Accurate predictions of iron redox state in silicate glasses: A multivariate approach using x-ray absorption spectroscopy

M. Darby Dyar¹, Molly McCanta², Elly Breves¹, CJ Carey³, Antonio Lanzirotti⁴

¹Department of Astronomy, Mount Holyoke College, South Hadley, MA 01075, U.S.A.
²Department of Earth and Ocean Sciences, Tufts University, Medford, MA 02159, U.S.A.
³School of Information and Computer Sciences, University of Massachusetts at Amherst, Amherst, MA 01003, U.S.A.
⁴Center for Advanced Radiation Sources, University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637, U.S.A.

ABSTRACT

Pre-edge features in the K absorption edge of x-ray absorption spectra are commonly used to predict Fe³⁺ valence state in silicate glasses. However, this study shows that using the entire spectral region from the pre-edge into the extended x-ray absorption fine structure region provides more accurate results when combined with multivariate analysis techniques. The least absolute shrinkage and selection operator (lasso) regression technique yields %Fe³⁺ values that are accurate to ±3.6% absolute when the full spectral region is employed. This method can be used across a broad range of glass compositions, is easily automated, and is demonstrated to yield accurate results from different synchrotrons. It will enable future studies involving x-ray mapping of redox gradients on standard thin sections at 1×1 μm pixel sizes.

INTRODUCTION

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It has long been a goal of geoscientists to develop a robust method for microanalysis of iron redox states, and decades of development in the synchrotron x-ray absorption spectroscopy (XAS) community have worked toward this goal. Glasses are of particular interest because of the direct relationship between Fe$^{3+}/\Sigma$Fe and the intrinsic oxygen fugacity ($f_{O2}$) of the melt, and the fact that glasses may record the oxidation state of their magma source region and, possibly, the additional effects of magma interaction with the near surface environment.

The geological community is especially interested in using XAS to quantify Fe redox states in magmatic and volcanic glasses of varying compositions. Berry et al. (2003) laid the framework for many subsequent studies by using XAS spectra of synthetic silicate glasses with independently-measured Fe$^{3+}/\Sigma$Fe ratios to calculate Fe$^{3+}$ from peak area-normalized centroids in the pre-edge region. Subsequent workers (e.g., Wilke et al. 2005, Cottrell et al. 2009, Lühl et al. 2014) also used internal standards to predict redox in glasses. These studies made incremental progress toward development of a more generalized approach because they used only small numbers of standards, so their results were applicable to only limited compositional ranges. They also focused only on the pre-edge portion of the Fe K absorption edge.

The challenge now at hand is to improve upon all prior approaches to Fe redox state determinations by exploiting information contained in the entire XAS spectrum, potentially extending into the EXAFS region. For example, Berry et al. (2010) suggest several empirical alternative approaches to calibration of garnet XANES spectra. They report that the average centroid energy of garnet pre-edges is relatively insensitive to Fe$^{3+}/\Sigma$Fe, and propose two alternative approaches to Fe$^{3+}/\Sigma$Fe prediction. The first is to use the main absorption edge energy at an arbitrary normalized intensity value of 0.9, and the second employs the ratio of spectral intensities at 7138.4 and 7161.7 eV. This work shows that valuable information is encoded in the
main edge and low-energy EXAFS regions.

Most recently, Dyar et al. (2012) demonstrated that a multivariate analysis method (partial last squares regression, or PLS) employing the full XAS spectra resulted in dramatic improvements in the accuracy of predicting Fe$^{3+}$/ΣFe in garnets. Results showed that PLS analysis of the entire XANES spectral region yields significantly better predictions of Fe$^{3+}$ in garnets, with both robustness and generalizability, than approaches based solely on pre-edges. Moreover, their PLS coefficients and loadings clearly demonstrate that the vast majority of the useful information in the XANES spectra for predicting Fe$^{3+}$/ΣFe in garnets is found in channels at the main edge and higher. The current study tests the broader applicability of this result on a system of great interest to geoscientists: silicate glasses.

This study seeks to overcome the limitations of the previous studies of Fe$^{3+}$/ΣFe by using 372 spectra from 60 different bulk glass compositions and comparing information found in the pre-edge region to that in the broader energy range covering the Fe K edge from 7100-7220 eV. We describe a robust model with well-justified error bars that allows determination of Fe$^{3+}$/ΣFe over a wide range of silicate glass compositions. Software available from the authors allows this calibration to be used on data from any synchrotron that outputs data in the ubiquitous χμ(*.xmu) standard format as output by the ATHENA program (Ravel and Newville 2005).

