silicate glass; (ii) a formation temperature that is 100° to 250°C lower than the temperature (~1150°C) required for a comparable borosilicate glass; (iii) a relatively good capacity of the molten glass for dissolving the elements found in both defense and commercial power reactor wastes; (iv) a melt viscosity and processing (that is, pouring) temperature in the range from 800° to 1000°C, significantly lower than the pouring temperature (~1150°C) of borosilicate glass; and (v) suitability for use for both commercial and defense-related nuclear waste disposal. Of greatest significance, it appears that the lead-iron phosphate glass waste form can be processed using a technology similar to that developed for borosilicate glass nuclear waste forms.

B. C. SALES
L. A. BOATNER

Solid State Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831

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X-ray Absorption Spectroscopic Investigation of Sulfur Sites in Coal: Organic Sulfur Identification

Abstract. *High-resolution x-ray absorption spectroscopy was used to probe the chemical and structural environments of sulfur in coal. Measurement of the sulfur K-edge spectra down to 2472.0 electron volts under nonvacuum conditions was made possible in an all-helium path, and a Stern-Heald type ion chamber was used for fluorescence detection. For a number of selected sulfur-containing minerals and organic model compounds, results show that near-edge spectral features are diagnostic for sulfur in specific organic moieties such as thiols, disulfides, and various heterocyclics, as well as in mineral sulfide and sulfate phases. The spectrum of a model system containing 35 percent iron pyrite and 65 percent benzothiophene was found to match the observed spectral features of a bituminous coal from the eastern United States.*

Sulfur takes on several forms in coal including elemental, mineral, and organic (*1*). Further classification is possible. Mineral sulfur forms include pyrite or sulfate groups; organic sulfur may occur in heterocyclic species, thiol moieties, or thioether units, among others (*2*). Because of the heterogeneity and opacity of coal, it has not been possible to determine directly the sulfur forms in coal by conventional techniques. Knowledge of the sulfur forms is indirect, based primarily on spectroscopic studies of pyrolytic or chemically degraded fragments of coal and model compounds. Even the simple quantification of organic versus inorganic sulfur in coal is usually indirect, because it relies upon sequential leaching of sulfate, then pyritic compounds, with organic sulfur presumed to comprise the residue. This assumption is subject to error since the occlusion of nanometer-sized mineral fragments in the organic matrix has been commonly observed (*3*).

Sulfur is one of the most pernicious elements in coal. When released into the atmosphere through combustion, it may produce so-called acid rain (*4*). Because of this possibility, several countries now limit sulfur emissions from coal-burning power plants. Some alkali sulfates have low-melting eutectics and may cause fouling and corrosion when in contact with hot metal surfaces (*5*). Sulfur-containing compounds may have deleterious environmental, health, and safety effects (*6*). Sulfur may poison catalysts during processing (*7*). It may also inhibit prolonged storage of coal by catalyzing spontaneous ignition (*8*). Acid mine drainage results from microbial degradation of metal sulfides in the coal (*6*).

For these reasons, several processes for the removal of sulfur in coal have been recently developed (*9*). Certainly, a better understanding of the nature and distribution of sulfur-bearing minerals and organic sulfur–containing functional groups and their concomitant chemistry will have a desirable impact on advanced coal preparation processes and the environmental acceptability of coal-derived energy.

The K-edge spectra of sulfur in coal have been measured by Hussain *et al.* (*10*), who used a total electron yield technique under ultrahigh vacuum conditions. In that study, the sulfur species in coal were not identified since organic compounds of sulfur, which are usually vacuum-incompatible, were not measured. The ability to obtain soft x-ray absorption spectra down to 2.4 keV under nonvacuum conditions with the use of a fluorescent ion-chamber detector arrangement has recently been shown by Lytle *et al.* (*11*). This nonvacuum procedure (*11*) may be summarized as follows. Spectra were obtained on beam line VII-3 wiggler side station at the Stanford Synchrotron Radiation Laboratory during a dedicated run of the Stanford positron electron accelerator ring (SPEAR) at an electron energy of 3.0 GeV and an injection current of ~75 mA. The synchrotron x-ray beam from SPEAR was monochromatized with double Si(111) crystals and a 1-mm entrance slit, which yielded a resolution of ~0.5 eV (*11*) at the sulfur K-edge of 2472.0 eV (*12*). Spectra of sulfur in coal and model compounds were measured by the fluorescence extended x-ray absorption fine structure (EXAFS) technique (*13*). This technique monitors the sulfur K_α fluorescence intensity, which is proportional to the degree of absorption of the incident beam, and hence monitors the x-ray absorption spectrum. A Stern-Heald type fluorescence detector (*13*) was used, the construction of which has been described (*11*). Helium and nitrogen were used as detector gases in the incident ion chamber and fluorescence detector, respectively. The incident beam was detuned up to 90 percent to minimize harmonic contents at the sulfur K-edge energy. An all-helium path from the beryllium window to the sample was used to minimize absorption and scattering by air. We prepared spectral specimens by packing powdered samples into 6-μm X-ray Polypropylene (*14*) envelopes sufficiently large that the x-ray beam impinged only on the sample (*15*).

