

Utilizing Linear Combination Fitting (LCF) To Model Highly Reduced, Multi-Component Mixtures Of Cation-Sulfide Species Relevant To Mercurian Melts. B. A. Konecke¹, K. E. Vander Kaaden², F. M. McCubbin¹ and P. Northrup³. ¹ARES, NASA Johnson Space Center, Houston, TX 77085, USA, ²Jacobs, JETS Contract, NASA Johnson Space Center, ³Stony Brook University (corresponding author: brian.a.konecke@nasa.gov)

Introduction: The oxidation state(s) and speciation of S imparts a major geochemical control on the chemical affinity and behavior of S in magmatic systems [1]. Under reducing conditions ($<IW-3$), oxygen (O^{2-}) is replaced by sulfide (S^{2-}) on the anion sublattice of the silicate melt, and complexes with cations [M], where: $0.5 S_2 + [M]O_{(silicate\ melt)} = 0.5 O_2 + [M]S_{(silicate\ melt)}$ ([2]; and references therein). The limiting solubility of sulfide in a silicate liquid is defined by the S content at sulfide saturation (SCSS), where: $[M]S_{(silicate\ liquid)} \rightleftharpoons [M]S_{(sulfide\ liquid)}$. The SCSS is sensitive to temperature (T), degree of melt polymerization (i.e., SiO_2 content), oxygen fugacity (fO_2), and FeO content; and to a minor degree pressure (P). In highly reducing systems ($IW-3$ to $IW-8$; relative to the iron-wüstite mineral redox buffer), the SCSS is highly sensitive to FeO concentrations of the melt (at fixed T - P -composition (X)- fO_2 ; [3]). The estimation of SCSS for low-Fe (< 2 wt. % FeO) systems is challenging, as most models rely upon accurate measurements of FeO content (and activity) of the melt [4]. As a result, SCSS estimates for mercurian lavas remain enigmatic, in part due to their low-FeO (< 2 wt. % FeO), high-S (> 1 wt. % S) and exceedingly low fO_2 ($IW-3$ to $IW-7$) characteristics [4–8]. Previous studies have proposed that the observed correlation between S, Ca, Mg, and Fe systematics in mercurian basalts is indicative of the presence of (Mg, Ca, Fe)S sulfide melts, suggesting that CaS and MgS are abundant (and potentially dominant; $[MgS, CaS] > FeS$) in the silicate melt [4, 8, 9]. However, few studies have investigated the influence of MgS and CaS species on the S solubility (e.g., SCSS) of highly reducing silicate melts. Here, we combine electron probe microanalysis (EPMA) and X-ray absorption near edge structures (XANES) spectroscopy at the S K -edge with data from petrologic experiments to constrain these intensive variables in order to develop a new model that provides additional constraints on the SCSS of mercurian melts.

Experimental Methods: Experimental run products represent an ideal situation where the P - T - X - fO_2 , are well known. We will perform experiments using piston-cylinder apparatuses to achieve a broad range of T (1100–2050°C), P (0.5–5 GPa), and fO_2 ($IW-5$ to -7). Starting compositions will range from simplistic diopside-like liquids to complex compositions representative of the largest volcanic field on the surface of Mercury (i.e., *Borealis Planitia*). Experimental charges

will be loaded with a range of sulfur and metal components to impart an intrinsic fO_2 on the system in order to examine the change of S speciation and melt structure as a function of P , T , X , and fO_2 (see [8] for discussion). We anticipate that the experimental run products will contain varying proportions of silicate liquid(s), silicate minerals, metals, and sulfides. All experimental run products will be analyzed using electron microprobe techniques to determine the major and minor elements, using the methods described by [8].

Analytical Methods: *In situ* μ -XANES spectroscopy measurements at the S K -edge will be performed at the TES 8-BM beamline at the National Synchrotron Light Source II (NSLS-II; Brookhaven National Laboratory). Spectra will be collected from 2460 to 2540 eV, with step sizes of 0.1–0.3 eV at the S K -edge (2464 to 2484 eV), and 0.5 eV for the pre-and-post edge regions using 0.5–3 s scan durations per energy step. Two to three scans will be collected per spot analyses, and step scan durations will be varied as a function of S content to produce high-quality spectra even for S-poor mineral phases or glasses [10].