**SAMPLES STUDIED**

Compositions of synthetic glass samples studied are shown in Figure 1 on a plot of total alkalis vs. SiO$_2$ and as-run compositions are provided in Table 1. Starting compositions were

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1Deposit item AM-15-xxxx, Table 1. Deposit items are available two ways: For a paper copy, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue for price information). For an electronic copy visit the MSA web site at http://www.minsocam.org, go to The American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.
produced by weighing out appropriate amounts of Alfa Aesar Puratronic oxide and carbonate powders, grinding the mixtures by hand in an agate mortar under ethanol for one hour, and decarbonating (if carbonates were present) at 800°C for 2 hours. Oxide mixes were used directly in the low-SiO₂ experiments without a glassing step. A mixture of sample powder (~100 mg) and polyvinyl alcohol (PVA) was used to adhere the sample to the wire loop. High-SiO₂ runs were first glassed at the appropriate \( f_{O2} \) and the resulting glass was placed on a wire loop (without PVA) and rerun to ensure homogeneity and lack of bubbles.

Equilibration experiments were run in a vertical 1-atm gas mixing furnace at Tufts University using the Pt (or Re) wire-loop technique. Re loops were used for low \( f_{O2} \) runs (\( f_{O2} < \) QFM [quartz-fayalite-magnetite]). Re wire was used as Fe solubility in the Re is low under the conditions of these experiments (Borisov and Jones 1999). Pt-loops were pre-doped using powders of the identical starting composition for 6 hours at \( T_{max} \) and the \( f_{O2} \) intended for the experiment. Glassy material was dissolved off the Pt-loop using a 50:50 mixture of heated HF and HNO₃ and the loop was then used for an experiment. These procedures were followed to reduce but, generally, not eliminate Fe losses to the wire during an experiment. A majority of the samples were equilibrated in multiple \( f_{O2} \)’s including air, CO₂, and at QFM and IW/Mo-MoO₂ buffers to vary the resulting Fe³⁺ contents.

In addition to those samples, we were fortunate to obtain probe mounts from the wet chemical redox study of Moore et al. (1995), which included many highly silicic samples. Our data set also includes five repeat XAS analyses on a homogeneous bead of volcanic glass from Apollo sample 15081; no Mossbauer analysis is available for that sample, but it is likely to be completely reduced, having formed at IW-0.5 (Sato et al. 1973).

METHODS
Samples were analyzed during several sessions at beamline X26A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, and beamline 13 ID-E (GSECARS) at the 7 GeV Advanced Photon Source, Argonne National Laboratory. At both beamlines, the beam was focused using mutually-orthogonal Kirkpatrick-Baez mirrors to a ~7×9 μm area (NSLS) or a 1×1 μm area (GSECARS). Incident beam energy was controlled by a water-cooled (9° C) Si(311) channel-cut monochromator. At the NSLS, monochromator energy drift was monitored with a magnetite standard that was analyzed before and after every 2-3 samples. An energy offset was determined using repeat measurements of the observed pre-edge centroid of the NMNH magnetite standard relative to a reference energy of 7113.25 eV (cf. Westre et al. 1997). At GSECARS, incident x-ray energy was calibrated on the first derivative peak of an iron metal foil standard (7110.75 eV, Kraft et al. 1996) and no energy drift was detected throughout the analytical session. Numerous samples were run at both facilities and the spectra are indistinguishable (Figure 2), indicating that the energy calibrations are comparable.

XANES spectra were collected in fluorescence mode using a 9-element high-purity Ge solid-state detector array. Acquisition parameters varied between sessions, but the structure of the Fe K absorption edge was scanned at a sampling resolution of at least 5.0 eV from 7020-7105 eV, 0.1 eV from 7105-7118 eV, 0.5 eV from 7118-7140 eV, and 1.0 eV from 7140-7220 eV. The maximum energy of the scan was chosen empirically to avoid any significant remaining oscillations in the absorption spectra to achieve reasonable edge-step normalization.

