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Radiation-Induced Changes in Vanadium Speciation in Basaltic Glasses: Implications for Oxybarometry Measurements Using Vanadium K-edge X-ray Absorption Spectroscopy

ANTONIO LANZIROTTI[1,*], STEPHEN SUTTON[1,2], MATTHEW NEWVILLE[1], AND ELISABET HEAD[3]

[1] Center for Advanced Radiation Sources, The University of Chicago, Argonne, IL 60439, USA

[2] Department of the Geophysical Sources, The University of Chicago, Argonne, IL 60439, USA

[3] Department of Earth Science, Northeastern Illinois University, Chicago, IL 60625, USA

ABSTRACT

Magmatic oxygen fugacity (fO_2) exerts a primary control on the discrete vanadium (V) valence states that will exist in quenched melts. Vanadium valence proxies for fO_2, measured using X-ray absorption near-edge spectroscopy (XANES), can provide highly sensitive determinations of the redox conditions in basaltic melts. However, X-ray beam-induced changes in V speciation will introduce uncertainty in the calculated average V valence (V*) that must be properly evaluated in order to make meaningful interpretations of the igneous evolution of the system. The study presented here showed that beam-induced modifications in V speciation are observed in silicate glasses that are dependent on the radiation dose rate used during analysis. Changes in V speciation are observed to be most pronounced at the highest flux density tested, 9.25 x10^{11} ph/s/μm^2 (photons per second per square micrometer), with rapid changes occurring in the first 200s of analysis. The high dose rate conditions result in changes in calculated V* ~0.3 valence unit for the most oxidized glass analyzed (V* = 4.94), which can correspond to ~ 0.5 log unit reduction in calculated fO_2. However, at flux densities ≤ 1.13x10^9 ph/s/μm^2, measured changes in V* were found to be < 0.03 for all standard glasses analyzed. The degree of reduction observed during analysis is also found to be progressively smaller as the initial V* of the glass

decreases, such that magmatic glasses with V* values ≤ 3.7 show no statistically-significant change in calculated valence during analysis at any flux density tested. For most terrestrial magmatic glasses, where V* is found to be < 4, beam induced changes in V* can be effectively minimized (< 0.04), within analytical uncertainty of the XAFS analysis, by limiting flux densities to be ≤ $1x10^9$ ph/s/μm^2.

INTRODUCTION

Accurate estimates of the intrinsic oxygen fugacity (fO_2) of magmas are important for constraining source composition and understanding the conditions under which melts are generated, their sub-liquidus evolution and crystallization history, and the composition and evolution of volcanic gases released to the atmosphere (Sato 1978; Mathez 1984; Christie et al. 1986; Ballhaus et al. 1990; Carmichael 1991; Kelley and Cottrell 2009). Oxybarometers of varying types provide geologists analytical approaches for indirectly constraining magmatic fO_2 through chemical analysis of varying primary igneous phases. Of the approaches currently available for oxybarometry, those based on X-ray absorption fine structure (XAFS) spectroscopy (Sutton et al. 2005, 2005, 2020; Cottrell et al. 2009; Bunker 2010; Jugo et al. 2010; Henderson et al. 2014; Trail et al. 2015; Lanzirotti et al. 2018) are particularly attractive due to the high sensitivity of XAFS in detecting subtle changes in the chemical speciation of redox-sensitive elements in igneous minerals and/or glasses in response to changing magmatic fO_2. Various XAFS oxybarometers have been developed for magmatic systems, including those based on measuring changes in chemical speciation of multivalent elements such as Fe, S, Ti, Mn, Cr, Eu, Ce and V (reviewed in Sutton et al. 2020 and references therein). Vanadium XAFS oxybarometry has broad applicability to terrestrial and extraterrestrial igneous materials since its valence varies continuously from V^{3+} to V^{5+} over a wide range of fO_2 (Giuli et al. 2004; Sutton et

al. 2005; Karner et al. 2006; Lanzirotti et al. 2018; Nakada et al. 2020). In terrestrial basaltic melts, the $V^{3+} \leftrightarrow V^{4+}$ and $V^{4+} \leftrightarrow V^{5+}$ multivalent couples span an oxygen fugacity range relative to the nickel-nickel oxide (NNO) buffer from about NNO-6 to NNO+3.5 (Papike et al. 2005).

An analytical complication in the application of XAFS oxybarometers with respect to mineral and glass analysis is the potential for inducing changes in the valence and/or crystal-chemical environment of the element of interest due to exposure of samples to the synchrotron X-ray beam. Such phenomena have been documented in several systems and have been found to be particularly pronounced for hydrous magmatic glasses. For example, sulfur valence state changes have been observed during XAFS analysis of volcanic glasses and melt inclusions (Rowe et al. 2007; Wilke et al. 2008; Klimm et al. 2012); most commonly reported is the generation of S^{4+} species in glasses, generally attributed to reduction of S^{6+} during irradiation (Wilke et al. 2008). In another example, Cottrell et al. (2018) showed that Fe^{2+} in hydrous silicate glasses can undergo rapid oxidation upon exposure to radiation. In the most hydrous basaltic glasses they analyzed, they showed that radiation-induced increase in $Fe^{3+}/\Sigma Fe$ ratio of up to 0.16 can be observed after several minutes of irradiation at X-ray flux densities of $\sim 2 \times 10^9$ ph/s/μm^2. They also showed that for Fe, the rate of oxidation also correlates with the product of water concentration and ferrous/ferric iron oxide ratio in the glass. Interestingly, in anhydrous glasses, they observed no statistically significant change in Fe valence under any beam conditions, which led them to infer that it is radiation-induced hydrolysis which may drive oxidation of Fe^{2+} in these magmatic glasses. Other studies have noted that anhydrous silicate glasses with high concentrations of Fe often do not show evidence of beam-induced changes in Fe valence (Camara and Oel 1984). However, in soda-lime silicate glasses where Fe is doped at trace element concentrations (150-5000 ppm), Fe^{3+} has been shown to undergo X-ray induced

reduction (Camara and Oel 1984; Gonçalves Ferreira et al. 2013). Such reduction was hypothesized to result from the production of localized defects within the glass matrix during irradiation, where electron-hole pairs associated with the defect sites act to change the valences of incorporated trace Fe. We hypothesize that other multi-valent trace elements in natural silicate glasses, such as V, may display similar behavior on irradiation.

This study presents new observations regarding X-ray beam-induced changes in V valence in silicate glasses. Although the potential for radiation-induced changes in V valence in the analysis of natural silicate glasses has been alluded to in published studies (Lanzirotti et al. 2018), we are unaware of any systematic study that has sought to describe and quantify the magnitude of any observed changes with radiation dose rate that are relevant to geochemical studies. For V XAFS oxybarometry to provide accurate and precise estimates of changing oxygen fugacity in magmatic systems, it is important to understand and quantify how irradiation during XAFS analysis can modify the spectral features used to calculate the average V valence of igneous systems.

