Origin of vanadium in coals: parts of the Western Kentucky (USA) No. 9 coal rich in vanadium

P. I. PREMOVIĆ[1], N. D. NIKOLIĆ[1], M. S. PAVLOVIĆ[2]
LJ. S. JOVANOVIĆ[1] & M. P. PREMOVIĆ[1]

[1] *Laboratory for Geochemistry and Cosmochemistry, Department of Chemistry, University of Niš, P.O. Box 91, 18000 Niš, FR Yugoslavia*
[2] *Institute of Nuclear Sciences Vinča, 11000 Beograd, FR Yugoslavia*

Abstract: The existence of vanadyl (VO^{2+})-non-porphyrins (P) in a thin band (enriched with vanadium) of the Western (W.) Kentucky (KY) No. 9 coal seam was shown by electron spin resonance (ESR). The ESR analysis indicates that VO^{2+}-non-P are associated with the coal organic insoluble fraction. ESR parameters show that VO^{2+} ion is in an environment with approximately axial symmetry and chelated possibly by carboxylic/phenolic oxygen ligand donor atoms. These parameters are compared with those of VO^{2+}-fulvic acid complexes and the model complexes with salicylic/phthalic acids reported by others. It is concluded that the vanadylation of W. KY No. 9 thin coal band occurred during its diagenetic (peat-forming) stage in the Pennsylvanian swamp. The extraordinary V enrichment of the top 15 cm, relative to the lower parts of the W. KY No. 9 coalbed is interpreted by a high V concentration of the past swamp water attained through a sudden and exceptional external supply. The predominant source of the metal was probably volcanic ash on the land that was weathered/leached of its vanadium. The association of V/Cr (together with their enrichment in the top of the seam) and Ni implies that the volcanic ash was derived from basalts. Abundant organic (humic) materials (with the high V enrichment factor) and low rate of deposition were the primary factors responsible for the high vanadium content of the coal. From the chemistry of VO^{2+}, FeS_2 and $CrOH^{2+}$ it is deduced that the oxidation potential Eh and pH of the ancient peat interstitial water were approximately -0.2 to -0.3 V and 5–6, respectively.

The presence of vanadium in US coals is well documented. Much analytical data (Zubović *et al.* 1961; Zubovic 1966; Cahill *et al.* 1976; Swaine 1976, 1977; Valkovic, 1983) have been compiled because the metal has a significant effect on coal conversion processes (catalyst poisoning) (references in Maylotte *et al.* 1981). In addition, vanadium contributes to harmful physiological effects (e.g. lung disease) arising from the industrial combustion of coal and the resultant ejections of vanadium derivatives into the atmosphere (Rehder 1991).

The discovery of the ESR signals of VO^{2+}-P in the petroleums and asphaltenes by O'Reilly (1958) prompted researchers to apply the technique for the detection and approximate quantification of low concentrations of VO^{2+}-P in various carbonaceous geological materials without recourse to extraction (Premović, 1978). Hocking & Premović (1978) were the first to use this technique to study VO^{2+}-P in the coal/coal-like inclusions of the Athabasca tar sand. Premović (1984) and Premović *et al.* (1986) applied ESR to estimate the distribution of VO^{2+}-P in the bitumen and kerogen fractions of ancient shaly-type sediments: the La Luna Mara

(LLM) limestone and Serpiano (Se) marl. Finally, Nissenbaum° *et al.* (1980) detected VO^{2+}-P in the DS asphalt float (Israel) using ESR.

The average V content of US coals is 20 ppm (Valković 1983). However, the concentration in certain parts of some seams exceeds 2000 ppm (Zubović 1966), e.g. the Western KY No. 9 seam. Recently, Maylotte *et al.* (1981) applied the V-XAFS to probe the chemical and structural environment of V in the parts of this coalfield (Providence mine, Union County, Fig. 2) enriched with V. According to these authors the metal exists as V^{3+} and VO^{2+} in both of which it is bound to oxygens. Maylotte *et al.* (1981) also found that the the predominant form of V in the so-called heavy fraction of the KY coal (specific gravity $\geq 1.4\,g\,cm^{-3}$) is very similar to roscoelite of V_2O_3 with V^{3+} with octahedral oxygen coordination. On the other hand, V in the light fraction ($\leq 1.3\,g\,cm^{-3}$) appears to be predominantly as VO^{2+} in an oxygen environment with no evidence for VO^{2+} coordinated with N (such as VO^{2+}-P) or S.

The purpose of the present report was to carry out a geochemical and other investigations of V and VO^{2+} ions (by ESR) present in the coal

parts (rich in V) of the W. KY No. 9 seam. It was expected that these studies might yield additional information of interest as a contribution to the general understanding of the origins of the coals enriched with V.

Experimental procedure

Sample preparation and pyrolysis

The coal samples were ground to a fine powder (200–400 mesh) with a ball mill and Soxlet extracted exhaustively with benzene/methanol azeotrope to remove soluble organic material (bitumen). The extracted rock was treated with 20% hydrochloric acid (HCl) to remove carbonates. After filtration and washing, the remaining minerals were acid leached by digestion for 72 hours at room temperature using 1:1 by volume mixture of concentrated hydrofluoric acid (HF): 48% and HCl: 20%. The mixture was filtered and the residue washed successively with boiling

distilled water to pH 7. After drying, the insoluble organic concentrate was again exhaustively extracted with benzene/methanol azeotrope until the solvent siphoning to the flask was clear. Material was dried at 80°C and stored in a desiccator.

Elemental analysis

Elemental analysis of the coal organic insoluble fraction (Table 1) for C, H and N was done on a LECO Model 600 CHN Determinator while S was determined on the LECO Model SC 32 Sulfur Analyzer. O was determined by difference.

