1   **Accurate predictions of iron redox state in silicate glasses: A multivariate approach using**

2   **x-ray absorption spectroscopy**

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11   REVISION 1

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13   **ABSTRACT**

14   Pre-edge features in the K absorption edge of x-ray absorption spectra are commonly

15   used to predict Fe^{3+} valence state in silicate glasses. However, this study shows that using the

16   entire spectral region from the pre-edge into the extended x-ray absorption fine structure region

17   provides more accurate results when combined with multivariate analysis techniques. The least

18   absolute shrinkage and selection operator (lasso) regression technique yields %Fe^{3+} values that

19   are accurate to ±3.6% absolute when the full spectral region is employed. This method can be

20   used across a broad range of glass compositions, is easily automated, and is demonstrated to

21   yield accurate results from different synchrotrons. It will enable future studies involving x-ray

22   mapping of redox gradients on standard thin sections at 1×1 μm pixel sizes.

23   **INTRODUCTION**

24   It has long been a goal of geoscientists to develop a robust method for microanalysis of

25   iron redox states, and decades of development in the synchrotron x-ray absorption spectroscopy

26   (XAS) community have worked toward this goal. Glasses are of particular interest because of the

27   direct relationship between $Fe^{3+}/\Sigma Fe$ and the intrinsic oxygen fugacity (f_{O2}) of the melt, and the

28   fact that glasses may record the oxidation state of their magma source region and, possibly, the

29   additional effects of magma interaction with the near surface environment.

30   The geological community is especially interested in using XAS to quantify Fe redox

31   states in magmatic and volcanic glasses of varying compositions. Berry et al. (2003) laid the

32   framework for many subsequent studies by using XAS spectra of synthetic silicate glasses with

33   independently-measured $Fe^{3+}/\Sigma Fe$ ratios to calculate Fe^{3+} from peak area-normalized centroids in

34   the pre-edge region. Subsequent workers (e.g., Wilke et al. 2005, Cottrell et al. 2009, Lühl et al.

35   2014) also used internal standards to predict redox in glasses. These studies made incremental

36   progress toward development of a more generalized approach because they used only small

37   numbers of standards, so their results were applicable to only limited compositional ranges. They

38   also focused only on the pre-edge portion of the Fe K absorption edge.

39   The challenge now at hand is to improve upon all prior approaches to Fe redox state

40   determinations by exploiting information contained in the entire XAS spectrum, potentially

41   extending into the EXAFS region. For example, Berry et al. (2010) suggest several empirical

42   alternative approaches to calibration of garnet XANES spectra. They report that the average

43   centroid energy of garnet pre-edges is relatively insensitive to $Fe^{3+}/\Sigma Fe$, and propose two

44   alternative approaches to $Fe^{3+}/\Sigma Fe$ prediction. The first is to use the main absorption edge energy

45   at an arbitrary normalized intensity value of 0.9, and the second employs the ratio of spectral

46   intensities at 7138.4 and 7161.7 eV. This work shows that valuable information is encoded in the

47   main edge and low-energy EXAFS regions.

48   Most recently, Dyar et al. (2012) demonstrated that a multivariate analysis method

49 (partial last squares regression, or PLS) employing the full XAS spectra resulted in dramatic

50 improvements in the accuracy of predicting $Fe^{3+}/\Sigma Fe$ in garnets. Results showed that PLS

51 analysis of the entire XANES spectral region yields significantly better predictions of Fe^{3+} in

52 garnets, with both robustness and generalizability, than approaches based solely on pre-edges.

53 Moreover, their PLS coefficients and loadings clearly demonstrate that the vast majority of the

54 useful information in the XANES spectra for predicting $Fe^{3+}/\Sigma Fe$ in garnets is found in channels

55 at the main edge and higher. The current study tests the broader applicability of this result on a

56 system of great interest to geoscientists: silicate glasses.

57   This study seeks to overcome the limitations of the previous studies of $Fe^{3+}/\Sigma Fe$ by using

58 372 spectra from 60 different bulk glass compositions and comparing information found in the

59 pre-edge region to that in the broader energy range covering the Fe K edge from 7100-7220 eV.

