O'Brien, *Mon. Weather Rev.* **109**, 1190 (1981)]. The finer resolution of the later study resulted in a finer resolution of the wind stress curl field. The areal extent and magnitude of prominent features of the eastern tropical Pacific wind stress curl are supported by the findings of S. Hastenrath and P. J. Lamb, *Climatic Atlas of the Tropical Atlantic and Eastern Pacific Oceans* (Univ. of Wisconsin Press, Madison, 1977). The climatic data presented by Hastenrath and Lamb are on a 1° by 1° grid, which covers the eastern tropical Pacific and tropical Atlantic oceans.

7. The mass transport model is given by $V = (1/\beta)$ curl $\hat{\tau}$, where V is the meridional mass transport, β is the northward variation of the Coriolis parameter, and $\hat{\tau}$ is the wind stress vector. From the V transports and continuity

$$\frac{\delta U}{\delta x} + \frac{\delta V}{\delta y} = 0$$

considerations, the zonal mass transport, U, was calculated. The U and V mass transports were used to calculate streamlines from the model $\nabla^2\psi = \xi$, where ψ is the stream-function and ξ is the mass transport vorticity

$$\frac{\delta V}{\delta x} - \frac{\delta U}{\delta y}$$

A streamline is a convenient scalar that can be used to visualize the vector mass transport field. The results of the mass transport calculations are presented in E. E. Hofmann and J. J. O'Brien, in preparation.

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9. The Intertropical Convergence Zone is the transition region between the northeast and southeast trade wind belts.
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11. Long-wavelength Rossby waves are long-period oscillations that may be excited by fluctuations of the wind stress curl. The restoring force for these waves is the β effect, where β is $(\delta f/\delta y)$, f is the Coriolis acceleration, and y is the meridional direction. At the latitude of the Costa Rica Dome, the phase speed and group speed of these waves is $c_R = c^2/\beta y^2$, where c is the baroclinic phase speed and y is the distance from the equator. The presence of annual Rossby waves in the tropical North Pacific is not unique in this study. The vorticity equation has been used [G. Meyers, *J. Phys. Oceanogr.* **9**, 663 (1979)] to model the combined response of local Ekman pumping and Rossby waves. Analysis of observational data established that the largest annual variations in depth of the 14°C isotherm occur near 6°N and 12°N. The depth variations at 6°N were found to propagate westward at the speed of a nondispersive baroclinic Rossby wave. The results of Meyers' model correlated well with the observations at 6°N.
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16. We thank E-Chien Foo, J. M. Klinck, and C. N. K. Mooers for their helpful comments, J. Merritt for computer programming assistance, P. Teaf for typing, and two anonymous reviewers. This research was supported by NSF grant ATM-7920485 and Office of Naval Research–Selected Research Opportunities contract N00014-80-C-0076. Contribution No. 174 of the Geophysical Fluid Dynamics Institute at Florida State University and contribution No. 3 of the Pacific Equatorial Ocean Dynamics Program.

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X-ray Absorption Spectroscopic Investigation of Trace Vanadium Sites in Coal

Abstract. *X-ray absorption spectroscopy was used to probe the chemical and structural environment of vanadium in coal. It was found that vanadium exists in at least two environments, in both of which it was coordinated to oxygens. There was no evidence of vanadium in nitrogen (porphyrin) or sulfide environments. It was also found that the vanadium environments in the raw coal did not survive unchanged in a liquefaction process. These findings have implications for coal cleaning processes and for trace element release into the liquefaction process stream.*

Coal contains nearly all the elements in the periodic table as impurities. Although the common inorganic elements in coal can be accounted for in the major minerals, the chemical and structural environments of many of the trace elements (those with a concentration ≤ 1000 ppm) cannot be confidently determined by conventional microscopic, spectroscopic, and diffraction techniques. An element that occurs in only a trace amount may, however, have a significant effect on coal conversion processes through its effects on corrosion, catalyst poisoning, and fugitive emissions. To deal rationally with these effects it is necessary to know the manner in which the element is held in coal and how its chemical environment changes during a process.

