**XANES spectroscopy of sulfides stable under reducing conditions**

**BRENDAN A. ANZURES**¹,*, **STEPHEN W. PARMAN**¹, **RALPH E. MILLIKEN**¹, **ANTONIO LANZIROTTI**², and **MATTHEW NEWVILLE**²

¹Department of Earth and Planetary Sciences, Brown University, Providence, Rhode Island 02912, U.S.A.
²Center for Advanced Radiation Sources, The University of Chicago, Argonne, Illinois 60439, U.S.A.

**Abstract**

X-ray absorption near-edge structure (XANES) spectroscopy is a powerful technique to quantitatively investigate sulfur speciation in geologically complex materials such as minerals, glasses, soils, organic compounds, industrial slags, and extraterrestrial materials. This technique allows non-destructive investigation of the coordination chemistry and oxidation state of sulfur species ranging from sulfide (2− oxidation state) to sulfate (6+ oxidation state). Each sulfur species has a unique spectral shape with a characteristic K-edge representing the s → p and d hybridization photoelectron transitions. As such, sulfur speciation is used to measure the oxidation state of samples by comparing the overall XANES spectra to that of reference compounds. Although many S XANES spectral standards exist for terrestrial applications under oxidized conditions, new sulfide standards are needed to investigate reduced (oxygen fugacity, fO2, below IW) silicate systems relevant for studies of extraterrestrial materials and systems. Sulfides found in certain meteorites (e.g., enstatite chondrites and aubrites) and predicted to exist on Mercury, such as CaS (oldhamite), MgS (niningerite), and FeCr2S4 (daubréelite), are stable at fO2 below IW-3 but rapidly oxidize to sulfate and/or produce sulfurous gases under terrestrial surface conditions. XANES spectra of these compounds collected to date have been of variable quality, possibly due to the unstable nature of certain sulfides under typical (e.g., oxidizing) laboratory conditions. A new set of compounds was prepared for this study and their XANES spectra are analyzed for comparison with potential extraterrestrial analogs. S K-edge XANES spectra were collected at Argonne National Lab for FeS (troilite), MnS (alabandite), CaS (oldhamite), MgS (niningerite), Ni24S6 (anhydrite), MgSO4, FeSO4, FeCr2S4 (daubréelite), Na2S, Al2S3, Ni7S6, and Ni2S3; the latter five were analyzed for the first time using XANES. These standards expand upon the existing S XANES end-member libraries at a higher spectral resolution (0.25 eV steps) near the S K-edge. Processed spectra, those that have been normalized and “flattened,” are compared to quantify uncertainties due to data processing methods. Future investigations that require well-characterized sulfide standards, such as the ones presented here, may have important implications for understanding sulfur speciation in reduced silicate glasses and minerals with applications for the early Earth, Moon, Mercury, and enstatite chondrites.

**Keywords:** XANES spectroscopy, chemical state of S, oxidation state of S, sulfides, sulfates, end-member variability

**Introduction**

Along with iron, sulfur is the most important heterovalent element in geologic systems. Due to its range of charges from 2− to 6+, the behavior of sulfur is complex. Under different redox conditions, sulfur can bond with both more electropositive and more electronegative elements in magmas, soils, industrial glasses and slags, and meteorites (Fleet 2005). This has significant effects on the partitioning behaviors of these elements between silicate melts (S²− and S⁶⁺), liquid metals and sulfides (S⁰ and S²−), gases (H₂S, S₂, SO₂, and SO₃), and solids (S²−, S⁰, S²⁺, S⁴⁺, and S⁶⁺). Under reducing conditions inferred for enstatite chondrite and auribrite meteorite parent bodies, as well as for lunar and Mercurian magmas, sulfur is stable as a number of different sulfide compounds not typically found on Earth, and S is the most abundant volatile element dissolved in silicate melts (>1 wt%). Sulfides stable below IW-3 include CaS (oldhamite), MgS (niningerite), MnS (alabandite), FeCr₂S₄ (daubréelite), NaCr₂S₄ (caswellsilverite), and djerfisherite [K₆Na(Fe²⁺,Cu,Ni)₂S₆Cl], all of which rapidly oxidize to sulfate and/or produce sulfurous gases in air under terrestrial surface conditions.

Reduced silicate systems have applications for terrestrial mid-ocean ridge basalt (MORB), meteorites such as enstatite chondrites and aubrites, and magmas on the Moon and Mercury. Mercury is the most extreme example with surface sulfur detections of 1.5–4 wt% (Nittler et al. 2011). Recent work on sulfide solubility in experimental Mercurian glasses (Namur et al. 2016b) predicts MgS and CaS should be the dominant sulfides in extremely reduced silicate melts, while our analyses of sulfide speciation have confirmed and quantified MgS and CaS...