Reflectance measurement

The coal sample was mixed with an epoxy binder in a plastic mould and cured overnight. The grain mount was ground and polished. Maximum reflectance measurement ($\% R_0$, max) was

Table 1. *Geochemical analyses of KY 9*

(a) *Chemical analysis*

Fraction	Cold HCl*	Boiling HCl	HF*	Organic
±1%	16.5	3	3	77.5
Organic fraction	soluble	insoluble		
±1%	6	94		

* The HCl/HF fraction

(b) *Distribution of V[±10 ppm], VO²⁺[±100 ppm], Cr[±10 ppm] and Ni[±10 ppm]*

	V	VO²⁺	Cr	Ni
Whole coal fraction	1000	500	70	40
HCl/HF	1800	n.d.*	135	130
Organic insoluble	800	650	50	15

* n.d. not detected

(c) *Elemental analysis (±0.5%, moisture free): organic insoluble fraction**

C	H	H/C	N	S	Mineral matter	O (diff.)
67.5	4.5	0.8	1.0	7.0	5.0	13.0

* Total acidity $1 \pm 0.4\,\mathrm{g\,eq\,kg^{-1}}$

(d) *Mössbauer analysis*

Form of Fe	FeS₂	Jarosite
±0.5%	96.0	4.0%

Sample number: 15

carried out by means of a Zeiss MPM II microscope, fitted with white halogen/UV HBO light sources and using an Epiplan (Neofluor) oil immersion objective ($n_{oil} = 1.518$ at 546 nm). (%R_0, max) was recorded on vitrinite.

Acidity determination

Total acidity of the coal organic insoluble fraction was determined by exchange with barium hydroxide measuring the amount of barium uptake (Schafer 1970).

Acid leaching

1 g of the coal organic insoluble fraction was refluxed for 30 days with 100 ml of 6 M HCl. The leached residue was removed by centrifugation, carefully washed with distilled water (again by centrifugation) until free of Cl⁻, and then thoroughly dried over P_2O_5 in a vacuum desiccator at room temperature. The dried residue was then analyzed for VO^{2+} by ESR.

Emission spectrometry

A PGS-2 plane grating spectrograph (Carl Zeiss, Jena) was used with an attachment for photoelectric detection, an arc plasma excitation source, and a Bausch and Lomb diffraction grating as the monochromator (Marinković & Vickers 1971).

Atomic absorption spectrometry (AAS)

A Perkin–Elmer model 4000 atomic absorption spectrometer was used with a Perkin–Elmer platinum hollow-cathode lamp and a nitrous oxide/acetylene burner head.

Electron spin resonance (ESR)

ESR measurements were performed on finely ground powders of (unheated and heated) geological samples which were transferred to an ESR quartz tube (4 mm o.d., 3 mm i.d.). Spectra were recorded on a Bruker ER 200D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz. The g-values and hyperfine coupling constants were determined relative to a solution of potassium

nitrosodisulfonate (Fremy's salt) for which $g = 2.0055 \pm 0.0001$ and the nitrogen hyperfine splitting, $a_N = 1.309 \pm 0.001$ mT (Faber & Fraenkel 1967). A quartz sample tube (approximately 2 mm o.d., 0.8 mm i.d.) was used for Fremy's solution ($c.\,10^{-3}$ M) that was taped on the exterior of the tube.

Scanning electron microscopy (SEM) and electron microprobe analysis

The coal sample was examined by SEM and energy-dispersive X-ray (EDX) spectroscopy with a JEOL JSM 5300 electron microscope equipped with a Link System QX 20003 EDX-spectrometer. Operating conditions for EDX analysis were 30 keV accelerating voltage, 0.1 μA beam current and a beam spot diameter of approximately 3 μm.

X-ray absorption fine structure (XAFS) spectroscopy

The S XAFS experiments were conducted at beam-line X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (New York, USA). Electron energies were 2.53 GeV and beam currents were typically 90–200 mA. A silicon (111) double-crystal monochromator was used to vary the X-ray energy from approximately 50 eV below to 300 eV above the S K-shell absorption edge (2472 eV). The experiments were done in the fluorescent mode, using a fluorescent ionization detector described elsewhere (Huffman et al. 1991). Further details concerning XAFS are found in Huffman et al. (1991).

Mössbauer spectroscopy

The Mössbauer absorption spectrum was obtained using a constant-acceleration Mössbauer spectrometer of standard design at US Steel Corporation, Research Laboratory, Monroeville (USA). The multichannel analyzer featured a dual-input module enabling simultaneous accumulation of a sample and calibration spectrum of an Fe foil; isomer shifts were measured with respect to metallic Fe at room temperature. Source consisted of $c.\,30$ to 80 mCi of ^{57}Co in a Pd matrix. Further details concerning Mössbauer analysis are found in Huggins & Huffman (1979).

Results and discussion

Depositional environments, and the coal samples' thermal history

The Springfield (W. KY) No. 9 coal of the Carbondale Formation (Middle Pennsylvanian, Fig. 1) in the W. KY coalfield (Fig. 2) of the Illinois Basin (correlative with the Illinois No. 5 and Indiana No. V coals) is the most abundant coal in the W. KY coalfield. The W. KY No. 9 coal was deposited when coastal/deltaic swamp environment (peat-forming system) covered large areas of the W. KY Basin (Rice *et al.* 1979). The climate at the time of the peat/coal deposition was tropical to subtropical (Hower & Wild 1982). Coal rank varies from high volatile A bituminous (hvAb) to hvCb bituminous. V (and Cr) is enriched in the ash at the top of the coal in the western portion of the field. Ni, Zn, Cu, and Co can also be concentrated in the top benches, but the trend is not as consistent as the V/Cr enrichment (Hower *et al.* 1990*b*). Hower *et al.* (1983, 1990*a*, *b*) considered that hydro-thermal metamorphism generated some of hvAb coals in the Union coalbed (near the W. KY Fluorspar District, Fig. 2) against the back-ground of hvCb rank. In addition, these authors suggested that the hydrothermal fluids deposited relatively high concentrations of metals such as Ba and Zn in this coalfield.