All spectra will be merged and normalized by using the software package Athena (Ifeffit package; [11]). Normalization of merged raw spectra involves setting the pre-edge and post-edge to 0 and 1, respectively. The normalized spectra of our experimental unknowns will be compared to the S K -edge energies (eV) of known reference materials, including: FeS (troilite; 2470.0 eV), MgS (niningerite; 2475.1 eV), and CaS (oldhamite; 2470.0 and 2477.4 eV; see Figure A; data from [1]). Linear combination fitting (LCF) will be used to evaluate the S-XANES K -edge (peak a) and multiple post-edge (peaks b–e) features that are characteristic to the speciation and bonding environment of reference minerals (Figure B). The LCF modeling will evaluate the edge and post-edge features (peaks a–e; see dotted lines in Figure B) because the consideration of a broad range of energy positions will improve the fitting parameters and statistics used to calculate the influence of S species in spectra of unknown samples. Considering the linear relationship between the S content and S-XANES absorption energy intensities, chemical data measured from EPMA can be combined with the LCF modeling to (semi-) quantify the molar proportions of CaS, MgS, and FeS of the experimental glasses [2, 12].

Results and Discussion: As a proof of concept, we simulated end-member and non-end-member mixing of sulfide species (i.e., Ca, Mg, and Fe) in S-XANES spectra to assess the reproducibility of the LCF (see Figure B; compare dotted lines [LCF model] to spectra of sulfide mixtures [solid lines]). First, we evaluated end-member CaS, MgS, and FeS spectra, and the modeled results yielded (normalized to 1) values that are within error of the ideal cation proportions (compare symbols to gray cross in Figure C). Second, we modeled non-end-member, two-component, and three component mixing of sulfide species, including: $(\text{Ca}_{0.50}, \text{Mg}_{0.50})\text{S}$, $(\text{Ca}_{0.50}, \text{Fe}_{0.50})\text{S}$, $(\text{Fe}_{0.50}, \text{Mg}_{0.50})\text{S}$, and $(\text{Ca}_{0.33}, \text{Mg}_{0.33}, \text{Fe}_{0.33})\text{S}$, to evaluate the overall quality of fitting for more complex mixing scenarios (Figure C). Similarly, these modeled values are within error of the ideal sulfide mixtures (denoted by gray crosses in Figure C), indicating that the LCF is a robust tool for modeling these multi-S-speciation component systems that are highly relevant to experimental and natural samples.

Implications: Currently, there are limited literature data that reports the speciation and oxidation state(s) of S in minerals and quenched silicate liquids (i.e., glasses) that crystallized in highly reduced, Fe-poor and high-S magmatic systems [e.g., 13]. The estimation of SCSS for Fe-poor systems remains highly problematic, and there is limited data regarding the influence of elevated MgS and CaS on the SCSS. We will combine experimental, analytical, and modeling methods to constrain the redox conditions where CaS and MgS shift towards abundant-to-dominant S species in silicate melts relative to Fe. This anticipated insight will help develop and test a novel SCSS calibration that also considers the molar proportion of MgS and CaS to improve our understanding of the geochemical behavior of S during mercurian magmatism.

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Figure Caption: (A) Normalized S-XANES spectra of end-member sulfide reference materials: CaS

(oldhamite), MgS (niningerite), and FeS (troilite)[1]. The S K-edge absorption peak is denoted by a, and the post edge features are denoted by b–e. (B) Normalized S-XANES spectra of mixtures of ideal 2 sulfide component mixture, and 3 component mixture (solid line). The dotted line represents the spectra of the linear combination fitting (model) of each mixture. (C) Modeled cation proportions versus ideal cation proportions. The LCF model successfully reproduced nearly all of the ideal sulfide-speciation mixtures within analytical error (1σ) for one-two-and three component mixing.