60 We describe a robust model with well-justified error bars that allows determination of $Fe^{3+}/\Sigma Fe$

61 over a wide range of silicate glass compositions. Software available from the authors allows this

62 calibration to be used on data from any synchrotron that outputs data in the ubiquitous $\chi\mu$

63 (*.xmu) standard format as output by the ATHENA program (Ravel and Newville 2005).

SAMPLES STUDIED

65   Compositions of synthetic glass samples studied are shown in Figure 1 on a plot of total

66 alkalis vs. SiO_2 and as-run compositions are provided in Table 1[1]. Starting compositions were

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[1]Deposit 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.

67   produced by weighing out appropriate amounts of Alfa Aesar Puratronic oxide and carbonate

68   powders, grinding the mixtures by hand in an agate mortar under ethanol for one hour, and

69   decarbonating (if carbonates were present) at 800°C for 2 hours. Oxide mixes were used directly

70   in the low-SiO_2 experiments without a glassing step. A mixture of sample powder (~100 mg) and

71   polyvinyl alcohol (PVA) was used to adhere the sample to the wire loop. High-SiO_2 runs were

72   first glassed at the appropriate f_{O2} and the resulting glass was placed on a wire loop (without

73   PVA) and rerun to ensure homogeneity and lack of bubbles.

74   Equilibration experiments were run in a vertical 1-atm gas mixing furnace at Tufts

75   University using the Pt (or Re) wire-loop technique. Re loops were used for low f_{O2} runs (f_{O2} <

76   QFM [quartz-fayalite-magnetite]). Re wire was used as Fe solubility in the Re is low under the

77   conditions of these experiments (Borisov and Jones 1999). Pt-loops were pre-doped using

78   powders of the identical starting composition for 6 hours at T_{max} and the f_{O2} intended for the

79   experiment. Glassy material was dissolved off the Pt-loop using a 50:50 mixture of heated HF

80   and HNO_3 and the loop was then used for an experiment. These procedures were followed to

81   reduce but, generally, not eliminate Fe losses to the wire during an experiment. A majority of the

82   samples were equilibrated in multiple f_{O2}'s including air, CO_2, and at QFM and IW/Mo-MoO_2

83   buffers to vary the resulting Fe^{3+} contents.

84   In addition to those samples, we were fortunate to obtain probe mounts from the wet

85   chemical redox study of Moore et al. (1995), which included many highly silicic samples. Our

86   data set also includes five repeat XAS analyses on a homogeneous bead of volcanic glass from

87   Apollo sample 15081; no Mossbauer analysis is available for that sample, but it is likely to be

88   completely reduced, having formed at IW-0.5 (Sato et al. 1973).

89   **METHODS**

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90   Samples were analyzed during several sessions at beamline X26A at the National

91   Synchrotron Light Source (NSLS), Brookhaven National Laboratory, and beamline 13 ID-E

92   (GSECARS) at the 7 GeV Advanced Photon Source, Argonne National Laboratory. At both

93   beamlines, the beam was focused using mutually-orthogonal Kirkpatrick-Baez mirrors to a ~7×9

94   μm area (NSLS) or a 1×1 μm area (GSECARS). Incident beam energy was controlled by a

95   water-cooled (9° C) Si(311) channel-cut monochromator. At the NSLS, monochromator energy

96   drift was monitored with a magnetite standard that was analyzed before and after every 2-3

97   samples. An energy offset was determined using repeat measurements of the observed pre-edge

98   centroid of the NMNH magnetite standard relative to a reference energy of 7113.25 eV (cf.

99   Westre et al. 1997). At GSECARS, incident x-ray energy was calibrated on the first derivative

100 peak of an iron metal foil standard (7110.75 eV, Kraft et al. 1996) and no energy drift was

101 detected throughout the analytical session. Numerous samples were run at both facilities and the

102 spectra are indistinguishable (Figure 2), indicating that the energy calibrations are comparable.

103   XANES spectra were collected in fluorescence mode using a 9-element high-purity Ge

104 solid-state detector array. Acquisition parameters varied between sessions, but the structure of

105 the Fe K absorption edge was scanned at a sampling resolution of at least 5.0 eV from 7020-7105

106 eV, 0.1 eV from 7105-7118 eV, 0.5 eV from 7118-7140 eV, and 1.0 eV from 7140-7220 eV. The

107 maximum energy of the scan was chosen empirically to avoid any significant remaining

108 oscillations in the absorption spectra to achieve reasonable edge-step normalization.

