

# XAS Spectra of Synthesized Glasses Bundle Description

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## *Research Purpose*

The experiments in this study were designed to produce glasses equilibrated over multiple oxidation states to constrain multivalent element abundance as a function of oxidation conditions. Oxygen is the most abundant element in solids of the Solar System, and is variable in abundance and isotopic composition (e.g., Mittlefehldt et al. 2008). Because it is difficult to measure quantitatively through direct methods, oxygen can best be evaluated through analysis of multivalent elements, which record oxygen potential and are quantified using the parameter of oxygen fugacity ( $f_{O_2}$ ). Oxygen fugacity is defined as the potential for a multivalent cation to occur in any of its valence states, either reduced, neutral, or oxidized. Quantification of  $f_{O_2}$  in geologic systems is of paramount importance as it reflects the degree of oxidation of the magma source region and, possibly, the additional effects of magma interaction with the near surface environment.

Terrestrially,  $f_{O_2}$  is most often quantified using the partitioning behavior of  $Fe^{2+}$  and  $Fe^{3+}$  in mineral and melt phases (e.g., Buddington and Lindsley, 1964; Sack et al., 1980; Christie et al., 1986; Kress and Carmichael, 1991; Cottrell et al., 2009; Dyar et al., 2016). As a major rock-forming element that is also multivalent, the variation of iron redox ratios as a function of  $f_{O_2}$  is well described and forms the basis for many of the oxygen buffers commonly employed in experimental work. Fe redox works well for terrestrial igneous materials due to the relatively high  $f_{O_2}$  of the Earth's atmosphere, crust, and upper mantle ( $f_{O_2} \geq$  quartz-fayalite-magnetite [QFM]) which results in large changes in  $Fe^{2+}/Fe^{3+}$  with relatively small changes in  $f_{O_2}$ . At  $f_{O_2}$  values  $<$  QFM though, Fe redox becomes less sensitive and analytical uncertainties may make it difficult to determine  $f_{O_2}$  differences between samples. Therefore, multivalent element redox couples that have valency changes at lower  $f_{O_2}$  values are sought to more precisely constrain lower  $f_{O_2}$  processes. However, these analytical tools are hindered by the lack of development and calibration of non-Fe multivalent element oxybarometers.

In this study, we apply multivariate techniques to enable accurate X-ray Absorption Spectroscopy (XAS) measurements of Fe, Cr, Mn, and Ti ratios across the whole spectral region through creation of a broad suite of experimentally homogenized glasses of geological relevance for use as XAS standards. We then correlate the measured redox ratios with experimental  $f_{O_2}$  to calibrate new multivalent element oxybarometers for use in low  $f_{O_2}$  glasses to assess their formation conditions. The data archived are the individual element spectra from each equilibration run. Oxidation state results and correlations with  $f_{O_2}$  derived from these spectra are

presented in Dyar et al. (2016) and McCanta et al. (in preparation for submission to American Mineralogist 2022).

### *Experimental and Analytical Methods*

Synthetic glass starting compositions were generated for a wide range of geologically-relevant compositions. Starting compositions were 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 at 800°C for two hours. Oxide mixes were used directly in the experiments without a glassing step.

A mixture of sample powder (~100 mg) and polyvinyl alcohol (PVA) was used to adhere the sample to wire loops for insertion into the furnace. Equilibration experiments were run in a vertical 1-atm gas mixing furnace at the University of Tennessee using the Pt (or Re) wire-loop technique. The  $f_{O_2}$  was measured using an SiO<sub>2</sub> yttria-doped zirconia oxygen sensor located adjacent to the sample and temperatures were measured using a type S thermocouple. Oxygen fugacities were fixed by flowing H<sub>2</sub>-CO<sub>2</sub> gas mixtures pegged at the QFM, IW, or IW-2 buffer for the maximum temperature of an experiment with the gas composition held constant during cooling. Each composition was run at all  $f_{O_2}$  conditions, producing a range of multivalent element concentrations in the resulting glasses.

All experiments were initiated by inserting the sample into the hot spot under the desired gas mixture at ~1000°C, followed by ramping to the composition-dependent peak temperature at 500°C/hr. Experiments remained at the peak temperature for the duration of the run necessary to ensure melt homogenization. Samples were then drop-quenched into deionized water and recovered run products were prepared for analysis.

Beads from glass equilibration runs were weighed and divided in half. One-half of each bead was embedded in epoxy and polished into a 1" thick mount for X-Ray Absorption Spectroscopy (XAS) analysis. Iron, Cr, Mn, and Ti were analyzed as epoxy-mounted polished glass beads using XAS at the GeoSoilEnviroCARS beamline at the Advanced Photon Source, Argonne National Lab using a spot size of ca. 1×1 μm. The beam current was minimized to limit any potential changes in oxidation conditions during glass analysis (estimated flux = 4 × 10<sup>10</sup> – 4 × 10<sup>11</sup> photons/s/μm<sup>2</sup>). A monochromator glitch is present in the Fe XAS data at ~7317 eV. Due to its location in the far extended X-ray absorption fine structure (EXAFS) region, it does not affect the data quality.

### *Data Product Formats*

Data that comprise this archive are formatted in accordance with PDS specifications (see References 1-3). All spectral data are ASCII text files in comma delimited (CSV) format. Documents are provided as PDF/A ([www.pdfa.org/download/pdfa-in-a-nutshell](http://www.pdfa.org/download/pdfa-in-a-nutshell)) or as plain ASCII text if no special formatting is required.

### *Bundle Organization and Naming*

This bundle is organized into 2 collections: a data collection and a document collection. The data collection contains the spectral data products in the bundle organized by element

(Chromium (Cr), Iron (Fe), Manganese (Mn), and Titanium (Ti)). The document collection contains the document you are currently reading.

All spectral data files have the following nomenclature: yy\_xas\_zzz.csv, where ‘yy’ is the element abbreviation (Cr, Fe, Mn, or Ti) and ‘zzz’ is the specimen id (4 to 13 characters). ‘xas’ indicates these are X-ray Absorption Spectroscopy measurements.

Each product in the bundle is accompanied by a PDS4 label. PDS4 labels are ASCII text files written in the eXtensible Markup Language (XML). Product labels are detached from the files they describe (with the exception of the Product\_Bundle label). There is one label for every product. A PDS4 label file has the same name as the data product it describes, but always with the extension “.xml”.

The information in the PDS4 labels includes complete software-readable descriptions of data file formats, so that users may write custom software to read the products if desired. Data may also be accessed and viewed with the PDS4 viewer available at [http://sbndev.astro.umd.edu/wiki/PDS4\\_Viewer](http://sbndev.astro.umd.edu/wiki/PDS4_Viewer).

Please see References 1-4 for additional information about archive organization, identifiers, and naming conventions in PDS4.

### References

1. Planetary Data System Standards Reference, Version 1.17.0, Oct. 14, 2021.
2. PDS4 Data Dictionary Document, Version 1.17.0.0, Sep. 30, 2021.
3. Planetary Data System (PDS) PDS4 Information Model Specification, Version 1.17.0.0, Sept. 30, 2021.
4. Data Providers' Handbook: Archiving Guide to the PDS4 Data Standards, Version 1.17.0, October 14, 2021.
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