The average vanadium content of U.S. coals is 20 ppm (*1*). However, the concentration in certain parts of some seams can be greater than 1500 ppm (*2*). Studies of coals by scanning electron microscopy and energy-dispersive x-ray analysis have found examples of vanadium-bearing silicates and iron pyrites (*3*). A number of density separation studies (*4*) have pointed to an organic environment for vanadium or a mixed organic-mineral environment. In an early study Triebs (*5*) found vanadyl porphyrin in a boghead coal. Vanadium is a well-known hot corrosion agent for metal parts (*6*) and has been identified as a factor in fibrogenesis affecting miners (*7*).

We took advantage of the unique atom selectivity of the x-ray absorption technique and used both the high-resolution near-edge K spectra and the extended x-ray absorption fine structure (EXAFS) (*8*) to probe the local atomic environments of trace vanadium in coal. Intense synchrotron radiation was used as the x-ray source. The technique is nondestructive and requires no sample preparation that could disturb the elemental environments. It does not require a vacuum system and thus can be used with coal processing products such as liquids and tars, and it examines the whole sample, not just isolated regions.

The coal used in this study came from the top 15 cm of the Kentucky No. 9 seam. Parts of the seam are unusually high in vanadium. The vanadium concentrations in the samples ranged from 1000 to 1800 ppm. In addition to the raw coal, density-graded samples were prepared. The coal was pulverized under nitrogen in glass equipment to below a mesh size of 200 μm and centrifuged with Certigrav liquids. Two sets of samples were prepared, one lighter than 1.3 g/cm^3 and one heavier than 1.4 g/cm^3. Samples of liquefied coal were also prepared. The pulverized coal was mixed with 1 percent (by weight) $SnCl_2$ and tetralin, then placed in a high-pressure bomb. The system was pressurized to 2000 pounds per square inch gauge with hydrogen, then heated to 300°C for 5 hours. At this time the coal had become plastic and tarry. Samples of the tarry product were used directly in the x-ray experiments.

The experiments were performed with the EXAFS-I-5 spectrometer (*9*) at the Synchrotron Radiation Laboratory at Stanford University during a dedicated run of SPEAR (the Stanford positron electron accelerator ring) at an electron energy of 3.0 GeV and a storage ring current of ~ 100 mA. The synchrotron x-ray beam from SPEAR was monochromatized with a channel-cut Si(220) crystal and a 1-mm entrance slit, which yielded a resolution of approximately 0.3 eV at the vanadium K edge at 5465 eV. Spectra of vanadium in coal were measured by the fluorescence EXAFS technique (*10*). This technique monitors the vanadium Kα fluorescence intensity, which is proportional to the degree of absorption of the incident beam, and hence monitors the x-ray absorption spectrum. A fluorescence detector similar to that of Stern and Heald (*11*) was used. Spectral specimens were prepared by packing the powdered coal into Al cells 1500 μm thick equipped with 6-μm Kapton windows, which were sufficiently large that the x-ray beam impinged only on the coal sample. The cells were placed in a sample chamber purged with helium to minimize absorption and scat-

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tering by air in the range 5 to 6 keV.

High-resolution near-edge spectra and EXAFS spectra of a series of selected vanadium compounds of known structure were also measured and used to model the chemical states and local atomic structure of vanadium in coal. Where the concentration of these samples was high enough, the EXAFS was measured by the standard absorption technique. Vanadium K-edge spectra for a series of selected model compounds are shown in Fig. 1. The zero of energy is taken at the first inflection point of vanadium metal, whose spectrum is also given for comparison. Two different types of near-edge spectra were observed, representing (i) octahedrally coordinated compounds, such as V_2O_3, which exhibit a weak pre-edge peak, and (ii) tetrahedrally coordinated compounds such as NH_4VO_3 or compounds with a short vanadyl bond in a square pyramid, such as V_2O_4 and vanadium tetraphenyl porphyrin, all of which exhibit a strong pre-edge peak. These edge features are due to transitions from the vanadium 1*s* level to the empty energy level manifold of the molecule and could be measured to ± 0.2 eV relative to vanadium metal. For a transition metal atom in octahedral symmetry the 1*s* to 3*d* dipole transition is forbidden but the much weaker quadrupole transition is allowed (*12*). The curves for V_2O_3 and roscoelite in Fig. 1 illustrate this type of spectrum. For tetrahedral complexes, the lack of a center of inversion permits a dipole transition between the 1*s* and T_2 orbitals (these can contain much metal 3*d* character) (*13*). This gives rise to the strong pre-edge peak shown for NH_4VO_3. Similar transitions can be expected in other compounds where the local environment around the central vanadium atom lacks a center of inversion (for instance, V_2O_4 and vanadium porphyrin).