109   Spectra were processed using the PAXAS (Python Analysis for XAS) software package

110 written for this project by Mirna Lerotic and CJ Carey. The program automates I_0 and edge-step

111 normalization and optional correction for over-absorption (OA). PAXAS works in batch

112 processing mode, taking as input a list of filenames of raw spectra, a list of sample compositions

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113 for OA correction, material type (garnet, amphibole, glass), and optional energy shifts for each

114 spectrum. Background removal and edge-step normalization in PAXAS were performed using a

115 linear fit to the pre-edge region (~7025-7085 eV) and a third-order polynomial fit to the post-

116 edge region (~7210-7215 eV) using the algorithm of Ravel and Newville (2005). The optional

117 OA correction uses an adaptation of the FLUO algorithm (Haskel 1999) with absorption cross-

118 sections used to approximate the absorption coefficient from McMaster et al. (1969). Input data

119 files are in the standard $\chi\mu$ (*.xmu) format as output by the ATHENA program (multi-column

120 data of energy bins, fluorescence intensities and incident flux intensities). PAXAS assumes that

121 input data has already been corrected for detector dead-time. The software is configured to

122 output predicted $\%Fe^{3+}$ using the optimal algorithm described in Dyar et al. (2012) for garnets,

123 Dyar et al. (submitted) for amphiboles, and this paper for glasses, and is available from the

124 authors.

125 Four variations of data input were employed: pre-edge data only vs. the full spectra, and

126 corrected for OA vs. uncorrected. Each of these four data sets was tested using two multivariate

127 techniques. The first is partial least squares regression (PLS), which calculates components that

128 maximize the covariance between the feature and response matrices (Wegelin 2000). It is

129 especially well suited for problems with many highly correlated features and multiple responses

130 (Kalivas 1999). PLS sequentially chooses directions, or components, of maximal covariance

131 from the feature matrix, **X**, and the response matrix, **Y**, to determine the model coefficients using

132 a two-step process. The first step is the shrinkage step, in which the shrinkage penalty determines

133 the number of factors to be included in the regression. This shrinks the feature matrix by

134 projecting it from the original p-dimensional space into a smaller q-dimensional vector space. In

135 this project, $p = 600$, the number of channels at which the signal is measured, and q, the number

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136   of components, is either allowed to vary from 1-10 or held constant at $q = 6$ in this study. The

137   second step follows ordinary least squares by regressing the response (here $Fe^{3+}/$ Fe) on the

138   components generated in the first step to minimize the residual sum of squared error.

139   The second multivariate technique tested was lasso regression, which is an ordinary least

140   squares regression model with an l_1 penalty on the model coefficients to induce sparsity (Hastie

141   et al. 2009). It produces a sparse model by shrinking some coefficients and setting most other

142   coefficients to zero. It is assumed that a smaller subset of the predictor variables is driving the

143   prediction results. Thus, other coefficients can be excluded from the model (i.e., set to zero) with

144   no significant performance loss. This reduces a sizable, largely uninterpretable model to a sparse,

145   more interpretable model. The lasso adds a regularizer to ordinary least squares to prevent the

146   model from overfitting the training data. It performs automatic feature selection by constricting

147   non-informative feature coefficients to zero. For problems with many features, the lasso can

148   eliminate noisy features that may otherwise hinder the model. These parsimonious models have

149   shown to be effective in many types of chemometric models (Filmozer et al. 2012). The lasso has

150   one hyperparameter, α, that controls the constriction level of the coefficient vector β.

151   The open-source machine learning Python library Scikit-learn (Pedregosa et al. 2011)

152   was used to train and test all models. Accuracy was evaluated using leave-one-out cross-

153   validation and calculated using the root mean square error of prediction (RMSEP), which is in

154   the units of absolute $\%Fe^{3+}$.