SAMPLES AND ANALYTICAL PROCEDURES

Four synthetic glasses and two natural volcanic glasses were analyzed by V K-edge XAFS at varying incident flux densities. The synthetic samples are from a suite of anhydrous forsterite-anorthite-diopside (FAD) composition glasses doped to provide V concentrations of ~ 3000 ppm. This suite of glasses were synthesized at 1 atm pressure, at equilibration temperatures of 1310 - 1320°C and at log fO_2 ranging from -15.5 to -4.55. Their synthesis is fully described in Hanson and Jones (1998). For this study, four glasses in the suite were evaluated for radiation-induced changes in V valence, chosen because they were equilibrated over a broad range of ~7 log units fO_2, (expressed here relative to nickel-nickel oxide buffer, NNO, Huebner and Sato, 1970):

FAD_V2a (log fO_2 -11.6, ΔNNO-5.3), FAD_V4 (log fO_2 -9.6, ΔNNO-3.3), FAD_V1a (log fO_2 -7.1, ΔNNO-0.7) and FAD_V3 (log fO_2 -4.6, ΔNNO+1.7). The two natural glasses studied are Smithsonian Institution NMNH National Rock Collection samples (Jarosewich et al. 1980) designated A-99 (NMNH 113498-1), a sample of fresh basaltic glass collected from the Makaopuhi Lava Lake, Hawaii, and VG-2 (NMNH 111240-52), a sample of fresh basaltic glass dredged from the Juan de Fuca Ridge. Published estimates for NNO-relative fO_2 for A-99 and VG-2, based on V XAFS oxybarometry, were ΔNNO-1.28 and ΔNNO-0.08 respectively (Lanzirotti et al. 2018). Absolute vanadium abundances have not been reported for these two glasses, but natural basaltic glasses generally have V concentrations between ~200–400 ppm, which is consistent with the X-ray fluorescence intensities measured for V K emission lines. All samples were prepared as polished (using 0.5 micron diamond-embedded polishing paper), epoxy embedded chips where the glass thickness was large compared to the sampling depth of V K-edge X-rays. Previous V K-edge XAFS analyses of these samples are described in Lanzirotti et al. (2018),Sutton et al. (2005) and Karner et al. (2006).

Vanadium K-edge XAFS spectra were measured using the 13-ID-E undulator-based microprobe at the GeoSoilEnviro-CARS sector, Advanced Photon Source (APS), Argonne National Laboratory, USA. The optical and instrumental configuration of the beamline are described in Lanzirotti et al. (2016, 2018) and (Sutton et al. 2017). Monochromatic radiation was provided by a cryogenically-cooled, double-crystal monochromator using a Si(111) monochromator crystal set. Beam focusing to the sample is provided by a pair of 240 mm long, highly polished, dynamically-bent bare silicon mirrors in a Kirkpatrick-Baez (KB) geometry capable of generating focused spot sizes of ~1 x 2 μm (FWHM) and of providing incident monochromatic flux (I_0) in excess of $5x10^{12}$ ph/s, which is measured in a helium-filled, 200 mm-

long ion chamber just upstream of the KB mirror optics. For the experiments described here, X-ray flux density delivered to the sample was controlled by dynamic defocusing of the beam, using the KB optics, and by filtering of the incident beam, using high-purity aluminum filters. For consistency with previous published data from the beamline, the sample-impinging flux densities that are reported here are calculated based on measured I_0, which is monitored upstream of the mirror focusing optics. Flux is calculated using measured current in the 200 mm long ion chamber, assuming 100% He gas at atmospheric pressure and effective ionization potential for He from Knoll (2010). The KB mirrors have reflection efficiencies of ~80%, so flux delivered to the samples is estimated to be 60% of the measured I_0 flux. The energy of the first derivative peak of V metal foil provided a V K-edge energy of 5463.76 eV, consistent with value determined by Kraft et al. (1996). Fluorescence spectra were collected using a Vortex ME4 and Canberra SX7 silicon-drift diode detector arrays coupled to a high-speed digital spectrometer system (Quantum Xpress3).

Full V K-edge XAFS spectra were collected at variable flux densities, 2.56 $x10^8$, 7.75 $x10^8$, 6.25 $x10^{11}$, and 9.25 $x10^{11}$ ph/s/μm^2, with each analysis conducted on a fresh sample spot. This allowed us to compare the final shape of the XAFS spectra with increasing radiation dose and evaluate any potential trends in changing V speciation over time. The XAFS spectra collected at flux densities of 2.56 $x10^8$ and 9.25 $x10^{11}$ ph/s/μm^2 scanned the incident beam from 5365-5455 eV in 2.5 eV steps, from 5455-5490 eV in 0.15 eV steps, and from 5490-5645 eV in 2.0 eV steps at 1 s per energy point. This allowed us to compare spectra with optimal signal/noise at the highest and lowest flux densities tested, with one spectrum being collected in ~6 minutes (Fig. 1). More rapid XAFS spectra were also collected at flux densities of 7.75 $x10^8$ and 6.25 $x10^{11}$ ph/s/μm^2, scanning the incident beam from 5420-5455 eV in 3.5 eV steps, from 5455-5475 eV in

140 0.15 eV steps, from 5475-5500 eV in 2.5 eV steps and from 5500-5700 eV in 5.0 eV steps at 0.5
141 s per energy point. This allowed us to evaluate changes in spectral shape more quickly at two
142 flux densities that differ by a factor of ~800, with slightly poorer signal/noise, but with one
143 spectrum being collected in only ~1.5 minutes (Figs. 2, 3 and 4).

144 V* values were calculated using the Sutton et al. (2005) calibration, derived from XAFS
145 spectra measured in synthetic glass standards produced under known fO_2 and temperature
146 conditions. Following the Sutton et al. protocol, each XAFS spectrum is first normalized to the
147 count rate measured at 5600 eV. The pre-edge peak intensity (I) is then measured as the
148 maximum intensity of the net pre-edge peak multiplet after normalized intensities are multiplied
149 by 1000 and after subtracting the edge step contribution. The effective vanadium valence, V* is
150 then calculated as:

$$I = -153 + 199(V^*) - 106(V^*)^2 + 22.4(V^*)^3 \quad (1)$$

151 Tests were also conducted to constrain rates of reduction in glasses showing evidence of
152 decreases in V* as a function of radiation dose rate using four flux densities covering more than
153 4 orders of magnitude: 1.69×10^6, 1.38×10^8, 1.13×10^9, and 9.25×10^{10} ph/s/μm^2. A protocol
154 similar to that described by Cottrell et al. (2018) for evaluating beam-induced changes in Fe
155 valence was used for this purpose. For evaluating beam-induced changes in Fe valence in silicate
156 glasses Cottrell et al. measured the change in the peak amplitude of the second multiplet pre-
157 edge peak of the Fe K-edge with time at differing flux densities. Here, we evaluated the time
158 dependence of the measured V spectral intensity at an energy of 5468.15 eV, which sits on the
159 pre-edge peak, as a function of flux density (i.e., dose-rate). Each time series consists of
160 measurements at 1s intervals over 1500s of total irradiation and with each curve measured at a
161 fresh spot on the sample that had not been previously irradiated. The 13-ID-E monochromator

has been demonstrated (Sutton et al. 2017) to have no significant energy drift (<0.05 eV) as a function of time, so that it is unlikely that any intensity changes measured are affected by energy drift. Although pre-edge peak energies also increase with increasing valence, the energy shifts are small (~1 eV from V^{3+} to V^{5+}, Sutton et al. 2005). Thus, although we are solely monitoring changing intensity of the pre-edge peak at an energy of 5468.15 eV in constructing the rate-of-change curves, this is the most convenient method for evaluating *potential* changes in valence at very short accumulation times of 1 s. Thus, for the purposes stated here, the uncertainties introduced by collecting intensities at a single energy are likely to be negligible.

