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XANES spectroscopy of sulfides stable under reducing conditions

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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 nondestructive 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 $s \rightarrow p$ 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, f_{O_2}, 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 $FeCr_2S_4$ (daubréelite), are stable at f_{O_2} 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), $Ni_{1-x}S$, NiS_2, $CaSO_4$ (anhydrite), $MgSO_4$, $FeSO_4$, $Fe_2(SO_4)_3$, $FeCr_2S_4$ (daubréelite), Na_2S, Al_2S_3, Ni_7S_6, and Ni_3S_2; 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