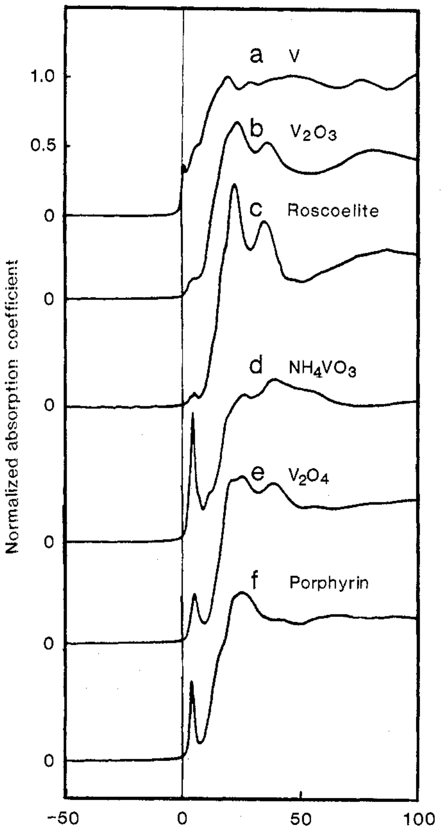

Fig. 1. Vanadium K-edge absorption spectra for (a) the metal, (b and c) octahedral coordination, (d) tetrahedral coordination, and (e and f) square pyramid coordination. Roscoelite is a vanadium mineral with the formula $KAlV_2Si_3O_{10}(OH)_2$.

Figure 2 shows K-edge spectra of vanadium in a coal, its sink and float fractions, and its liquefaction residue. All the coal samples in this study had a pre-edge peak at 4.5 ± 0.2 eV, which varied in intensity with the particular sample. Relative to raw coal, the light fractions all showed an increase in peak height and the heavy fraction showed a decrease. This behavior indicates the presence of more than one environment for vanadium in this coal. The trend in Fig. 2 indicates that a clean heavy fraction would be very similar to roscoelite or V_2O_3, that is, V^{3+} in octahedral oxygen coordination. The position of the main absorption edge is compatible with this assignment. Because rafting may occur, the light fraction may contain some of the mineral found in the heavy fraction, so that the pre-edge peak height cannot be determined accurately. The energy of this feature is, however, 4.5 eV. This excludes V^{5+} (as in V_2O_5, NH_4VO_3, and vanadium 8-hydroxyquinoline) from consideration because their pre-edge peak occurs at 5 to 6 eV. It also excludes V^{4+} with some nitrogen ligands, as in vanadium phthalocyanine and porphyrin, where the peak occurs at 3.5 to 4.0 eV. The pre-edge peak position and intensity are in good agreement with V^{4+} in oxygen coordination with one short vanadyl bond. In Fig. 2 it is also possible to compare the edge spectrum before and after liquefaction. It is clear that the vanadium environment in the raw coal did not survive liquefaction, but appeared reduced totally to a trivalent state like that in V_2O_3 or roscoelite. Reactivity during liquefaction is probably not restricted to vanadium and may be a general path by which inorganic elements from coal minerals are liberated into the product stream.