RESULTS

Observed Spectroscopic Changes Following Irradiation

In V K-edge XAFS spectroscopy, increases in V valence are generally indicated by increases in the net, normalizedintensity of the pre-edge peak and shifting of the main absorption edge to higher energy, although other changes in spectral shape are also noted (Wong et al. 1984; Sutton et al. 2005; Lanzirotti et al. 2018). The pre-edge peak results from the dipole forbidden ls→3*d* transition and is coupled to metal-ligand symmetry; V species in regular octahedral coordination with the O^{2-} ligand have the smallest observable pre-edge intensity while species in tetrahedral coordination have the largest intensity. In glasses, these changes in coordination are coupled to changes in V valence. Figure 1 shows edge-step normalized V K-edge XAFS spectra collected for FAD_V3, the most oxidized glass analyzed, and FAD_V2a, the most reduced glass analyzed, measured at flux densities of 2.56 $x10^8$ (in red) and 9.25 $x10^{11}$ (in blue) ph/s/μm^2. In oxidized glass FAD_V3, a decrease in the energy of the main absorption edge (E_0) of -1.1 eV and a decrease in normalized, pre-edge peak intensity of -0.26 is observed (i.e., 26% decrease of the above edge normalization level). These spectral changes and the observed changes in intensity

and energy of spectral resonances in the main absorption peak, the "white line," are consistent with reduction in V valence (Lanzirotti et al. 2018) as the radiation dose rate increases. Reduced glass FAD_V2a displays a roughly similar decrease in E_0 of - 0.8 eV, but a small increase in pre-edge peak intensity is also observed with increasing dose rate if the spectroscopic background is not subtracted from the pre-edge peak. The inset plots in Fig. 1 show the relative magnitude of the measured pre-edge peaks for both glasses after subtracting the edge step contribution via spline fitting of the rising absorption edge. Although the background subtracted spectra for oxidized glass FAD_V3 indicate an ~30% reduction in pre-edge peak intensity after subtraction of the spectral background, the background subtracted peak intensities for reduced glass FAD_V2a displays a <1% difference at the two flux densities tested.

Both the reduced and oxidized glass display increases in the intensity of a spectroscopic low energy shoulder at ~ 5475 eV with increasing dose-rate. This feature sits on the rising absorption edge just above the pre-edge peak (Fig. 1, dashed line). The increasing intensity of this shoulder at ~5475 eV has the potential for elevating the pre-edge peak baseline, an effect that is more significant in highly reduced glasses where the pre-edge peak intensities are small. In V XAFS, the spectral shoulder that is observed on the rising absorption edge has been attributed to a $1s \rightarrow 4p$ shakedown transition (Wong et al. 1984) and these features are thought to be associated with charge transfer from the ligand to the metal. Thus observed changes in the absolute intensity of these shoulder peaks potentially indicate that changes in vanadium-oxygen complexing are occurring in these glasses with increasing radiation dose-rate.

To better evaluate the rate at which any observed spectroscopic changes occur, a series of more rapid XAFS analyses were conducted at both low (7.75×10^8 ph/s/μm^2) and high (6.25×10^{11} ph/s/μm^2) flux density. Results of these analyses are shown in Fig. 2 for the reduced

synthetic glasses (FAD_V2a and FAD_V4), Fig. 3 for the oxidized synthetic glasses (FAD_V1a ad FAD_V3) and in Fig. 4 for natural MORB glass VG-2. Shown are a series of 10 edge-step normalized V K-edge XAFS spectra that were measured sequentially, with each scan acquired in ~1.5 minutes, collected at low (left) and high (right) flux density. Acquisition of 10 total spectra requires the glass to undergo irradiation at each flux density for a total time of ~15 minutes. The inset plots on each figure show the pre-edge peak portion of each scan and provide calculated V* for each scan using the Sutton et al. (2005) calibration, which subtracts the pre-edge background. We estimate that the uncertainty in calculated V* from fitting the pre-edge peak intensity for any individual scan under the conditions used is ~ 1.5% (1σ error, which is what is reported for uncertainties below).

Observed trends in these spectra are consistent with those from Fig. 1. The most reduced glass analyzed, FAD_V2a (log fO_2 -11.6), gives a calculated mean V* of V* 3.13 (± 0.01) at low flux density and V* 3.10 (± 0.03) at high flux density (Fig. 2, top). Fig. 5 shows how the relative calculated V* for this series of analyses changes with time. For FAD_V2a, the first two spectra collected at the high flux condition yield slightly more reduced V*, but these are still within error of the calculated mean for all 10 spectra in the series. Glass FAD_V4 (log fO_2 -9.6), which was equilibrated under slightly more oxidizing conditions, gives a calculated mean V* of 3.62 (± 0.01) at low flux density and V* 3.47 (± 0.01) at high flux density (Fig. 2, bottom). After 200 seconds of irradiation, the FAD_V4 high flux sequence yields V* values that are clearly more reduced than what is measured at low flux, outside of the fitting uncertainties (Fig. 5).

In more oxidized glasses, this difference is accentuated with increasing valence. FAD_V1a (log fO_2 -7.1) gives a calculated mean V* of 4.30 (± 0.01) at low flux density and V* 4.02 (± 0.03) at high flux density (Fig. 3, top). FAD_V3 (log fO_2 -4.6) gives a calculated mean V* of

231 4.94 (± 0.01) at low flux density and V* 4.65 (± 0.08) at high flux density (Fig. 3, bottom). For
232 these glasses, all the high flux analyses are statistically distinct from what is measured at low
233 flux at all measured time points (Fig. 5). Natural MORB glass VG-2 provides calculated mean
234 V* of 4.33 (± 0.03) when measured at low flux density and 4.14 (± 0.05) at high flux density,
235 very similar to results given by synthetic glass FAD_V1a, although uncertainties are slightly
236 higher due to the lower V abundance in MORB glass.

237 Other studies have also utilized time series measurements of pre-edge intensities measured
238 rapidly at a single energy to help evaluate rates of speciation changes for multi-valent elements
239 in silicate glasses as a function of flux density (Cottrell et al. 2018; Moussallam et al. 2019;
240 Gaborieau et al. 2020). By monitoring intensity changes at a single incident energy, rapid
241 changes that occur at the onset of X-ray exposure can be evaluated. Figure 6 shows such time
242 series analyses for the two most oxidized synthetic glasses analyzed (Fig. 6 top) and for the two
243 natural basaltic glasses (Fig. 6 bottom). Changing spectral intensities of the V pre-edge were
244 monitored at an incident energy of 5468.15 eV for four different flux densities (described above).
245 Accumulated counts were collected at 1s intervals over 1500s of total irradiation, and then
246 plotted as the relative fractional change in measured change intensity over time. It should be
247 noted, however, that although such time series can be used to monitor changes at very short time
248 intervals, such analyses can have large associated uncertainties due to low signal/noise
249 (particularly when absorber concentrations are low) and can be difficult to accurately correlate to
250 valence (V*) due to an inability to evaluate potential changes in pre-edge spectral background.