The coal samples used in this study came from the top 15 cm of the W. KY No. 9 seam at Providence mine containing 1000 ppm V (Table 1). Parts of the seam are exceptionally high in V up to 1800 ppm (Maylotte, pers.

system	formation
PERMIAN	
PENNSYLVANIAN — U	
PENNSYLVANIAN — M	Carbondale — KY 9
PENNSYLVANIAN — L	
MISSISSIPPIAN	

Fig. 1. KY 9 within the Pennsylvanian system.

comm.). The elemental analysis of the coal is shown in Table 1. The coal is rich in vitrinite (around 80%). Vitrinite maximum reflectance measurement (%R_0, max = 0.60) indicates that the coal under study belongs to hvCb rank.
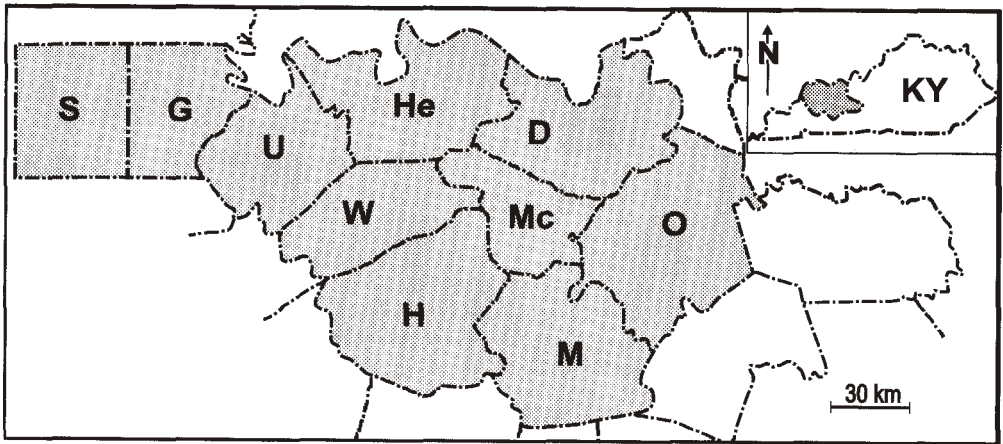
Fig. 2. The W. KY and Illinois (Saline and Gallatin counties) coalfields (approximate (shaded) outline of the lateral distribution of coal samples rich in V). KY: U(nion), W(ebster), H(opkins), D(avies), He(nderson), Mc(lean), M(uhlenberg) and O(hio) counties; Illinois: G(allatin) and S(aline) counties.

Throughout this paper the top 15 cm part of the W. KY No. 9 coal (enriched with both V and VO^{2+}) will be referred to as KY 9 unless otherwise specified.

ESR of VO^{2+} and V-XAFS study

Figure 3 shows the ESR spectrum of VO^{2+} incorporated into the KY 9 matrix. One sees five of the weak parallel components of the spectrum at the extremites, two at low field and three at high field. The remaining ones are masked by the much stronger perpendicular components in the centre of the spectrum. There are two obvious points. First, all of the coal VO^{2+}-non-P sites have the same magnetic parameters since there is only one set of lines in the spectrum. Second, the absence of any small splittings of the perpendicular components of

the spectrum implies that the VO^{2+}-non-P sites have axial symmetry, aside from any possible rhombic distortions much smaller than the linewidth of 1 mT. In this case all the spin-Hamiltonian parameters can be derived from this ESR spectrum using the axially symmetric spin-Hamiltonian

$$\mathscr{H} = \beta_0[g_\parallel H_z S_z + g_\perp(H_x S_x + H_y S_y)]$$
$$+ A_\parallel(S_z I_z) + A_\perp(S_x I_x + S_y I_y)$$

where $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ are the parallel (z) and perpendicular (x, y) components of g and ^{51}V hyperfine coupling tensors, respectively. H_i, S_i and I_i represent the vector components of the magnetic field, electron spin, and ^{51}V nuclear spin along the $i(=x, y, z)$ axes.

Experimental ESR spin-Hamiltonian parameters for the VO^{2+} compounds in KY 9 (given in Fig. 3), however, differed significantly from
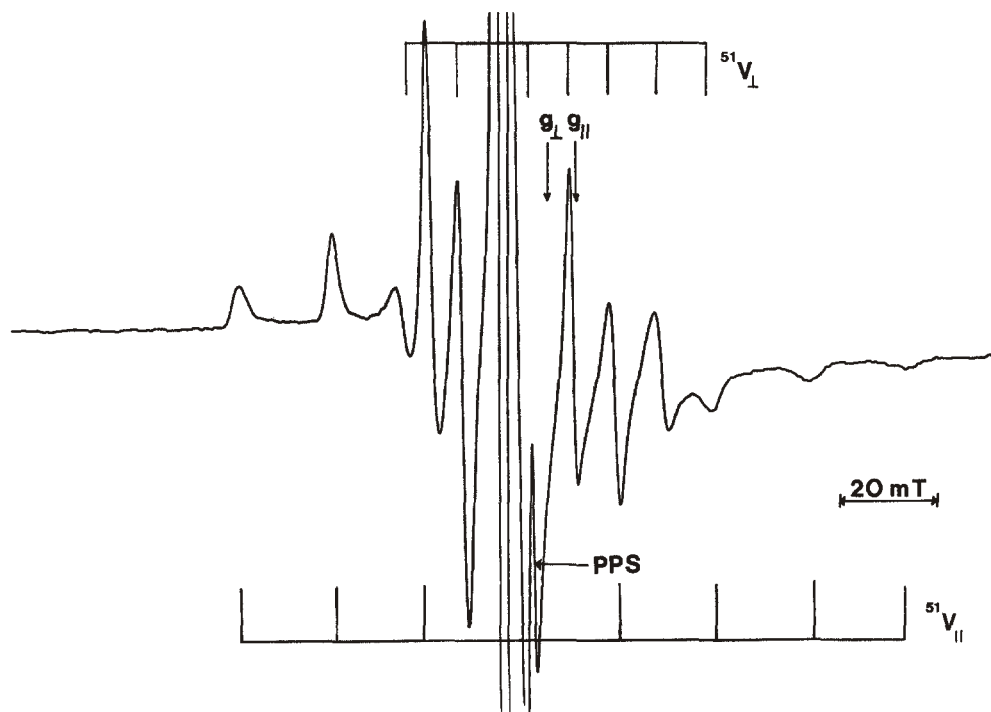