Figure 1 shows the K-edge absorption spectra of sulfur for four model organic sulfur-containing compounds used in this study. These compounds contain, respectively, a thiol S–H group, sulfur in a five-membered heterocycle, a disulfide linkage, and a sulfur-heterocycle bridging two aromatic rings. The spectra are well differentiated in terms of pre-edge features and in the height and shape of various near-edge absorption characteristics. Thus, they provide the opportunity to discriminate among organic sulfur–bearing functional groups in coal. Figure 2 shows the sulfur K-edge spectra of iron pyrite and potassium sulfate (K_2SO_4). Sulfate is the oxidized form of pyritic sulfur in coal, and its sulfur K-edge spectrum is expected to vary little with different counter cations, for example, K^+ or Fe^{2+}, since the edge spectrum of the central atom is most strongly dependent on bonding to its nearest neighbors. The pyrite spectrum consists of two characteristic absorption peaks at 1.4 and 11.8 eV and a shoulder at 8.8 eV. The sulfur spectrum of K_2SO_4 exhibits an edge shift of ~10 eV with respect to elemental sulfur, yielding a sharp peak at 11.5 eV and a doublet feature just below 20 eV. The large edge shift is expected because of the high formal oxidation state of sulfur in the sulfate ion. This reflects a higher energy requirement to photoionize the innermost core electron due to an increase in nuclear attraction at the oxidation state of S(VI).

Figure 3a shows the spectrum obtained on Winifrede seam coal from Lambric, Kentucky. The coal is classified as high volatile A bituminous and was taken as two large lumps from the bottom 25 cm of a channel cut in a freshly exposed seam. The lumps were stored under nitrogen and ground just prior to being transported to the synchrotron laboratory. The spectrum of this coal (Fig. 3a) illustrates the x-ray absorption near-edge spectroscopy (XANES) technique but should not be construed as typifying all eastern U.S. bituminous coals. This coal was chosen primarily because it had been mined and stored in such a way as to minimize decomposition (*16*). Wet chemical analysis indicated that this sample contained 0.5 percent pyritic sulfur and 0.94 percent organic sulfur (by weight), or 35 percent pyritic sulfur and 65 percent organic sulfur. To elucidate the nature of the organic sulfur species in the coal, a series of XANES simulations was made to match the normalized spectrum of sulfur in coal (Fig. 3a) with a linear combination of the pyrite spectrum (Fig. 2a) and each of the various organic model compounds shown in Fig. 1. Based on the absorption features at 3.0 and 11.8 eV and the shape of the edge in the coal spectrum, the best simulation was obtained by a linear summation of the spectrum representing the five-membered heterocyclic thianaphthene (Fig. 1b) and the spectrum for iron pyrite (Fig. 2a). Indeed, when for the simulated spectrum we used the percentages determined by chemical analysis (35 percent pyritic and 65 percent organic), a reasonably quantitative fit was obtained (Fig. 3b). Heterocycles of this sort have been proposed (*17*) as likely candidates for organic sulfur functional groups in coal. In that