251 At the highest flux density tested for these time series, $9.25e^{10}$ ph/s/μm^2, the two oxidized
252 synthetic glasses again show clear decreases in V pre-edge peak intensities with increasing
253 accumulated dose. An intensity change of ~ -11% is noted for FAD_V1a and -18% for FAD_V3

after 1500s of irradiation (Fig. 6 top). These are consistent with the full XAFS results. Although the full XAFS scans were collected using up to a factor of 10 higher flux density, the shorter accumulation time used in collecting the time series means that roughly similar levels of total photons were delivered to the analysis point. The time series measurements, however, more clearly show that the decreases in measured intensity changes at the pre-edge energy are non-linear with continued irradiation. The curves measured for both glasses flatten over time, suggesting they may have reached an equilibrium condition after 400s of exposure at the highest flux densities tested. Natural basaltic glasses VG-2 and A-99 both show small decreases in count rates at the pre-edge at the highest tested flux density of ~ -5%. However, at the lower tested flux densities, intensity changes are difficult to discern in these natural glasses within the analytical uncertainty of measuring V Kα fluorescence at the short 1s integration times used.

DISCUSSION

Evaluating Potential Changes in Vanadium Valence During XAFS Analysis

We used the empirically-derived formula of Sutton et al. (2005) to evaluate the potential impact of the observed beam-induced changes in V speciation on the calculated average V valence (V*) of the glasses studies. The Sutton calibration calculates V* on the basis of measured, edge-step normalized, pre-edge peak intensities after subtraction of the rising edge background. For V XAFS oxybarometric studies, the pre-edge peak intensity is found to have high valence sensitivity, although it is important to recognize that changes in V coordination within the glass network will also alter pre-edge peak intensities. The study by Sutton et al. (2005) shows that in silicate glasses changes in the V pre-edge peak intensity changes are predominately due to valence changes; the intensities for V^{4+} are about the same in VI and V coordination and V^{5+} is about the same in IV and V. However, lower coordination numbers tend

277 to provide slightly more intense pre-edge peak intensities, so although the intensity changes are
278 dominated by changes valence, the magnitudes of valence effects reported here will be
279 overestimates if some of the observed intensity changes are also due to coordination changes.
280 It is clear from these analyses that V in silicate glasses will undergo measurable beam-
281 induced reduction at high flux densities when the average V valence in the glass, V*, is greater
282 than ~ 3.7. The degree of reduction is also observed to increase with increasing V* of the glass.
283 The rapid XAFS measurements of the most oxidized glass analyzed, FAD_V3 (Fig. 3), gives a
284 mean V* of 4.94 when measured at a low dose condition of 7.75 x10^8 ph/s/μm^2 and 4.65 at a
285 high dose condition of 6.25 x10^{11} ph/s/μm^2. Therefore, an observed reduction in calculated V
286 valence (ΔV*) of -0.3 when the flux density is increased by a factor of ~800. With decreasing V*
287 in the glass, the degree of observed reduction as a function of flux density at these conditions is
288 also observed to be smaller. In FAD_V1a the change in mean V* similar, from 4.30 to 4.02
289 (ΔV*=0.28), in FAD_V4 from 3.62 to 3.47 (ΔV*=0.15), and in FAD_V2a from 3.13 to 3.10
290 (ΔV*=0.03). The results of both rapid XAFS scanning (Figs. 3 and 5) and from time series
291 analyses at the pre-edge peak (Fig. 6) also show that at flux densities at or below 7.75 x10^8
292 ph/s/μm^2, changes in V* are not statistically discernable over 1500s of irradiation. Extrapolation
293 of the observed trends suggests that glasses with starting V* values near ~ 3.7 will display only
294 minimal change in pre-edge peak intensity with increasing dose.
295 Highly reduced glasses with calculated V* less than 3.7 also likely undergo changes in V
296 speciation with irradiation. This is reflected by measured changes in overall spectral shape, shifts
297 in the energy of the rising absorption edge and changes in the intensity of the spectral
298 background near the pre-edge peaks. However, it remains unclear in these samples to what
299 degree these changes in speciation also involve changes in valence state. For the most reduced

300 glass analyzed, FAD_V2a, it was noted that calculated mean V* only changes from 3.13 to 3.10
301 (ΔV*=0.03), arguably within statistical uncertainty. We also noted from the rapid XAFS analysis
302 (Figs. 2 and 5) that the first two spectra in this series, collected at the high flux condition, yield
303 slightly more reduced V*, but still within error of the calculated mean for all 10 spectra in the
304 series. Thus some degree of beam-induced oxidation (as opposed to reduction) in these highly
305 reduced glasses cannot be discounted. However, the impact on calculated average valence
306 appears small.

307 In the natural basaltic glasses studied the degree of reduction observed appears comparable to
308 what is observed in the synthetic FAD glasses. In MORB glass VG-2 the mean V* decreases
309 from 4.33 to 4.14 (ΔV*=0.19), very similar to what is observed in FAD_V1a, which yields a
310 generally similar mean V*. Observed trends are proportionally similar for both synthetic and
311 natural glasses even though there are large differences in Fe concentration in the glasses
312 analyzed, which is significant in that it suggests that differences in Fe concentration have little
313 impact on the observed effect. Although Fe is present at only trace element concentrations in the
314 FAD glasses analyzed here (Lanzirotti et al. 2018), in natural basaltic glasses Fe concentrations
315 typically exceed 10 wt% and will be the most abundant multi-valent element present. It is worth
316 noting, however, that it is unknown if the degree or direction of beam-induced changes in V
317 valence in silicate glasses are impacted by the water content of the glass. All the glasses analyzed
318 here are relatively anhydrous, including the natural glasses. In studies of Fe valence in natural
319 glasses there is a clear correlation between water content and increasing degrees of Fe oxidation
320 with increasing flux density (Cottrell et al. 2018),

321 ***Discussion of Potential Mechanisms for Beam-Induce Changes in V Valence***

Studies examining the structural and chemical changes that occur in glasses exposed to ionizing radiation have shown that irradiation can generate free electrons and holes which can then be trapped in defect sites (Bishay 1970). These electron-hole pairs can act to change the valences of incorporated trace elements spatially correlated with such defects (Camara and Oel 1984; El Batal and Naf 2005; Zhang et al. 2007; Abdelghany and ElBatal 2012; Gonçalves Ferreira et al. 2013). It has been hypothesized that the free electrons can reduce multivalent transition metals while reduced ions in the glass can potentially capture the positive hole centers to transform to more oxidized species.

The XAFS spectral changes observed here in glasses with starting V* greater than ~3.7 are consistent with beam-induced reduction of V valence and is the dominant change observed in V speciation due to irradiation. The pronounced decreases in pre-edge peak intensity, the shifting of E_0 to lower energy and the changes observed in white line structure are all expected to occur with V reduction (Lanzirotti et al. 2018). We hypothesize that V^{4+} and V^{5+} ions in these glasses are able to capture available free electrons produced during irradiation to convert to V^{3+} and V^{4+} ions, respectively. Such valence reductions are potentially accounted for by electron capture reactions, consistent with what has been suggested from previous glass irradiation studies (El Batal and Naf 2005; Abdelghany and ElBatal 2012). That the degree of beam-induced reduction decreases with decreasing V*, so that glasses with initial V* value < 3.7 show only small changes in V XAFS pre-edge peak intensity with increasing dose, imply that this is the point at which the fraction of V^{3+} becomes significant and the effects of continued oxidation of V are near the uncertainty level.