Fig. 3. First derivative, room temperature, X-band spectrum of VO^{2+}-non-P within the insoluble organic fraction of KY 9. ESR parameters: $A_\parallel = 17.6 \pm 0.2$ mT, $A_\perp = 5.7 \pm 0.4$ mT; $g_\parallel = 1.951 \pm 0.003$, and $g_\perp = 1.985 \pm 0.010$ (for VO^{2+}-P, Premović 1984); $A_\parallel = 19.2 \pm 0.3$ mT and $A_\perp = 6.9 \pm 0.5$ mT; $g_\parallel = 1.937 \pm 0.005$, and $g_\parallel = 1.991 \pm 0.010$ (for VO^{2+}-non-P); $A_\parallel = 19.3$ mT, $A_\perp = 7.5$ mT (for VO^{2+}-soil humic, McBride 1978); $A_\parallel = 19.3$ mT and $A_\perp = 6.7$ mT (for the VO^{2+}-fulvic acid in the podzol soil, Templeton & Chasteen 1980); $A_\parallel = 19.9$ mT and $A_\perp = 7.5$ mT (for the VO^{2+}-fulvic acid in the deep peat, Abdul-Halim et al. 1981); and $A_\parallel = 19.2$ mT, $A_\perp = 6.8^*$ mT (for the VO^{2+}-phthalate/salicylate mixture, Templeton & Chasteen 1980).

* Calculated as mean value of hyperfine couplings (A_{xx} and A_{yy}) derived from a non-axial spin-Hamiltonian.

those of VO^{2+}-P (Fig. 3). It has been shown that these parameters are particularly sensitive to direct ligand substitution in VO^{2+} complexes (Holyk 1979). Thus, the differences in ESR parameters, especially $A_\parallel$ (which is the most sensitive parameter to the bonding) can represent the differences in the bonding ligands around VO^{2+} in a VO^{2+} complex. Model compound studies have shown this to be valid (Holyk 1979). For this reason, a comparison of the spin-Hamiltonian parameters for VO^{2+} in KY 9 and VO^{2+}-P of various bituminous sedimentary rocks (Fig. 3) implies that VO^{2+} compounds in the coal are of non-P type. Our ESR signal intensity indicates that the concentration of VO^{2+}-non-P incorporated into KY 9 is around 600 ppm of VO^{2+}, that most of the metal (60%) resides in an organic-insoluble phase and that 80% of this V is in the VO^{2+} form (Table 1).

The high value for $A_\parallel$ (19.2 mT, Fig. 3) indicates that the VO^{2+} ion incorporated into KY 9 coal is probably complexed with oxygenated functional groups such as carboxylic/phenolic. The $A_\parallel$ and $A_\perp$ of VO^{2+}-non-P are very similar to those reported VO^{2+} ions incorporated into the structure of soil humic acid (McBride 1978) and fulvic acid isolated from either a podzol soil (Templeton & Chasteen 1980) or an organic-rich deep peat (90% organic matter, Abdul-Halim *et al.* 1981) (Fig. 3). It is suggested by these authors that these ions are bound to (carboxylic/phenolic) oxygen ligand donor atoms in the humic/fulvic acid structures. It is interesting to note that most of V is concentrated in the fulvic fraction of modern peat (Cheshire *et al.* 1977).

In an effort to model the binding environment, ESR spectra of many fulvic acid solutions containing a variety of ligand mixtures were studied by Templeton & Chasteen (1980). Particular emphasis was placed on the salicylate/phthalate mixture because, it is generally thought that carboxylic/phenolic structures are the probable functional groups present in fulvic acid. In addition, as these authors pointed out the fulvic acid used in their investigation are characterized by a preponderance of such groups. For this reason the ESR ($A_\parallel$ and $A_\perp$) hyperfine parameters for this model salicylate/phthalate complex are given in Fig. 3. The similarity in the ($A_\parallel$ and $A_\perp$) values (Fig. 3) suggests that the ligand fields about VO^{2+} are comparable for VO^{2+}-non-P and for the fulvic acid complexes on the model (salicylic/phthalate) compound. The ESR data, of course, alone do not constitute proof that carboxylic/phenolic groups make up the first coordination sphere of

VO^{2+} in VO^{2+}-non-P. However, they are certainly consistent with this interpretation.

