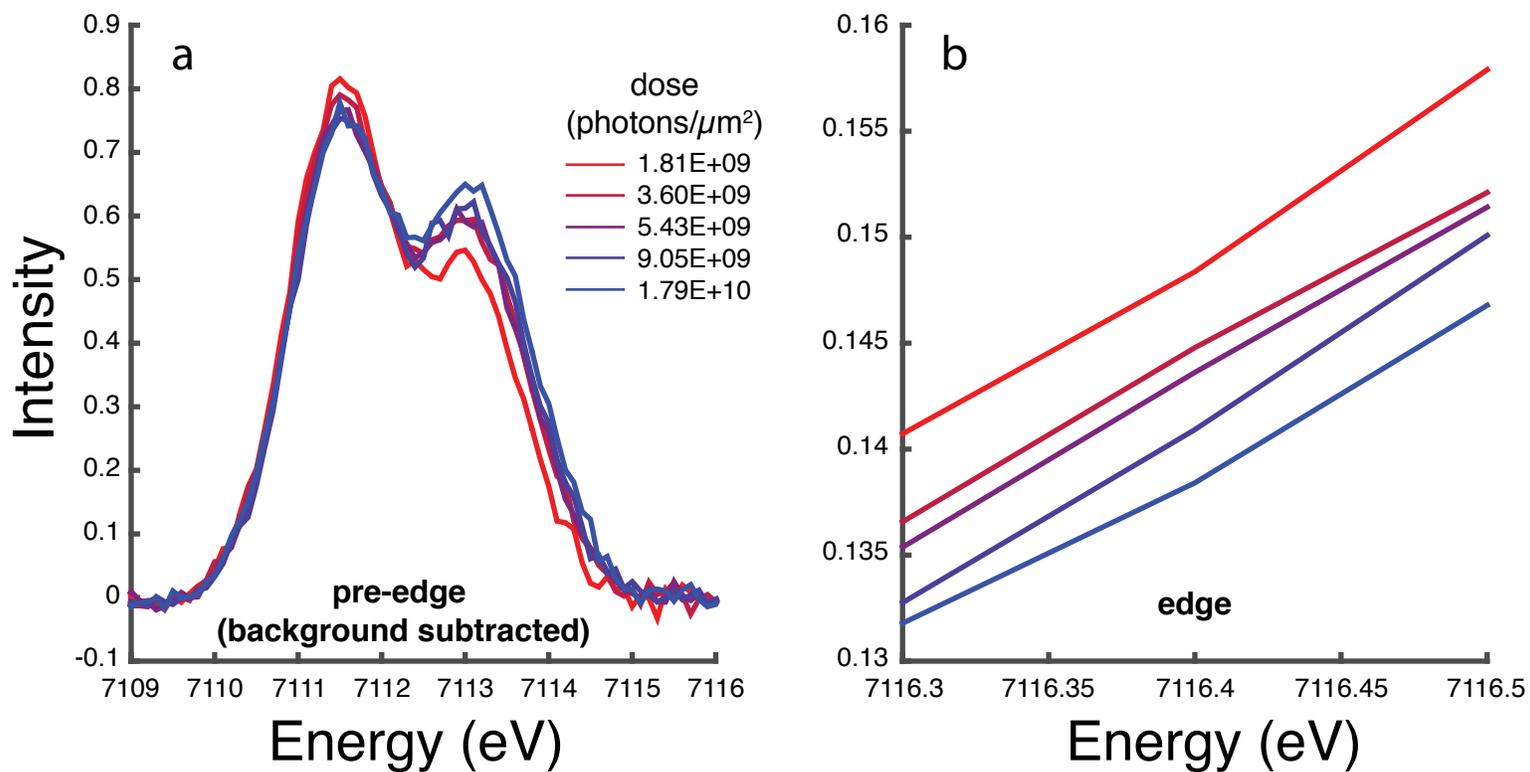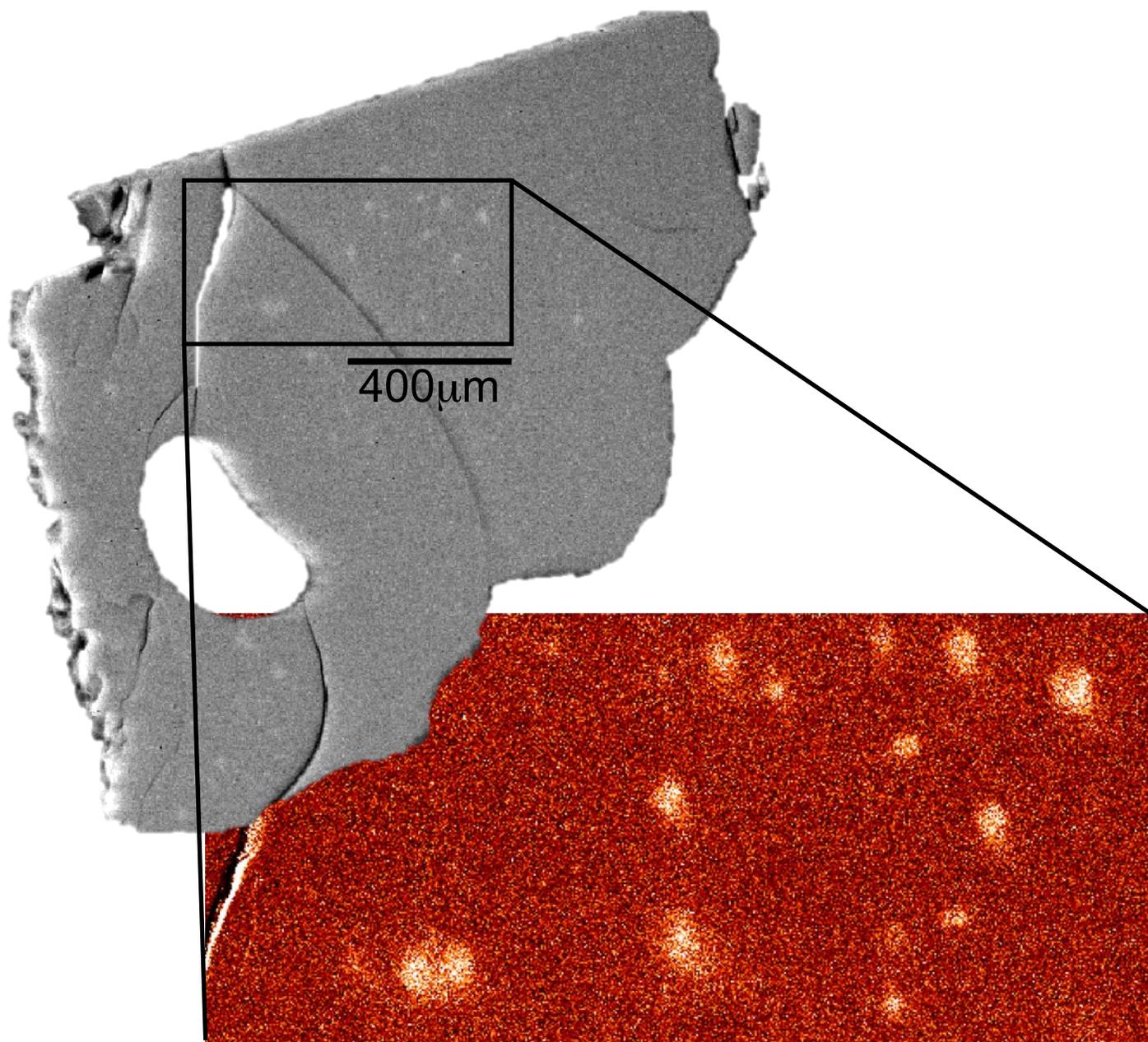