The possibility that some small degree of beam-induced oxidation of V^{3+} is occurring in the most reduced glasses analyzed cannot be conclusively discounted. Studies have shown that

irradiation of synthetic silicate, borate and soda lime glasses may result in the potential oxidation of reduced multivalent elements such as Fe^{2+}, Ce^{3+}, Cu^{+} and Mn^{2+} (Bishay 1970; El Batal and Naf 2005), hypothetically attributed to the reduced ions trapping holes via photochemical reactions. However, any such oxidation in the glasses studied here is within analytical uncertainty in fitting the pre-edge peaks. Oxidation of V^{3+} also appears to be inconsistent with the measured decreases of the E_0 absorption edge in the V XAFS with increasing dose, by as much as -0.8 eV for the most reduced glass analyzed here.

Even so, these more reduced glasses do display continued spectroscopic changes with irradiation, even though not clearly associated with changes in valence. There are observed increases in spectral intensity of the low energy shoulder at ~ 5475 eV, most likely reflecting changes in vanadium-oxygen complexing and coordination within the glass network during irradiation. Such effects can elevate the spectral backgrounds on the rising absorption edge and may account for the small increases measured in instantaneous count rate near the pre-edge peak with increasing dose. These changes in speciation seem to occur in all the glasses analyzed, regardless of valence.

IMPLICATIONS

Although V K-edge XAFS is highly sensitive to detecting small variations in V valence due to changing magmatic redox conditions, beam-induced changes in V speciation are likely to introduce systematic errors in calculated V* estimates, particularly in oxidized systems, that must be properly evaluated and/or mitigated in order to make meaningful interpretations with regards to the igneous evolution of the system.

The study presented here demonstrates that there are clear changes in V speciation that can occur during XAFS analysis of silicate glasses and that the magnitude of the observed beam-

induced modifications is dependent on both the radiation dose over the period of analysis and the starting valence of the samples being analyzed. The highest observed changes in valence occurred at flux densities > 6 x10^{11} ph/s/μm^2, resulting in reductions in calculated V* on the order of 0.3 valence units for the most oxidized glasses analyzed (V* = 4.94). A difference in assumed V* of 0.3 valence units can translate to differences in calculated fO_2 of as much as ~ 0.5 log units for terrestrial magmatic glasses equilibrated at ~1200 °C (Sutton et al. 2005), depending on redox conditions at equilibration, illustrating the importance of identifying the potential for such alterations to occur at the time of analysis. However, for the majority of terrestrial basaltic melts where V* is expected to be < 4, the impact on calculated oxygen fugacity will be significantly smaller.

Our low flux density data show that the radiation alteration effects can be mitigated by doing the measurements under these conditions. At the lower flux densities that we tested, ≤ 1x10^9 ph/s/μm^2, measured changes in V* were found to be < 0.04 for repeated analyses in a series, typically within the analytical uncertainty in calculating V* for any individual spectra using the Sutton et al. (2005) calibration. It was also found that magmatic glasses with V* values near 3.7 show the smallest degree of change in speciation, and thus calculated V*, with dose. This is an average V valence that is generally similar to that often measured for terrestrial basaltic glasses. For example, the terrestrial basaltic glasses analyzed in Sutton et al. (2005) and Lanzirotti et al. (2018), equilibrated at fO_2 from NNO-1.6 and NNO-0.5, provide V* values between 3.7 and 4.1.

These results allow us to infer negligible impact of potential radiation-induced effects on previously published results, studies which didn't account for possible beam-induced changes in V valence. For the glasses analyzed as part of the Sutton et al. (2005), we estimate that the beamline configuration used for the majority of their analyses, with a roughly 4 x 4 μm focused

beam, would have been conducted using a flux density of < $2x10^9$ ph/s/μm^2. At this flux density the most oxidized glasses analyzed may be expected to experience reductions in V* of < 0.05, within the quoted uncertainty of the analyses used to build their calibration curve. A study by Righter et al. (2006) examining the oxidation state of vanadium in coexisting spinel and basaltic melt reports V K-edge XAFS data collected at the same beamline at roughly the same time. The three standard spinels presented in the Righter et al. (2006) study, which are expected to be fairly resistant to beam-induced changes in speciation, are shown to lie very close to the Sutton 2005 calibration curve. Consistent with the hypothesis that at the flux density conditions used in the Sutton 2005 study, beam-induced reduction in the glass data was likely negligible. The study by Lanzirotti et al. (2018) developed V oxybarometry calibration models using multivariate analysis to predict the fO_2 of equilibration in glasses of basaltic composition and then tested the models on a suite of natural basaltic glasses. Recognizing the potential for beam-induced changes in V valence, the XAFS data collected on reference glasses for this study used a defocused beam of 30 x 30 μm and purposely reduced incident flux, so that flux densities to the standards was estimated to be ~$1x10^8$ ph/s/μm^2, so that changes outside of analytical uncertainty are not expected. Some of the analysis of natural glasses in this study did use a focused beam of ~ 2 x 2 μm, which would increase flux density to ~$2x10^{10}$ ph/s/μm^2. The natural glasses analyzed in that study, however, yield V* close to 4.1, so that beam reduction effects would be expected to reduce pre-edge peak intensities by <5%. A study by Head et al. (2018) included some V XAFS analyses of magmatic melt inclusions from Nyamuragira volcano, Africa using stated flux density of ~$2.5x10^{10}$ ph/s/μm^2, with calculated V* values between ~ 3.1 and 3.8. Although some reduction in V* would be expected at these flux densities, given calculated V* are < 4 it would be expected to reduce pre-edge peak intensities by <5%.

The results presented here provide researchers a framework for conducting V K-edge XAFS oxybarometry studies of natural magmatic glasses that will yield the most accurate estimate of the fO_2 at which the magma quenched. For most terrestrial magmatic glasses, where V* is found to be near 4, beam induced changes in valence can be effectively minimized to be within analytical uncertainty of the XAFS analysis if incident flux densities are kept at $\leq 1x10^9$ ph/s/μm^2. These results illustrate the importance of documenting not only the focused spot size used in V XAFS analysis of silicate glasses but the incident flux as well, so that the flux density can be estimated. This is a recommendation that has also been made for all XAFS analyses of magmatic melt inclusions (Rose-Koga et al. 2021).

The results of this study also have potential implications for the irradiation behavior of other multivalent trace elements in silicate glasses during XAFS analysis. Potential valence proxies for fO_2 in igneous systems include several multivalent elements that can be measured using XAFS. These are summarized in a review by Papike and coworkers (Papike et al. 2005, 2016) and include elements such S, Ti, Mn, Cr, Eu, and Fe in addition to V. With the increasing availability of brighter synchrotron sources and improved focusing optics capable of providing sub-micrometer focused X-ray beams for spectroscopic analysis (and thus potentially higher flux densities), it is important for researchers to accurately evaluate potential beam-induced changes in valence state and speciation for the elements being measured in each geochemical system, whether targets are magmatic silicate glasses or minerals.