Further support for this notion comes from XAFS investigation of V in KY 9 by Maylotte *et al.* (1981). This study shows that there is no evidence of V in the N environment (such as VO^{2+}-P). The limit of detection using the V XAFS method was about 50 ppm for VO^{2+}. Therefore, one may safely conclude that VO^{2+}-non-P are located within the KY 9 organic structure and that they are coordinated with the oxygen ligand donor atoms. These atoms are arranged in a nearly octahedral system with a strong tetragonal compression along the V–O bond of VO^{2+}. It is probable that coordination is primarily by carboxylate/phenolate groups with their four oxygen ligand donor atoms in the equatorial plane of VO^{2+}-non-P, which concurs with the known chelating functional groups of unoxidized/oxidized coals. In the free axial position, perhaps, there is one water molecule/hydroxyl ion (OH^-).

Pyrite (FeS_2) and other S compounds

EDX analysis shows that the KY 9 sample contains relatively high Fe (≥ 2% of total sample weight); SEM and chemical analysis indicates that most of this Fe is in an unoxidized form. Mössbauer spectroscopy reveals that 96% of total Fe present in KY 9 is pyritic Fe and only 4% appears as jarosite (the iron sulphate mineral). This mineral is usually present in weathered coals; presumably weathering product of FeS_2 (Huggins & Huffman 1979). According to Smith & Batts (1974) the Fe sulphates (as weathering products of FeS_2) in the coals are only of significance in relationship to very recent secondary processes.

Very recently, we have initiated *in situ* XAFS measurements of KY 9 part. Analysis of the data are still under way and only a few preliminary results will be discussed here. The S K-edge XAFS spectrum of KY 9 (Fig. 4) can be resolved in terms of two major general form components, unoxidized and oxidized. One of the unoxidized forms is the inorganic sulphide derived principally from FeS_2 (associated with the organic insoluble part). The SEM and EDX analyses indicate that all macerals of KY 9 contain substantial FeS_2, especially inertinite in which FeS_2 is the dominant S form. The other unoxidized forms are aliphatic sulphides and aromatic thiophenes. Oxidized forms include sulphate which can conceivably be derived from both inorganic and organic S compounds. The fact that sulphate is present in KY 9 (Fig. 4)
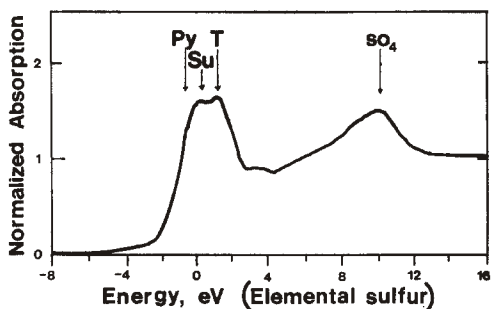
Fig. 4. XAFS spectrum of S in KY 9: Py (FeS$_2$); Su (sulphide); T (thiophene); and, SO$_4$ (sulphates).

strongly suggests that this part has been altered by natural weathering or induced oxidation.

Experimental evidence suggests that primary sedimentary FeS$_2$ forms in anoxic depositional environments provided that organic matter, dissolved sulphate, S-reducing bacteria and a source Fe co-occur in sufficient quantities (Berner 1970). Many authors have noted that peats accumulating in brackish to marine environments tend to be enriched with S content, while fresh-water, peat-forming systems tend to produce coal with a lower S content. Studies of modern peat-forming environments, however, show a substantial increase in the FeS$_2$ content of peats forming in marine-influenced environments (such as ancient W. KY swamp) (Casagrande *et al.* 1977; Altschuler *et al.* 1983). A 150 to 600 mm thick marine bituminous shale overlies the W. KY No. 9 coal over much of its extent. Since the marine sediment lies directly above the roof of W. KY No. 9 coalbed, it is probable that encroachment by the sea occurred very soon after, or even terminated, the final peat-forming stage. In this event, the organic material could be expected to be extremely reactive and a very rapid and complete reduction of sulphate to sulphide (H$_2$S/FeS$_2$) by organic/biological reactions could occur. It is, also, probable that some sulphate necessary for bacterial production of H$_2$S/FeS$_2$ in the W. KY No. 9 ancient swamp had arisen as a result of the downward diffusion of the dissolved sulphate in the overlying seawater. High contents of FeS$_2$, VO^{2+} and polyaromatic paramagnetic structures (PPS): $c. 45 \times 10^{19}$ spins g^{-1} in the coal, as determined by ESR, is consistent with this depositional model (Premović 1992; Premović *et. al.* 1993). Thus it seems reasonable to conclude that FeS$_2$ is formed during early diagenesis of KY 9, especially that incorporated into the maceral matrixes.

Origin of VO^{2+}-non-P

Coals have two major stages of formation: (a) a diagenetic or peat-forming stage that is controlled by biological activities; (b) coalification stage in which temperature, time and pressure are important. In the coalification sequence: peat → lignite → subbituminous coal → bituminous (hvCb → hvBb → hvAb) coal the content of oxygenated functional groups dramatically decreases, reaching its minimum with bituminous material. Hence, the first three members of this sequence have a much higher capacity of complexing VO^{2+} ions from aqueous solution than the fourth one (Szalay & Szilagyi 1967). Thus, VO^{2+} ions could be incorporated into KY 9 in any of these sequential phases.

The hvb coals subjected to air oxidation at moderate temperatures ($<150°$C) are characterized with good cation-exchange properties. This is attributed to acidic (carboxylate/phenolate) groups (the cation-exchange sites) formed during the oxidation process (Chandra 1982). In fact, these groups are excellent coordinating sites in the coal structure which would be rapidly filled by VO^{2+} ions (and other cations) through uptake from aqueous solution under suitable physicochemical conditions. Preliminary measurements indicate that total (carboxylic/phenolic) acidity of the KY 9 organic insoluble fraction is 1 ± 0.4 g eq kg^{-1} (Table 1) which may (theoretically speaking) bond up to 33 500 ppm of VO^{2+} ions from the aqueous solution.