RESULTS

156   Results of the 12 permutations on multivariate analyses are given in Figure 3: six models

157   using the full spectrum (lasso, PLS with q floating, and PLS with $q = 6$ either with or without the

158   over-absorption correction) and the same six using only the first 120 channels that comprise the

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159   pre-edge region. The PLS models with q held constant at 6 are very similar to those in which q

160   was allowed to float. In fact, for both full-spectrum models the floating q converged on a value

161   of 6, the same as the value held constant. The pre-edge models converged on $q = 5$ when that

162   parameter was allowed to vary, but the RMSEP is very similar. We conclude that models with q

163   = 6 are most broadly useful.

164   Overall, the pre-edge-only prediction models yield uniformly inferior results, with the

165   lasso performing slightly better than the PLS models. The full spectrum models all have

166   significantly smaller (better) RMSEP values and the R^2 values of those predictions when plotted

167   against Mössbauer %Fe^{3+} are >0.94. For the 600-channel models, the lasso performs the best,

168   with RMSEP = 3.55 for samples without the over-absorption correction, and ±3.59 for corrected

169   data. On the basis of these results, the two lasso models will be used in the PAXAS software

170   package; errors on prediction of %Fe^{3+} in glasses can be cited as ±3.6 for either model.

171   Our data also provide an opportunity to check the applicability of our model to data from

172   two facilities. Figure 4 shows plots of predicted vs. measured %Fe^{3+} for the two lasso models,

173   with different colors for data from NSLS and APS. There is no appreciable difference between

174   the two data sets, which were acquired on overlapping sets of samples.

175   Figure 5 shows the results of the models in graphical format. All data are plotted in blue

176   for the full spectra (top panels) and the pre-edge region only. For the lasso models, lasso

177   coefficients are indicated as vertical red lines; selected channels (energies) are indicated by the x

178   axis and the magnitudes of those coefficients are indicated by the length of the bar and the end-

179   point relative to the right-hand y axis. Only a few coefficients are located in the energy region

180   corresponding to the pre-edge signal, indicating that the bulk of information in the spectra about

181   Fe valence state is found in the main edge and EXAFS regions. The same trend is observed to

182   some extent in the PLS model loadings and coefficients. In contrast, the pre-edge models

183   (bottom panels in Figure 5), while less accurate, are remarkably sparse. Note that although the

184   pre-edge centroids have negative rather than positive PLS coefficients (bottom panels of Figure

185   5), that does not they do not influence the predictions. In general, the magnitudes of PLS

186   coefficients are much informative that their signs.

187   **IMPLICATIONS**

188   There is great diversity in standards and methods used by different research groups for

189   prediction of $Fe^{3+}/$ Fe in glasses, and this has resulted in a general lack of consistency and

190   accuracy across different studies. This work provides a broadly-applicable and widely accessible

191   method that is easily implemented using standard XAS file formats and does not require time-

192   consuming fitting of pre-edge features. Moreover, data from previous studies can easily be re-

193   analyzed to assess the reliability of existing numbers. The new calibration should ensure that

194   cross-comparisons can be made among researchers and synchrotron facilities with known

195   accuracy.

196   Moreover, the automated nature of this technique and its optimal performance from the

197   lasso sparse prediction method open the door to the long-awaited possibility of creating maps of

198   Fe^{3+} at high resolutions. The lasso calibration uses ~100 of the 600 channels acquired in this

199   study. Even if adjacent channels are included in a data-acquisition protocol, the time needed for

200   analyzing a single spot will be halved. At ~45 seconds per location (including moving the

201   sample) and 1×1 μm resolution, it will be possible to create a map of Fe^{3+} on a 50 μm glassy area

202   in a thin section in ~35 hours. Understanding redox gradients in silicate glasses should provide

203   exciting new insights into magmatic processes at microscales.