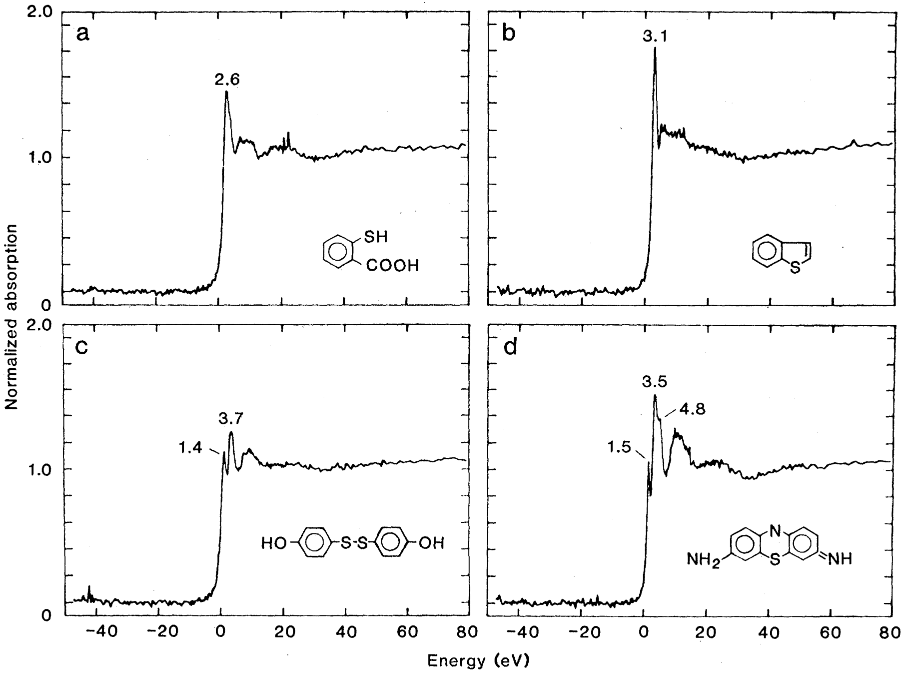
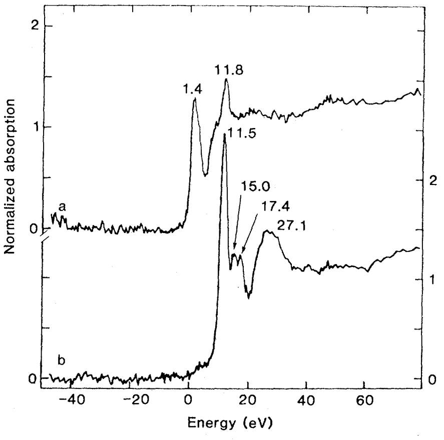


Fig. 1. K-edge spectra of sulfur in various organic bonding and coordination environments: (a) in a terminal thiol S–H group in thiosalicylic acid; (b) in a five-membered heterocyclic ring in thianaphthene (benzothiophene); (c) in a –S–S– bridge in bis(4-hydroxyphenyl)disulfide; and (d) in a ring bridging configuration in thionin. The zero of energy is taken at the first inflection point of elemental sulfur at 2472.0 eV (*12*). The absorption intensity of each spectrum was normalized to its respective EXAFS background extrapolated at 0 eV.



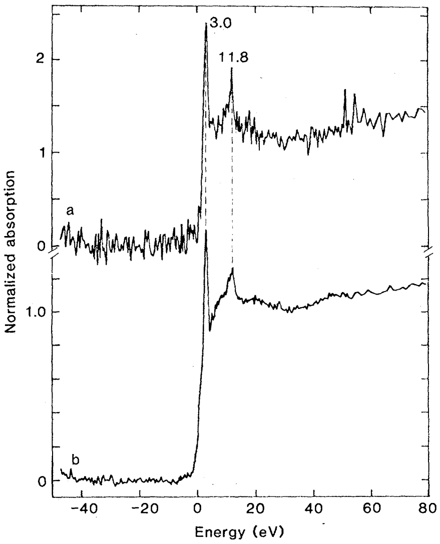


Fig. 2 (left). Normalized K-edge spectra of sulfur in (a) iron pyrite and (b) K_2SO_4. The zero of energy is taken at the first inflection point of elemental sulfur at 2472.0 eV.
Fig. 3 (right). K-edge spectrum of sulfur in (a) Winifrede seam coal; (b) a simulated sulfur spectrum obtained by forming a linear combination of the thianaphthene spectrum (Fig. 1b) and that of iron pyrite (Fig. 2a) in a ratio of 65 to 35 percent.

indirect study, coal was oxidatively degraded with sodium dichromate and the esterified products were identified as benzo- and dibenzothiophene derivatives by mass spectral analysis. The investigators concluded (*17*, p. 380) that "thiophene derivatives must be indigenous to coal." The direct XANES results reported here support these conclusions.