The near-edge absorption features discussed above indicate that vanadium in coal is most likely bound to oxygens as ligands. This finding can be examined more quantitatively from the EXAFS data on the high-energy side of the absorption edge. In the single-scattering approximation (*14*) the observed EXAFS, $\chi(k)$, may be given by

$$\chi(k) = \frac{-1}{k} \sum_j A_j \sin\left[2r_jk + \phi(k)\right] \quad (1)$$

where $k = \hbar^{-1}\sqrt{2m\,(\hbar\nu - E_b)}$ is the wave vector of the photoelectron, $\hbar$ is Planck's constant divided by 2π, m is mass, $\hbar\nu$ is the x-ray photon energy; E_b is the binding energy of the K electron of vanadium in the compound or coal; r_j is the distance of the atom or atoms in the jth coordination shell, $\phi(k)$ is a phase shift due to both central and backscattering atom potentials on the photoelectron, and A_j is a magnitude term given by

$$A_j = \frac{N_j}{r_j^2} f(k,\pi) \exp\left(\frac{-2r_j}{\lambda}\right) \exp\left(-2\sigma_j^2k^2\right) \quad (2)$$

where N_j is the coordination number; $f(k,\pi)$ the amplitude due to backscattering atoms only, λ the mean free path, and σ_j a Debye-Waller type root-mean-square displacement term. By using model compounds of known structure (known r_j, N_j, and σ_j), a set of backscattering amplitude and phase shifts may be derived empirically by fitting their EXAFS spectra to Eq. 1. These scattering parameters can then be used to fit the

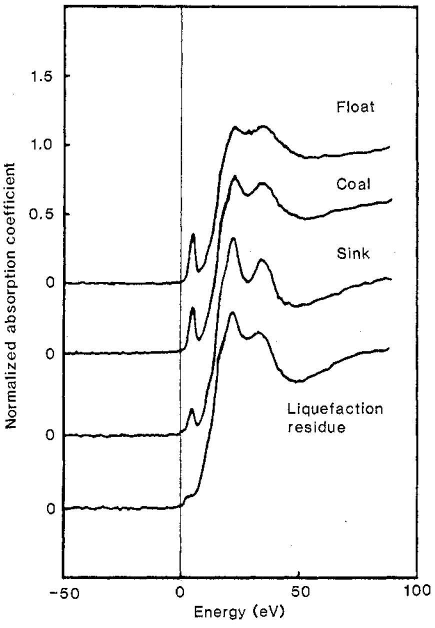

Fig. 2. Vanadium K-edge absorption spectra in coal, its sink and float fractions, and its liquefaction residue.

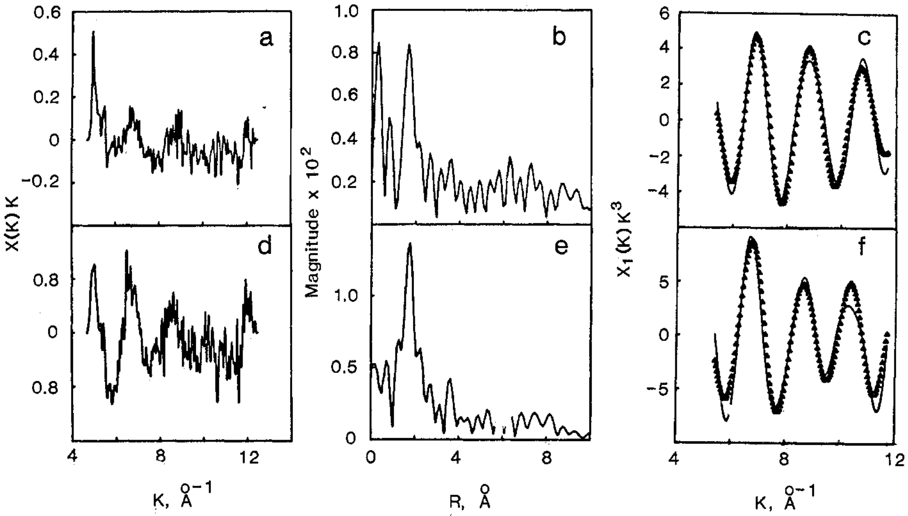

Fig. 3. X-ray absorption fine structure data for (a to c) float and (d to f) sink fractions of coal samples. (a) Normalized $\chi(k)k$ versus k; (b) Fourier transform of (a); (c) k^3-weighted inverse transform in the k range 4.7 to 11.7 $Å^{-1}$ of (b) in the region 1 to 2.5 Å and (▲) fitted data. A similar sequence is shown in (d) to (f).