204   **ACKNOWLEDGMENTS**

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FIGURES AND FIGURE CAPTIONS

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269   **FIGURE 1.** Total alkali vs. SiO$_2$ diagram showing compositions used for XANES calibration. Green

270   circles indicate samples equilibrated at up to four different f_{o2}'s, resulting in glasses with nearly the

271   same composition but very different Fe^{3+} contents. Purple squares represent compositions from other

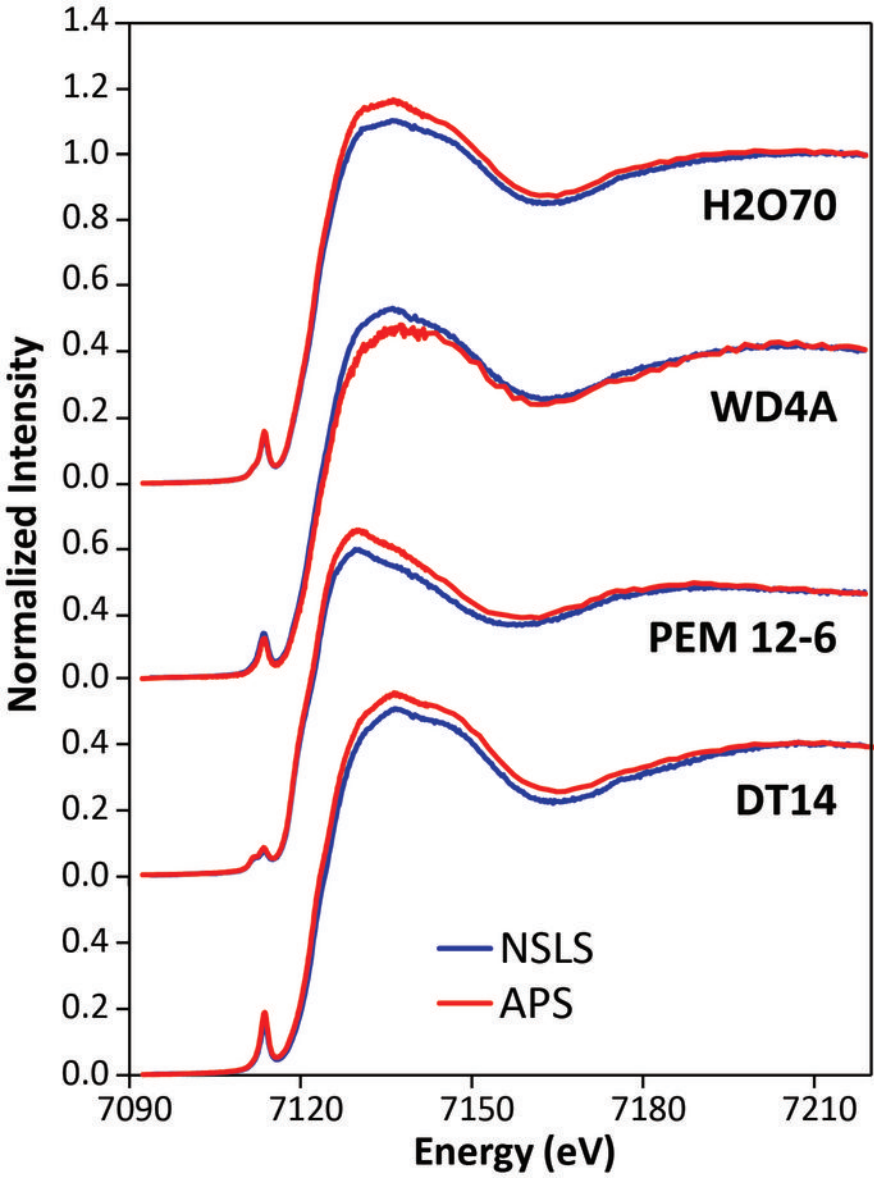272   studies (see text) for which only a single glass was used. Full compositional information for all

273   standards is given in Table 1.

274   **FIGURE 2.** Comparison of over-absorption-corrected XAS spectra acquired at two different

275   synchrotrons: beamlines x26a at the National Synchrotron Light Source at Brookhaven National