Hower & Davies (1981) estimated that the W. KY Pennsylvanian coals attained maximum burial (2–3 km) by the end of the Permian and were uplifted to near the present surface by the middle of the Cretaceous. It is clear that prolonged weathering of KY 9 had to be initiated/advanced during this near-surface stage of its burial. In aerated natural (subsurficial/meteoric) waters (such as those which have been in contact with KY 9 since its uplifting by middle of the Cretaceous), V is predicted to occur in the +5 oxidation state as the vanadate H$_n$VO$_4^{n-3}$ ion (Wanty & Goldhaber 1992). As a consequence, the V species involved in the adsorption process in an oxic milieu appear to be anionic, resulting in a relatively low affinity for the cation-exchange (carboxylate/phenolate) sites in the coal (Van der Sloot 1976).

At this stage it is more likely that the vanadylation of KY 9 occurred during its peat-forming stage. It is unlikely that a process would be introduced *via* subsurface water during the lignite/subbituminous phases of the coal-forming process. The subsurface water contains no appreciable amount of V, regardless whether

the source of water is meteoric (including vadose), connate or juvenile (White 1965; Overton 1973). Casagrande & Erchull (1977) in their study of metals (including V) in the subtropical Okefenokee (comprised of a wooded swamp environment) peat-forming system (Georgia, USA) pointed out that the peat-forming environment is of major importance for the distribution of metals ultimately found in coal. It is well-established that the Okefenokee represents a suitable model system that approximates ancient peat-forming systems that have ultimately given rise to coals. In fact, the tropical/subtropical low-land paralic swamps were at their maximum development in the Pennsylvanian (Johnson 1980).

Under typical swamp/peat physicochemical conditions, the most stable form of V in aqueous solution is generally vanadate ions ($H_n VO_4^{n-3}$) but the peat humic/fulvic components can reduce $H_n VO_4^{n-3}$ to VO^{2+} in an aqueous phase (Wilson & Weber 1979). VO^{2+} (and other V^{4+}) ions can then form stable complexes with many biogeochemical compounds (e.g. humic/fulvic acids, lignins, porphyrins etc.) through chelation, metal exchange reactions and redox reactions. The fact that >70% of VO^{2+} ions are incorporated into the organic insoluble fraction of KY 9 infers two important points: (a) the swamp/peat milieu was highly reducing (see below) and with a high reducing/complexing capacity through a mediation of its humic substances (i. e. highly enriched with humics); and, (b) VO^{2+} ions must be bonded to geochemically stable oxygenated groups of the coal in order to survive both the coal-forming process (about 200 Ma) and prolonged weathering (100 Ma). The lack of change of $A_{\parallel}$ of VO^{2+}(-non-P) upon prolonged (six months) heating at 100°C (and accompanied dehydratation) of KY 9, is evidence that VO^{2+} is strongly bound to the coal insoluble organic structure. The fact that extensive laboratory leaching with 6M HCl had no effect on the ESR signals attributed to VO^{2+}-non-P incorporated into insoluble organic part of KY 9 lends further support to this interpretation.

Source of V, volcanism and the origin of fusinites

Zubović (1966) found that V was enriched in the thin top block (generally ≤15 cm) of six sites of the Springfield (W. KY No. 9, Illinois No. 5) coal in a relatively large area (>50 000 km²) of the southern Illinois Basin (KY counties: Union, Webster, Hopkins, Davies, Henderson, McLean, Muhlenberg and Ohio; Illinois counties: Saline, Gallatin), (Fig. 2). Zubović (1966) pointed out

that there is no indication that the bituminous shale which overlies W. KY No. 9 coal is a likely source of the coal V enrichment. He argued that this bituminous rock 'of comparable thickness is present throughout Illinois, but there is no comparable V enrichment of the underlying coals'. Published analyses by Hower *et al.* (1990*b*) show the V enrichment in the top benches relative to lower benches at 42 of the 44 sites of W. KY No. 9 coal where the bench samples were collected. It is quite unlikely that a source of V in the W. KY No. 9 coal was ordinary shallow (<100 m) swamp waters (the *from within* theory). The levels of metals in the modern swamp (stagnant) waters are indeed very low (<1 ppm) (Casagrande & Erchull 1976, 1977). The principal arguments against the hydrothermal origin of V are: (a) hydrothermal fluids contain a rather low concentrations of V similar to seawater (Wedepohl 1971; Jeandel *et al.* 1987); (b) numerous intensive hydrothermal sources are necessary to supply the metal for about 10^4 years (a time interval sufficient for the deposition of the ≤15 cm of the coal for an assumed coal deposition rate of 1–2 cm ky⁻¹) over a large area (in the range of 5×10^4–10^5 km²) which is quite unlikely; Fe oxides that precipitates from the hydrothermal fluids are an excellent sink for V (Dymond & Roth 1988; Trefry & Metz 1989) and (c) it is difficult to believe that a thin coal band, extending over ten thousands square kilometres would be enriched by (circulating) hydrothermal fluids while the underlying (and much thicker) parts of the same coal remain unaffected. Local hydrothermal/surface-water activities, however, might have caused some epigenetic enrichments. The coalfields in Union and Webster counties are adjacent to the W. KY Fluorspar District which is the known area of extensive hydrothermal activities which occurred possibly as late as Upper Cretaceous (Brecke 1962).