Fourier-filtered EXAFS data of the unknown material and to derive structural parameters r_j, N_j, and σ_j for the jth coordination shell. Details of the Fourier analysis and fitting routine have been published (*15*). Here we outline the procedure for the vanadium EXAFS in coal.

From qualitative inspection of the coal data and analysis of the pre-edge results, it was decided to attempt to fit the EXAFS data with oxygen, sulfur, or nitrogen as the ligand. The backscattering amplitudes and phase shifts for these atoms were obtained from model compounds. The oxygen and sulfur backscattering amplitudes were obtained from V_2O_3 and V_2S_3. The vanadium-oxygen phase shift was extracted by using the known distances in V_2O_3; the vanadium-sulfur distance was not known in V_2S_3 and was therefore determined from the phase shifts reported by Lee *et al.* (*16*). The nitrogen parameters were determined from vanadyl mesotetraphenyl porphyrin, which has a vanadyl oxygen at 1.62 Å and four nitrogens at an average distance of 2.10 Å in the first shell. The vanadium-oxygen distance is known and the other oxygen parameters were taken from the V_2O_3 work. The approximate nitrogen backscattering amplitude and phase shift were obtained from calculated values and were refined by fitting to the porphyrin data. The nitrogen parameters were then used to fit vanadyl phthalocyanine and satisfactory results were obtained. These parameters for oxygen, sulfur, and nitrogen were then used to fit the coal data.

The EXAFS data for typical sink and float coal samples are shown in Fig. 3 along with the Fourier transforms and the inverse transforms 4.7 to 11.7 $Å^{-1}$ of the region of the first coordination shell, 1 to 2.5 Å. Although the data were noisy they were transformed into a complex first shell peak that could be isolated by Fourier inversion. By using these inverse transforms, the function $\chi_1(k)k^3$ was fitted with the parameters from the model compounds (*15*). The near-edge data showed that a short vanadium-oxygen bond was present. Hence two separate distances were varied simultaneously: a short vanadium-oxygen bond and an average distance with oxygen, nitrogen, or sulfur. The coal EXAFS could not be fitted with sulfur in any combination. Equally good fits could be obtained with oxygen or nitrogen as the remaining ligand with similar values of N, r, and σ. Because these elements are adjacent in the periodic table, they have similar backscattering and phase shift parameters and are difficult to distinguish. However, the pre-edge peak position in the data discussed above excludes nitrogen ligands, so we conclude that vanadium is coordinated to oxygen in this coal.

Within the estimated uncertainty, the light and heavy fractions appear similar, with one short vanadyl bond at about 1.6 Å and five longer bonds to oxygen at about 2.0 Å; however, there is less of the short-bonded oxygen in the heavy fraction. This simply reflects the fact that the vanadium "compounds" were only partially separated by the sink-float technique. We anticipate that with a finer initial particle size, the separation can be improved with progressive enrichment of the V_2O_3 or roscoelite-like phase in the heavy fraction. The EXAFS results for the light fraction yield an average vanadium-oxygen bond length of 1.93 Å in the coal fractions. This, together with the pre-edge peak intensity of about 1.0 for the light fraction, corresponds well with a tetravalent vanadium in an oxygen environment similar to that in V_2O_4—a conclusion consistent with that based on the pre-edge peak position discussed above.

The results reported here were obtained for selected coals with an abnormally high vanadium content, and the vanadium environment we found could be peculiar to this coal. Through a combination of improved detector efficiency, higher x-ray flux at wiggler stations, and longer signal integration times, it should be possible to obtain quality spectra of trace metals in coal to about 10 ppm, the approximate concentration of many elements in many coals and coal-derived products.

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