276   Laboratory, and the GSECARS beamline at the 7 GeV Advanced Photon Source, Argonne
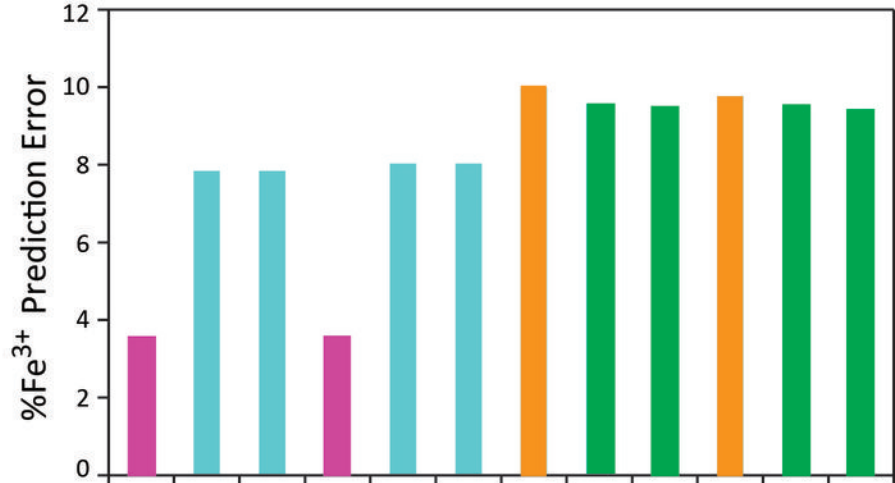
277   National Laboratory.

278   **FIGURE 3.** Graphs of leave-one-out cross-validation results from twelve different models showing

279   prediction errors calculated as root mean square errors (top panel) and the R^2 values for a best-fit line

280   comparing the XAS-predicted %Fe^{3+} values to those from Mössbauer spectroscopy (bottom panel).

281   These results demonstrate that sparse prediction models significantly outperform PLS for this data set.
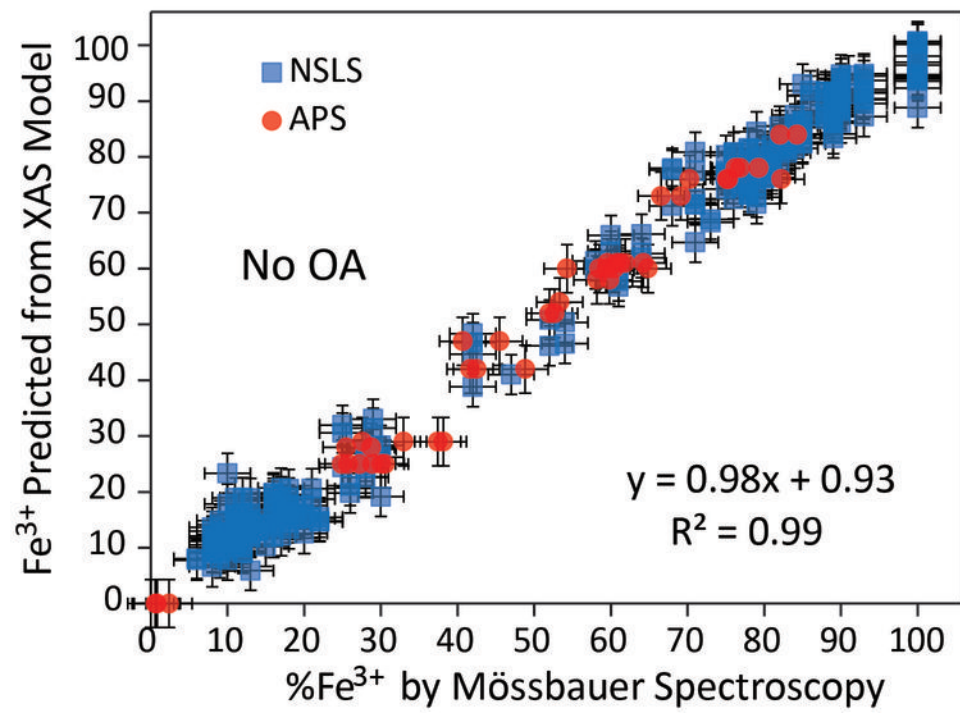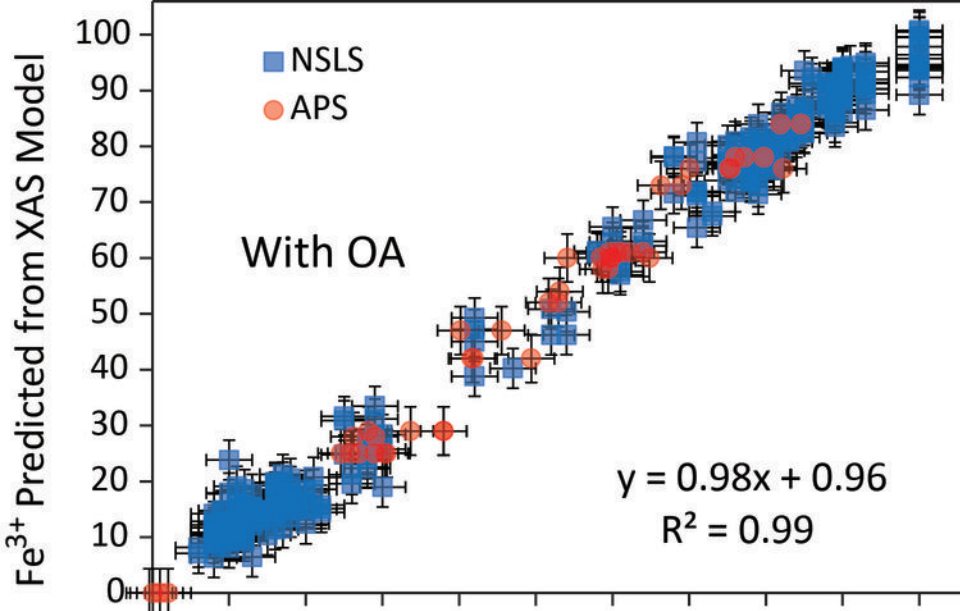
282   **FIGURE 4.** Example plots of predicted Fe^{3+} by the lasso models using the full spectra for data without