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FIGURE CAPTIONS

Figure 1: Measured edge-step normalized V K-edge XAFS spectra collected for FAD_V3, the most oxidized glass analyzed (top), and FAD_V2a, the most reduced glass analyzed (bottom), measured at flux densities of 2.56 $x10^{8}$ (in red) and 9.25 $x10^{11}$ (in blue) ph/s/μm^2. The inset plots on each show the relative magnitude of the measured pre-edge peaks for both glasses after subtracting the edge step contribution via spline fitting of the rising absorption edge. Although the background subtracted spectra for oxidized glass FAD_V3 indicate an ~30% reduction in pre-edge peak intensity after subtraction of the spectral background, the background subtracted peak intensities for reduced glass FAD_V2a displays a <1% difference at the two flux densities tested. Glass FAD_V3 also displays a decrease in the energy of the main absorption edge (E_0) of 1.1 eV with increasing radiation dose. Glass FAD_V2a displays a decrease of 0.8 eV in E_0 with increasing dose. The dashed line shows a low energy shoulder at ~ 5475 eV on the rising

absorption edge that increases in intensity with increasing dose in both samples. This increasing shoulder in FAD_V2a may be responsible for the increasing background under the pre-edge peak and the decrease in E_0.

Figure 2: Series of rapid V K-edge XAFS spectra collected on reduced synthetic glasses FAD_V2a (top) and FAD_V4 (bottom) conducted at a low density of 7.75 $x10^8$ ph/s/μm^2 (left) and a high flux density of 6.25 $x10^{11}$ ph/s/μm^2 (right). Shown are a series of 10 edge-step normalized V K-edge XAFS spectra that were measured sequentially, with each scan acquired in ~1.5 minutes. Acquisition of 10 total spectra requires the glass to undergo irradiated at each flux density for a total time of ~15 minutes. The inset plots on each figure show the pre-edge peak portion of each scan and provide calculated V* for each scan using the Sutton et al. (2005) calibration, which subtracts the pre-edge background.

Figure 3: Series of rapid V K-edge XAFS spectra collected on oxidized synthetic glasses FAD_V1a (top) and FAD_V3 (bottom) conducted at a low and high flux density as described in Fig. 2.

Figure 4: Series of rapid V K-edge XAFS spectra collected on natural MORB glass VG-2 at a low and high flux density as described in Fig. 2.

Figure 5: Plots of the relative calculated V* for the rapid synthetic glass XAFS analyses FAD_V2a (blue), FAD_V4 (red), FAD_V1a (gray) and FAD_V3 (green) shown in Fig. 2 and 3 as a function of time. Calculated V* from the low flux density series are shown as open squares

592 and from the high flux density series as filled circles. Error bars show estimated 1σ uncertainties
593 in calculating V*.
594
595 Figure 6: V pre-edge intensity rate-of-change curves for oxidized FAD_V1a, and FAD_V3 and
596 for natural basaltic glasses VG-2 and A-99, collected at varying flux densities. Flux densities
597 tested are labeled, covering more than 4 orders of magnitude. Intensities were measured at the V
598 pre-edge peak at an energy of 5468.15 eV. Each time series consists of measurements at 1s
599 intervals over 1500s of total irradiation. The vertical axis shows the relative change in the pre-
600 edge peak intensity over time, so that for each curve the intensity of the first analysis point plots
601 at a value of 1.0.

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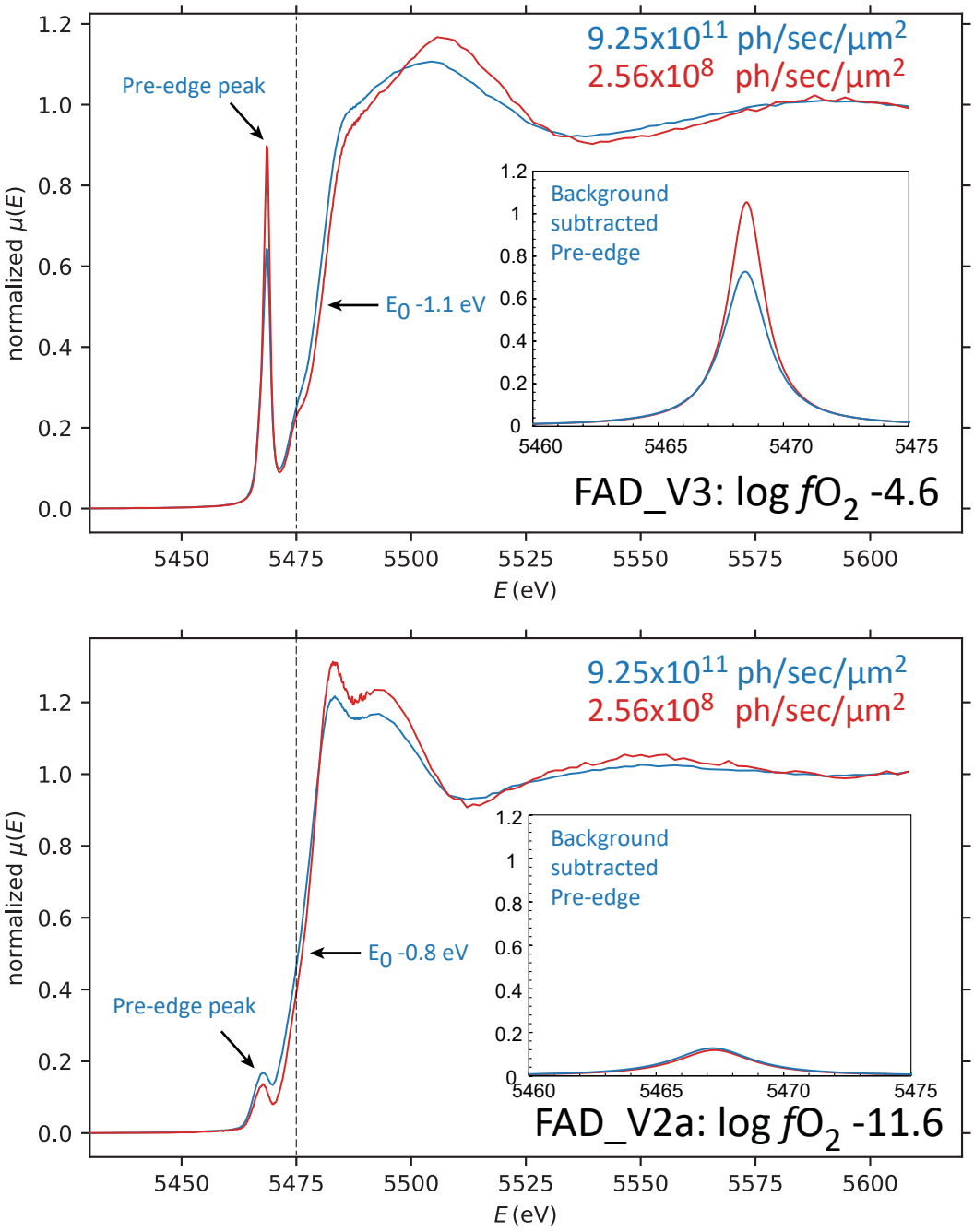
Figure 1