Spectra were processed using the PAXAS (Python Analysis for XAS) software package written for this project by Mirna Lerotic and CJ Carey. The program automates I₀ and edge-step normalization and optional correction for over-absorption (OA). PAXAS works in batch processing mode, taking as input a list of filenames of raw spectra, a list of sample compositions...
for OA correction, material type (garnet, amphibole, glass), and optional energy shifts for each spectrum. Background removal and edge-step normalization in PAXAS were performed using a linear fit to the pre-edge region (~7025-7085 eV) and a third-order polynomial fit to the post-edge region (~7210-7215 eV) using the algorithm of Ravel and Newville (2005). The optional OA correction uses an adaptation of the FLUO algorithm (Haskel 1999) with absorption cross-sections used to approximate the absorption coefficient from McMaster et al. (1969). Input data files are in the standard $\chi\mu$ (*.xmu) format as output by the ATHENA program (multi-column data of energy bins, fluorescence intensities and incident flux intensities). PAXAS assumes that input data has already been corrected for detector dead-time. The software is configured to output predicted $\%Fe^{3+}$ using the optimal algorithm described in Dyar et al. (2012) for garnets, Dyar et al. (submitted) for amphiboles, and this paper for glasses, and is available from the authors.

Four variations of data input were employed: pre-edge data only vs. the full spectra, and corrected for OA vs. uncorrected. Each of these four data sets was tested using two multivariate techniques. The first is partial least squares regression (PLS), which calculates components that maximize the covariance between the feature and response matrices (Wegelin 2000). It is especially well suited for problems with many highly correlated features and multiple responses (Kalivas 1999). PLS sequentially chooses directions, or components, of maximal covariance from the feature matrix, $X$, and the response matrix, $Y$, to determine the model coefficients using a two-step process. The first step is the shrinkage step, in which the shrinkage penalty determines the number of factors to be included in the regression. This shrinks the feature matrix by projecting it from the original $p$-dimensional space into a smaller $q$-dimensional vector space. In this project, $p = 600$, the number of channels at which the signal is measured, and $q$, the number
of components, is either allowed to vary from 1-10 or held constant at \( q = 6 \) in this study. The second step follows ordinary least squares by regressing the response (here \( \text{Fe}^{3+}/\text{Fe} \)) on the components generated in the first step to minimize the residual sum of squared error.

The second multivariate technique tested was lasso regression, which is an ordinary least squares regression model with an \( l_1 \) penalty on the model coefficients to induce sparsity (Hastie et al. 2009). It produces a sparse model by shrinking some coefficients and setting most other coefficients to zero. It is assumed that a smaller subset of the predictor variables is driving the prediction results. Thus, other coefficients can be excluded from the model (i.e., set to zero) with no significant performance loss. This reduces a sizable, largely uninterpretable model to a sparse, more interpretable model. The lasso adds a regularizer to ordinary least squares to prevent the model from overfitting the training data. It performs automatic feature selection by constricting non-informative feature coefficients to zero. For problems with many features, the lasso can eliminate noisy features that may otherwise hinder the model. These parsimonious models have shown to be effective in many types of chemometric models (Filmozer et al. 2012). The lasso has one hyperparameter, \( \alpha \), that controls the constriction level of the coefficient vector \( \beta \).

The open-source machine learning Python library Scikit-learn (Pedregosa et al. 2011) was used to train and test all models. Accuracy was evaluated using leave-one-out cross-validation and calculated using the root mean square error of prediction (RMSEP), which is in the units of absolute \( \%\text{Fe}^{3+} \).

**RESULTS**

Results of the 12 permutations on multivariate analyses are given in Figure 3: six models using the full spectrum (lasso, PLS with \( q \) floating, and PLS with \( q = 6 \) either with or without the over-absorption correction) and the same six using only the first 120 channels that comprise the
pre-edge region. The PLS models with \( q \) held constant at 6 are very similar to those in which \( q \) was allowed to float. In fact, for both full-spectrum models the floating \( q \) converged on a value of 6, the same as the value held constant. The pre-edge models converged on \( q = 5 \) when that parameter was allowed to vary, but the RMSEP is very similar. We conclude that models with \( q = 6 \) are most broadly useful.

Overall, the pre-edge-only prediction models yield uniformly inferior results, with the lasso performing slightly better than the PLS models. The full spectrum models all have significantly smaller (better) RMSEP values and the \( R^2 \) values of those predictions when plotted against Mössbauer \( \%Fe^{3+} \) are >0.94. For the 600-channel models, the lasso performs the best, with RMSEP = 3.55 for samples without the over-absorption correction, and ±3.59 for corrected data. On the basis of these results, the two lasso models will be used in the PAXAS software package; errors on prediction of \( \%Fe^{3+} \) in glasses can be cited as ±3.6 for either model.