283   over-absorption correction (no OA) and with it (with OA). In both cases, the regression line has an R^2

284   value of 0.99.

285   FIGURE 5. All XAS data in full spectrum and pre-edge-only models are plotted in blue against the

286   locations and magnitudes of lasso coefficients (vertical red lines ending in circles) in square plots and

287   the loadings and coefficients for PLS models (red dashed lines) with $q = 6$, in rectangular plots. The red

288   features indicate the energies at which the prediction of Fe^{3+} is most weighted in the x direction; the y

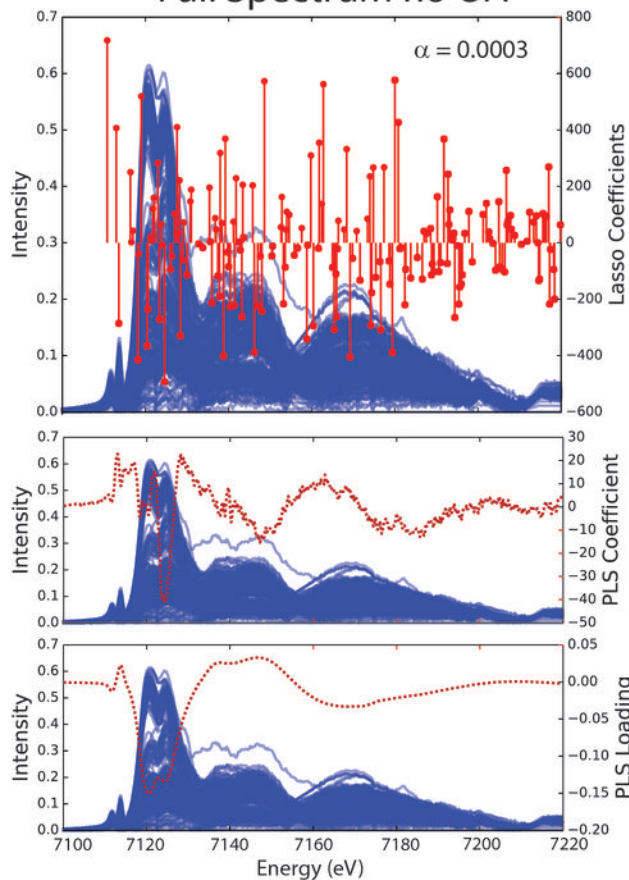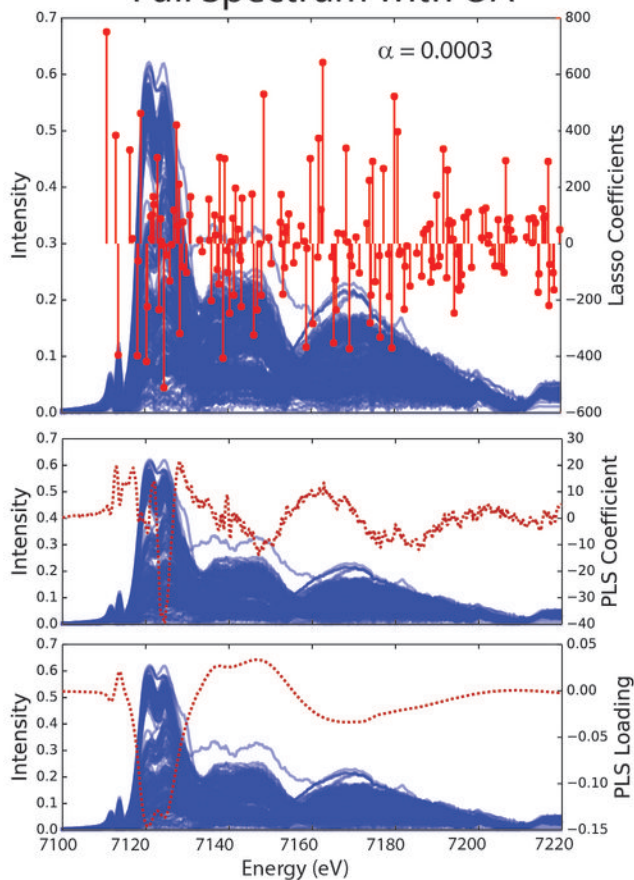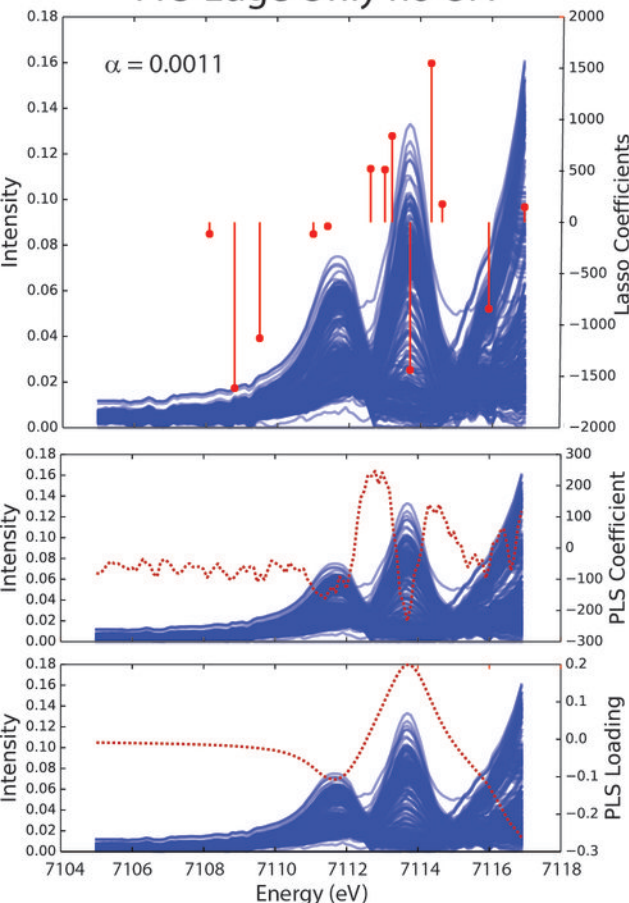289   direction shows the magnitude of the coefficient or loading at that energy.

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NSLS —
APS —

X-axis: Energy (eV), ranging from 7090 to 7210

Y-axis: Normalized Intensity, ranging from 0.0 to 1.4

Curves labeled: H2O70, WD4A, PEM 12-6, DT14

With OA

$y = 0.98x + 0.96$
$R^2 = 0.99$

No OA

$y = 0.98x + 0.93$
$R^2 = 0.99$