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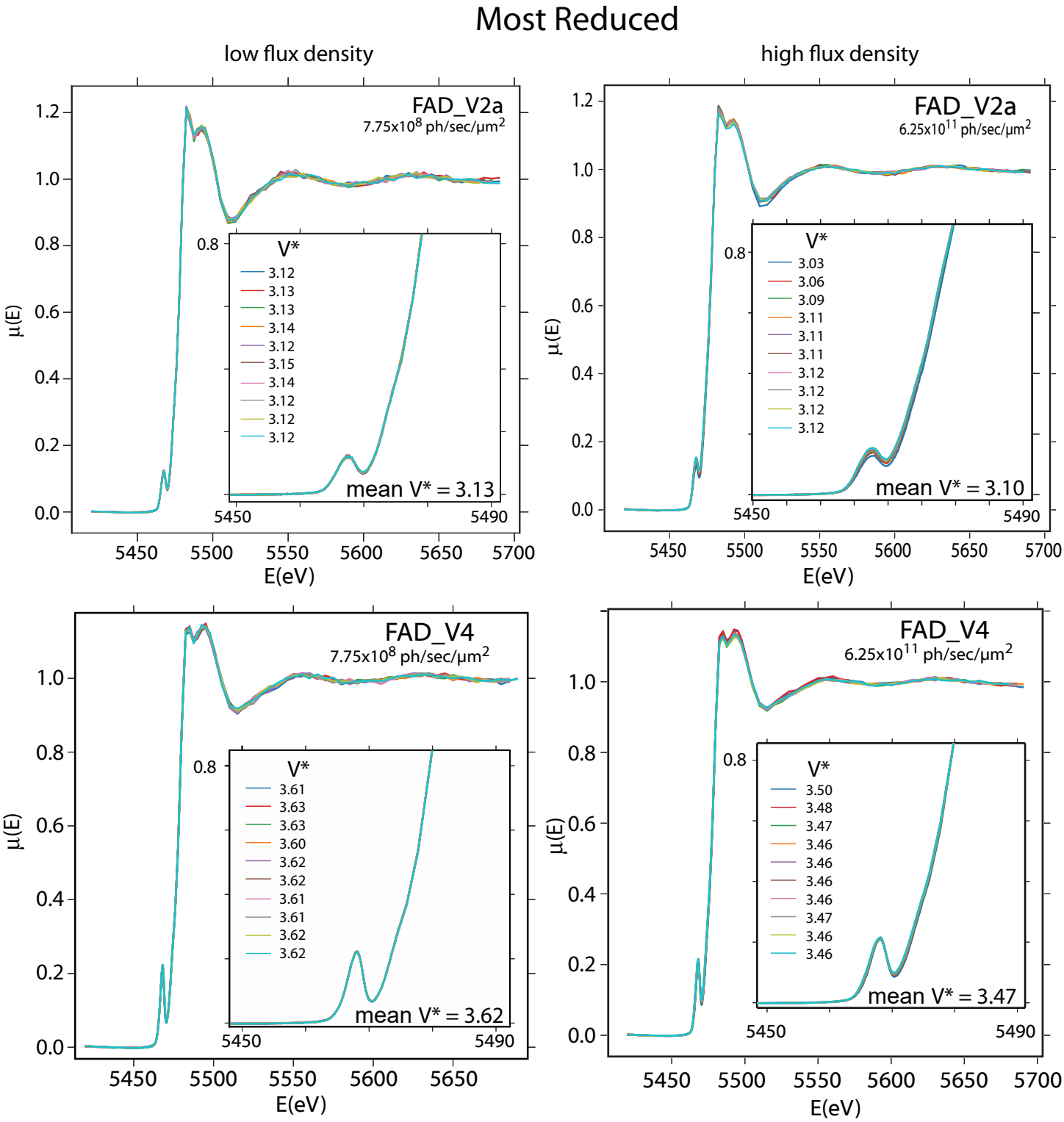