We must, therefore, postulate an (extraordinary) external supply of V of the past swamp/peat water of the W. KY No. 9 coal. We propose two views on the V source problem which we term *from below* and *from above*. According to the first concept, V was derived from either volcanic water or volcanic ash. Extensive and intense volcanism is known to have occurred in the Middle Carboniferous of North America. The other concept, perhaps more actualistic, presumes that the surface (water) processes were adequate to extract, concentrate and transfer V through weathering/leaching volcanoclastic materials from adjacent land areas. This view was formulated by Premović *et al.* (1986, 1993) to explain the

abnormal V enrichment of some ancient sedimentary rocks of marine origin. The appeal to volcanism as a source of V arises from the presumed inadequacies of ordinary processes to supply and transport V in sufficient quantities. The evidence for a volcanic source is the presumed close association in time and space of the V enrichment in a particular sediment and volcanism (Premović *et al.* 1993). As far as we are aware, there is no direct mineralogical (or other) evidence in favor of volcanism. However, the fact that this coalbed enriched with V cover an area of at least >50 000 km² (Fig. 2) may suggest a relatively intensive source. In this case, the main source of V would be the ash containing the ejected materials which were carried downwind from the distant eruptive centre. It is, then, the exception rather than the rule to find these fine volcanic materials in the conditions in which they were when freshly deposited. Their porosity and the (physical/chemical) instability of their constituents make them prone to alteration, especially in (chemically speaking) acidic environment such as the swamp/peat-forming milieu (see below).

Hower & Wild (1982) observed (macroscopically) the increase in fusinite in the top benches relative to the middle/bottom benches. Many authors consider that fusinites achieved their high carbon contents before deposition and most probably by exposure to elevated temperatures. A commonly held view of the origin of some fusinites is that natural pyrolysis occurred as a result of forest fires, ignited by lightning or meteorites. If this concept is adequate for the W. KY No. 9 coal fusinites then it is difficult to escape the conclusion that forest fires swept through the ancient swamp of the W. KY Basin in the later stages (Des Moinesian) of the peat accumulation. It is clear, then, that these fires could be readily triggered by volcanic eruptive materials. In addition, some of the erratic lateral trends observed for V (and Cr) distribution of the W. KY No. 9 coal could be due to the V concentrating effects of the forest fires through the formation of the charcoal/ash materials.

The W. KY No. 9 coalbed at the Providence mine is about 210 cm thick and has a marine black shale roof immediately on top of the coal (Maylotte, pers. comm.). According to this author, only coal samples from the top 15 cm have high V content and even then not all samples from that level showed it. For this reason, we analyzed a coal sample of the top 10 cm part from another (near-by) site. The absolute value of the V (100 ppm) concentration (and, of course, VO^{2+} content: <10 ppm) in this sample is substantially less then at the first location (Table 1). This erratic horizontal distribution of V in the top 15 cm bench samples, which were accumulated in the same freshwater basin though separated only by less than 10 km (Hower *et al.* 1990b), suggests that perhaps the reducing/complexing capacity of humics in the particular locations of past swamp/peat forming basin may have played an important role in concentrating V. This, on the other hand, may reflect the local divergence of vegetational cover within this area of ancient forest swamp (Casagrande & Erchull 1977). In addition, a sample of bituminous roof shale covering KY 9 contains <100 ppm of V, supporting Zubović's suggestion (Zubović 1966) that V in this and other V enriched coal(s) is not derived from this sedimentary cover.

Primary and secondary V

As noted above, V occurs in high concentrations at the top (≤150 mm) of the coalbed throughout much of the western half of the coalfield. A typical example is the V enrichment (1240 ppm) in the 126 mm top bench at a site in the Hopkins County, as opposed to the rest of six (lower) benches (total thickness *c.* 154 cm) in which the V content (Fig. 5) varies between 9 to 39 ppm (24 ppm used in discussion) (Hower *et al.* 1990b) and it is similar to the level of V (20 ppm) reported by Valković (1983) for the average US coals. Thus, V (1240 ppm) in the top bench rises over the V level (24 ppm) in lower benches by a factor of >50. The most spectacular example of the V enrichment (Zubović 1966) was in the top 150 mm section of the near-by Hopkins site, where it reached 2080 ppm and dropped to <9 ppm below the top. Such enormous V enrichments in the top portions of the W. KY No. 9 coal could only be explained by an abrupt and high influx of V into the W. KY Pennsylvanian swamp/peat-forming system and its subsequent localized chemical accumulation into the peat humics. This proposition, on the other hand, can only support the eruptive volcanism view. If this concept is correct then the volcanic event must have taken place during the Middle Pennsylvanian (Des Moinesian) about 300 Ma ago and therefore preceded the deposition of the uppermost portion of the W. KY No. 9 coal. The volcanic ejecta cannot, however, have stayed aloft for more than 6 months, and by Stokes's Law should have settled through <100 m of the Pennsylvanian swamp water in less than one week. These time intervals are much shorter than those assumed (*c.* 10⁴ years) for the sedimentation of the top 150 mm section
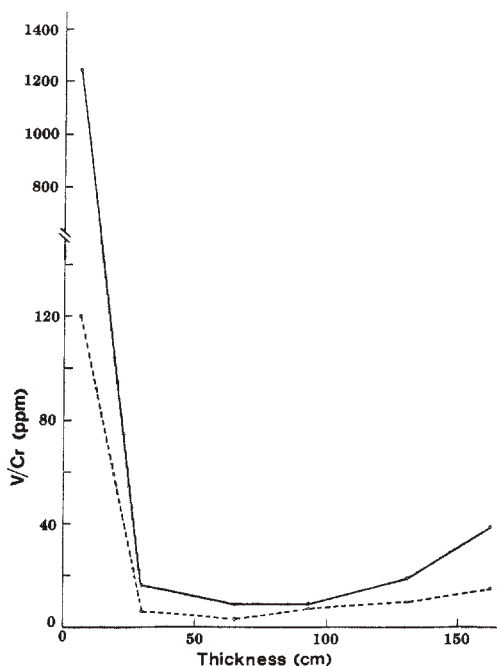
Fig. 5. The V/Cr distribution for benches at site 19, Hopkins County (Hower *et al.* 1990*b*): — — —, V; - - - - -, Cr

benches themselves: explosive volcanic activity was at a minimum during most of the KY 9 time and geochemical volcanic activity at a maximum. Had the activities been reversed the uppermost portions of the W. KY No. 9 coal would be associated with a relatively large mass of volcanic ash. In brief, volcanic ash and V-rich solution were the products of volcanic activity during the KY 9 time; ash was product of brief period (<1 year) of explosive activity; V-rich solution was the product of long sustained period (10^4–10^6 years) of geochemical activity. The ultimate cause of volcanic activity of a type resulting in large-scale discharge of ash rich in V remains a volcanological problem.