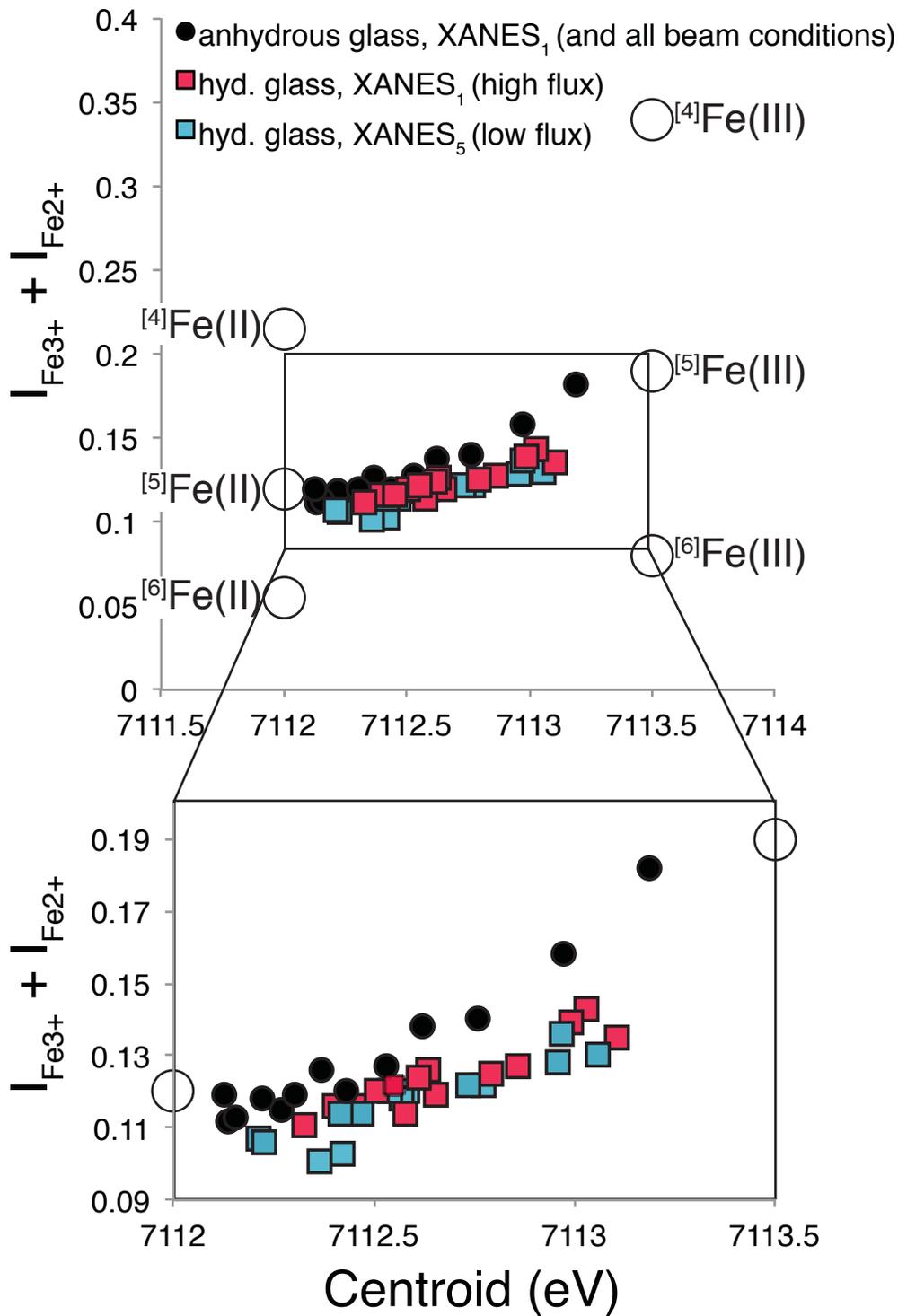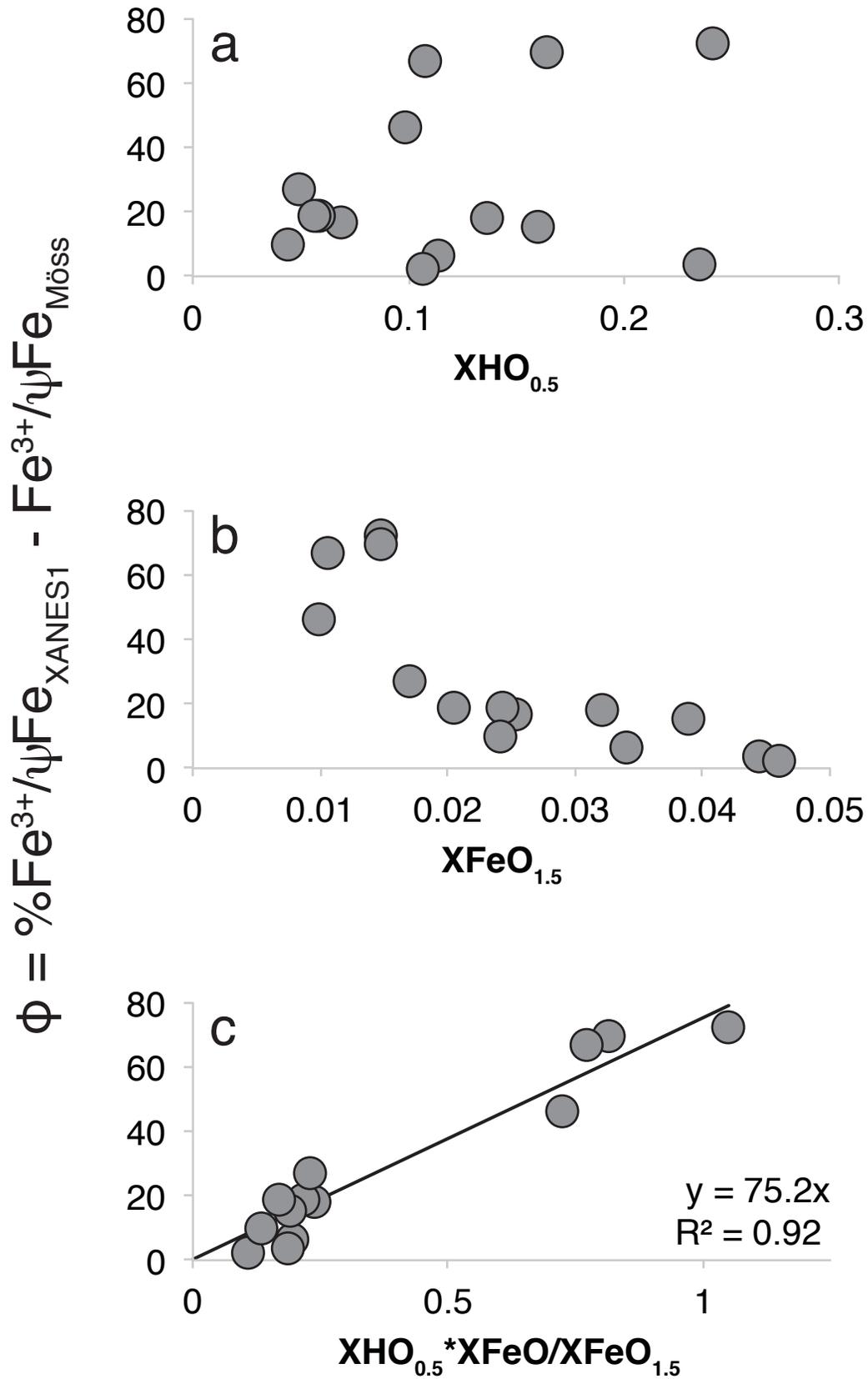**Anhydrous LW and All Glasses**

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

400μm

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10