Figure 2

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Figure 3

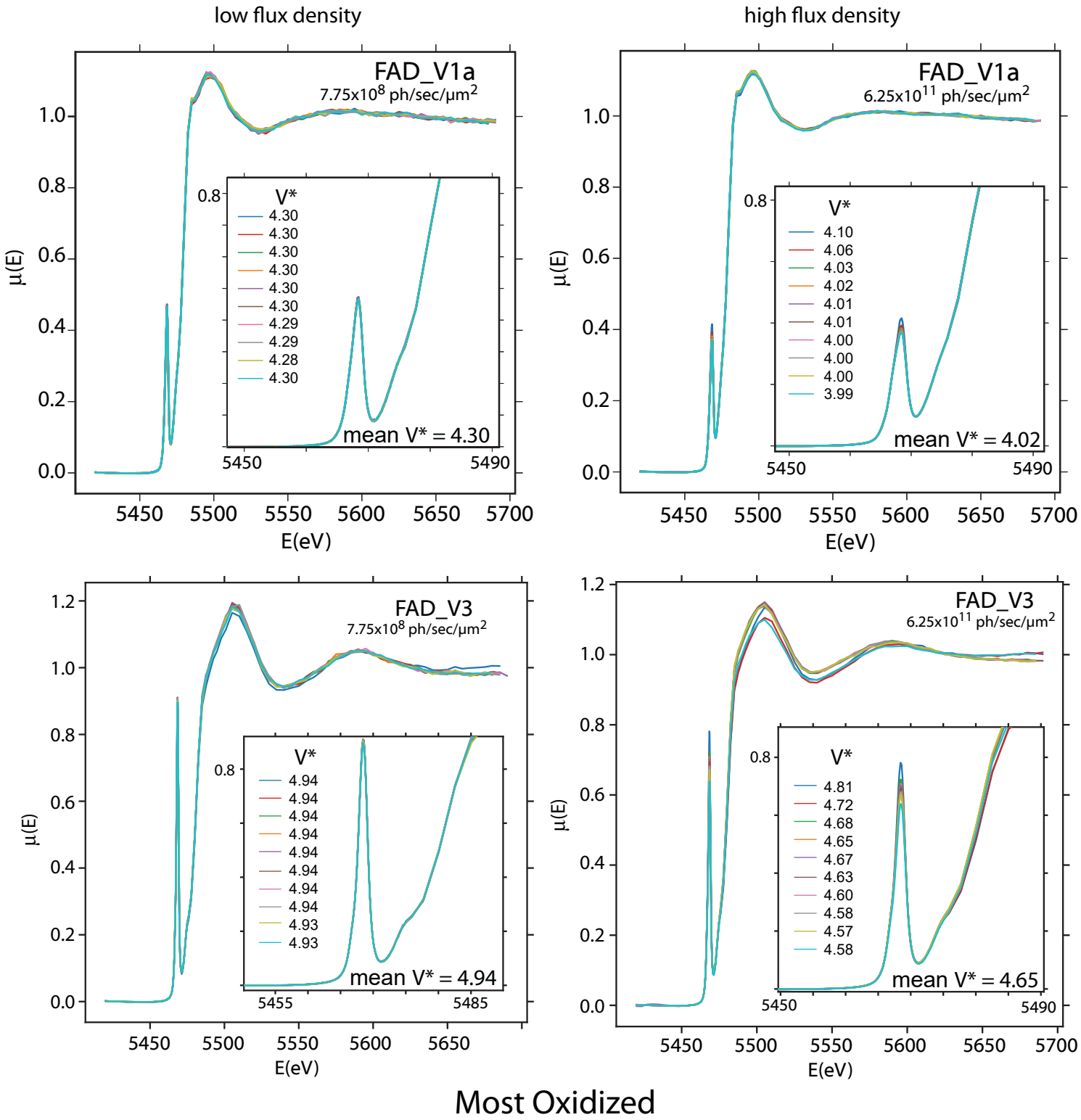

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Figure 4

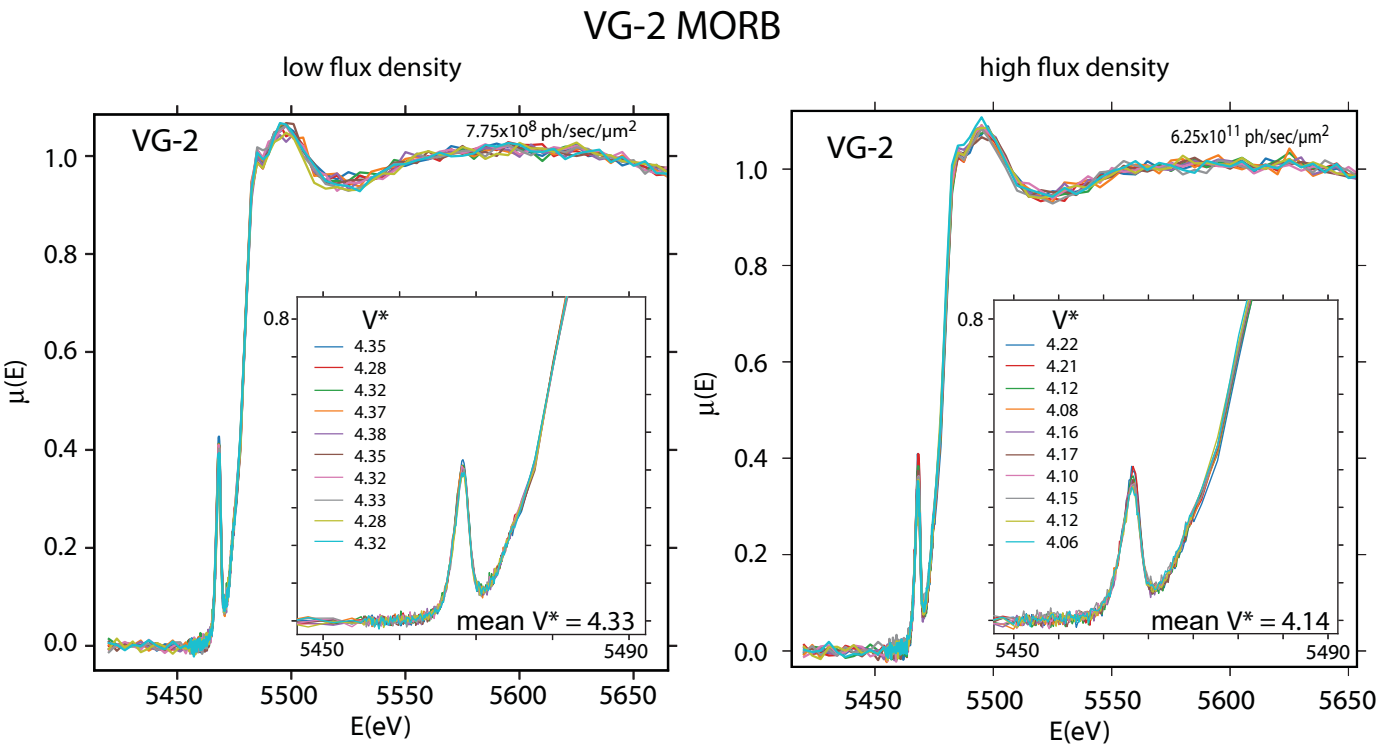

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Figure 5

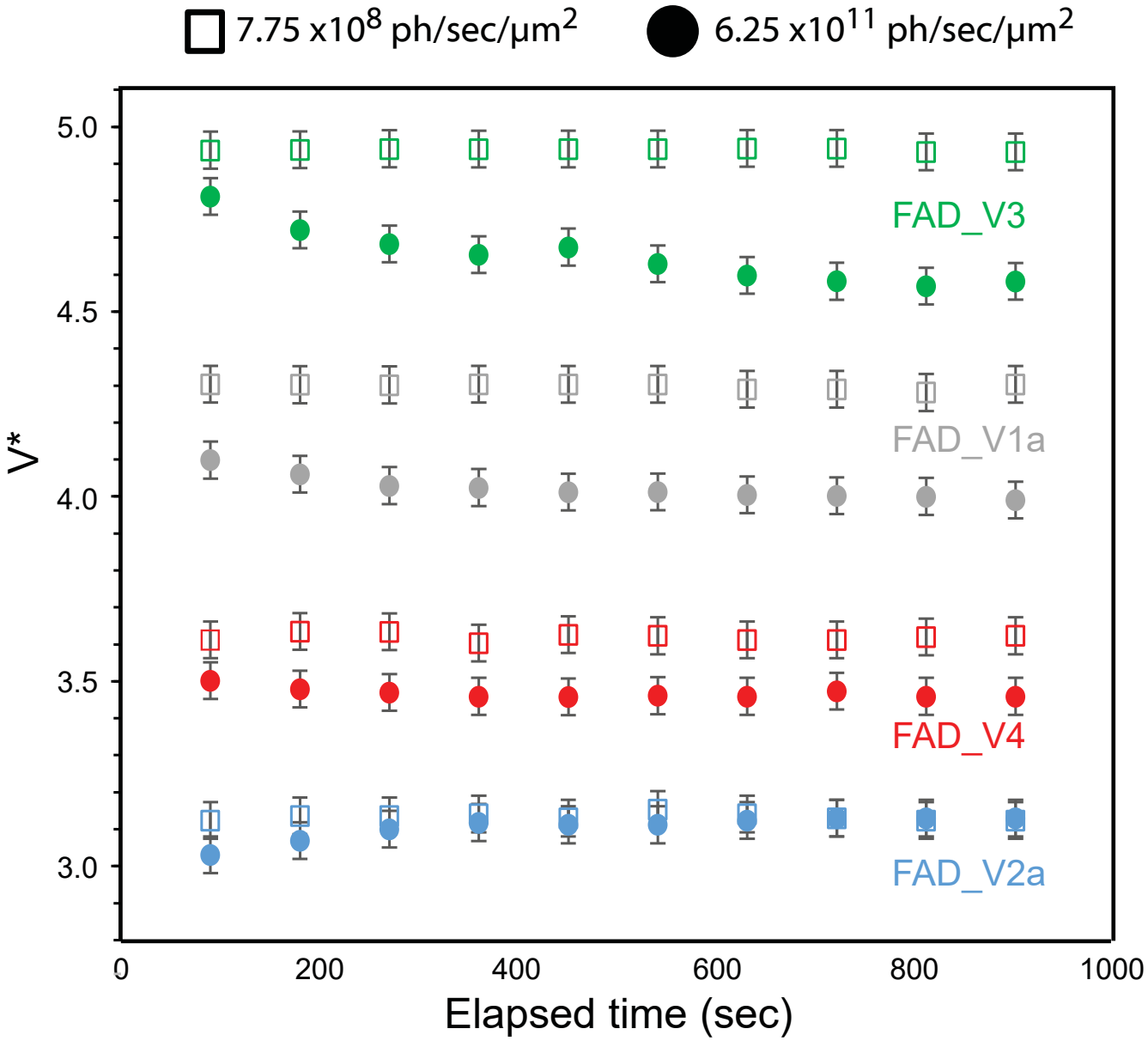

Figure 6

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