Our data also provide an opportunity to check the applicability of our model to data from two facilities. Figure 4 shows plots of predicted vs. measured \( \%Fe^{3+} \) for the two lasso models, with different colors for data from NSLS and APS. There is no appreciable difference between the two data sets, which were acquired on overlapping sets of samples.

Figure 5 shows the results of the models in graphical format. All data are plotted in blue for the full spectra (top panels) and the pre-edge region only. For the lasso models, lasso coefficients are indicated as vertical red lines; selected channels (energies) are indicated by the \( x \) axis and the magnitudes of those coefficients are indicated by the length of the bar and the endpoint relative to the right-hand \( y \) axis. Only a few coefficients are located in the energy region corresponding to the pre-edge signal, indicating that the bulk of information in the spectra about Fe valence state is found in the main edge and EXAFS regions. The same trend is observed to
some extent in the PLS model loadings and coefficients. In contrast, the pre-edge models (bottom panels in Figure 5), while less accurate, are remarkably sparse. Note that although the pre-edge centroids have negative rather than positive PLS coefficients (bottom panels of Figure 5), that does not they do not influence the predictions. In general, the magnitudes of PLS coefficients are much informative that their signs.

**IMPLICATIONS**

There is great diversity in standards and methods used by different research groups for prediction of Fe$^{3+}$/Fe in glasses, and this has resulted in a general lack of consistency and accuracy across different studies. This work provides a broadly-applicable and widely accessible method that is easily implemented using standard XAS file formats and does not require time-consuming fitting of pre-edge features. Moreover, data from previous studies can easily be re-analyzed to assess the reliability of existing numbers. The new calibration should ensure that cross-comparisons can be made among researchers and synchrotron facilities with known accuracy.

Moreover, the automated nature of this technique and its optimal performance from the lasso sparse prediction method open the door to the long-awaited possibility of creating maps of Fe$^{3+}$ at high resolutions. The lasso calibration uses ~100 of the 600 channels acquired in this study. Even if adjacent channels are included in a data-acquisition protocol, the time needed for analyzing a single spot will be halved. At ~45 seconds per location (including moving the sample) and 1×1 μm resolution, it will be possible to create a map of Fe$^{3+}$ on a 50 μm glassy area in a thin section in ~35 hours. Understanding redox gradients in silicate glasses should provide exciting new insights into magmatic processes at microscales.

**ACKNOWLEDGMENTS**

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We are grateful to Gordon Moore for the loan of the samples from his thesis and 1995 paper. We acknowledge funding from NSF grants EAR-1219761 and EAR-1219850.

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FIGURES AND FIGURE CAPTIONS

**FIGURE 1.** Total alkali vs. SiO$_2$ diagram showing compositions used for XANES calibration. Green circles indicate samples equilibrated at up to four different f$_{O_2}$’s, resulting in glasses with nearly the same composition but very different Fe$^{3+}$ contents. Purple squares represent compositions from other studies (see text) for which only a single glass was used. Full compositional information for all standards is given in Table 1.

**FIGURE 2.** Comparison of over-absorption-corrected XAS spectra acquired at two different synchrotrons: beamlines x26a at the National Synchrotron Light Source at Brookhaven National Laboratory, and the GSECARS beamline at the 7 GeV Advanced Photon Source, Argonne National Laboratory.

**FIGURE 3.** Graphs of leave-one-out cross-validation results from twelve different models showing prediction errors calculated as root mean square errors (top panel) and the R$^2$ values for a best-fit line comparing the XAS-predicted %Fe$^{3+}$ values to those from Mössbauer spectroscopy (bottom panel). These results demonstrate that sparse prediction models significantly outperform PLS for this data set.

**FIGURE 4.** Example plots of predicted Fe$^{3+}$ by the lasso models using the full spectra for data without over-absorption correction (no OA) and with it (with OA). In both cases, the regression line has an R$^2$ value of 0.99.

**FIGURE 5.** All XAS data in full spectrum and pre-edge-only models are plotted in blue against the locations and magnitudes of lasso coefficients (vertical red lines ending in circles) in square plots and the loadings and coefficients for PLS models (red dashed lines) with $q = 6$, in rectangular plots. The red features indicate the energies at which the prediction of Fe$^{3+}$ is most weighted in the x direction; the y direction shows the magnitude of the coefficient or loading at that energy.
With OA

\[ y = 0.98x + 0.96 \]
\[ R^2 = 0.99 \]

No OA

\[ y = 0.98x + 0.93 \]
\[ R^2 = 0.99 \]