Simulations carried out with other model compounds yielded spectra that bore little resemblance to the coal spectrum. For example, simulations that used sulfate as the inorganic component yielded incorrect relative intensities for the absorptions at 3.0 and 11.8 eV, together with peaks at 15.0, 17.4, and 27.1 eV that are not present in the coal spectrum (*18*). Simulations with other organic models shown in Fig. 1 and in other ratios yielded peak positions or intensities, or both, that did not correspond to those observed in the coal spectrum. We therefore conclude that the thiophene unit is the most likely candidate as the main organic sulfur functional group in this particular coal.

The results described above illustrate the applicability and usefulness of high-resolution x-ray absorption spectroscopy, based on the use of intense synchrotron radiation for direct, nondestructive determination of the nature of organic sulfur in coal. It remains to be determined how sulfur in coal transforms through natural and various thermochemical processes during coal conversion and combustion. We expect that, by signal-averaging multiply scanned spectra, it will be possible to improve the signal-to-noise ratio shown in Fig. 3a so that quality spectra in the EXAFS region at high energy may be obtained and analyzed to complement the near-edge data.

C. L. SPIRO
J. WONG
Corporate Research and Development, General Electric Company, Post Office Box 8, Schenectady, New York 12301
F. W. LYTLE
R. B. GREEGOR
Boeing Company, Post Office Box 3999, Seattle, Washington 98124
D. H. MAYLOTTE
S. H. LAMSON
Corporate Research and Development, General Electric Company

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El Niño–Southern Oscillation Events Recorded in the Stratigraphy of the Tropical Quelccaya Ice Cap, Peru

Abstract. *Snow accumulation measured during 1982–1983 on the Quelccaya ice cap, Peru, was 70 percent of the average from 1975 through 1983. Inspection of 19 years (1964 through 1983) of accumulation measured near the summit of Quelccaya reveals a substantial decrease (~30 percent) in association with the last five El Niño–Southern Oscillation (ENSO) occurrences in the equatorial Pacific. The ENSO phenomenon is now recognized as a global event arising from large-scale interactions between the ocean and the atmosphere. Understanding this extreme event, with the goal of prediction, requires a record of past occurrences. The Quelccaya ice cap, which contains 1500 years of annually accumulated ice layers, may provide a long and detailed record of the most extreme ENSO events.*

The years 1982 and 1983 were characterized by large, coherent climate anomalies over much of the earth (*1*, *2*). Synthesis of atmospheric data (pressure, temperature, and rainfall) and oceanic data (sea-surface temperatures) has led to the view that the El Niño–Southern Oscillation (ENSO) is a large-scale interaction between the atmosphere and ocean in the tropics (*3*). Recently these interactions have been linked with extraordinary weather conditions in diverse locations over the globe (*4*). Understanding these interactions with the goal of predictability requires a long history of past events. Currently this record encompasses 116 years (*5*), of which only the last 60 are well documented.

Results from the glaciological investigation of the tropical Quelccaya ice cap in Peru (*6*) since 1976 indicate that major ENSO occurrences may be recorded on this ice cap in the form of substantially reduced annual snow accumulation. The annual mass balance of this ice cap is an integration of the annual precipitation and radiation balances. The purpose of this report is to examine the temporal relation between the amount of mass accumulation on Quelccaya and these tropical Pacific ENSO events.

Each year since 1976, ~25 water samples representing 1 year of snow accumulation on Quelccaya have been collected for analysis of the microparticle concentration, oxygen isotopic abundance ratios, and beta radioactivity (*7*, *8*). Figure 1 is a composite of the microparticle concentrations in eight pits (1976 through 1983) that are joined to produce a continuous time series. The dry season (July) horizons (Fig. 1), easily identified by visual inspection within the snow pits, result from the concentration of microparticles during the dry season (*7*). The thicknesses of these annual dust layers reflect the annual snow accumulation (Fig. 1, dashed lines). Using measured densities, one can convert snow accumulation into water equivalent accumulation estimates (Fig. 1).

The 8 years of pit data yield an annual average of 1.10 m of water per year. Precipitation was sharply reduced (~30