The highest V contents (1000–2000 ppm) in the top benches of the W. KY No. 9 coal (Zubović 1966; Hower *et al.* 1990*b*; this work) are much higher than those of average volcanic ash-fall (200 ppm, Leventhal *et al.* 1983). This suggests that V in the Des Moinesian volcanic ejecta was greater than normal and/or that the humics of Pennsylvanian W. KY swamp/peat-forming basin had a great reducing/complexing capacity for the corresponding V ions from the swamp aqueous solution. Relative to ordinary US coal (Valković 1983), the top ≤ 150 mm portions of the W. KY No. 9 coal are enriched by a factor >50 for V (Zubovic 1966; Hower *et al.* 1990*b*; this work). If the 'normal' concentration of V in the Pennsylvanian swamp water was enhanced by a factor 100, most of the extraordinary V concentrations of these sections would be easily explained by involvement of three factors: (a) high V geochemical enrichment factor ($>50 000 : 1$) of peat (Szalay & Szilagyi 1967); (b) relatively low sedimentation rate; (c) relatively high input of organic matter and V. Consequently, it is reasonable to assume that the V concentrations in this ancient swamp had not exceeded 0.2 ppm.

In general, volcanic ashes have a chemical composition similar to that of the igneous rocks of the same family. Vanadium in these rocks is present predominantly as V(III) which ionic species are, however, relatively immobile. On the other hand, $H_n VO_4^{n-3}$ are readily soluble and can migrate far in the ash weathering/leaching solution and over a wide range of pH. Thus we suggest that V reached reducing bottom of ancient W. KY swamp/peat as $H_n VO_4^{n-3}$ where it was reduced to VO^{2+} by humic/fulvic components of the peat (see above). The fact that the HCl/HF soluble fraction of KY 9 contains exceptionally high V content (1800 ppm, Table 1) i.e. that 40% of total V in the coal resides in this fraction (Table 1) indicates that substantial amount of V(III)

of the W. KY No. 9 coal. When volcanic ash fell weathering/leaching of the metal should have occurred in 10^4–10^6 years (Zielinski 1979). That is, removal of V must have taken place during, geologically speaking, in a short time interval, relatively soon (10^4–10^6 years) after the Des Moinesian volcanism that produced the ash. Consequently, the high V concentration in this 150 mm top section apparently represents an admixture of primary V (derived directly from the primary ash fallout) and secondary V (which could be derived from other primary fallout deposits and eroded from elevated land sites near the W. KY Pennsylvanian forest swamp). It seems reasonable to suppose: (a) both kinds of V came from a single volcanic eruption and (b) the V contribution of the secondary ash fallout to the total coal V is much larger than that of the primary material.

Thus, we suggest that the main mass of V in the top benches of W. KY No. 9 coal appears to have been added to the Pennsylvanian swamp/peat basin as a product of volcanic activity mainly through geochemical alteration of volcanic ash. The absence of readily recognizable volcanic material (such as ash) explains, in a sense, the existence of these V-rich upper

(initially located in ash-fall) was released and altered into hydrated oxides and/or vanadates which may be adsorbed on the clay particles or precipitated in $CaCO_3$ (Evans 1978). These species are relatively labile and, as such, soluble in cold HCl. The release and associated alteration had to occur during the weathering/leaching process of ash in the O_2 saturated aqueous solution.

Cr, V, Ni and basaltic volcanic ash

Apart from V, W KY No. 9 coal is also enriched in other metals, notably Cr. 60% of total Cr in KY 9 resides in the organic insoluble fraction (Table 1). Cr follows the V enrichment pattern in the top benches of the 42 sites of W. KY No. 9 coalfield. For instance, there is a 15-fold increase of the Cr content in the top section (120 ppm) of the Hopkins site over the mean value (8 ppm) for six benches below (total thickness 154 cm, Fig. 5) (Hower et al. 1990b). In fact, V/Cr/Ni are expected to be concentrated from basaltic volcanic ashes (Wedepohl 1971). Thus, we tentatively suggest that the V/Cr/Ni enrichment of the HCl/HF soluble fraction of KY 9 (Table 1) is associated with basaltic volcanic activity which characterizes the Middle Carboniferous volcanism of (Eastern) USA.

Physicochemical conditions of deposition of Pennsylvanian W. KY peat-forming system

Numerous Eh–pH diagrams for V are present in the literature. A critical review of thermodynamic data for aqueous V species has been presented by Wanty & Goldhaber (1992). They focused their attention on the results of experimental studies of V chemistry, especially on those for which experimental physicochemical conditions are similar to naturally occurring conditions. According to Baas-Becking et al. (1960), who made a thorough study of Eh and pH in many natural aqueous environments, the acidity of the swamp/peat waters and the interstitial waters in the peat is unlikely to vary outside the range pH 4–8. Moreover, they found that the Eh values of most peat-forming systems do not exceed +0.6 V. We have constructed the Eh–pH diagram for total V concentrations of 0.2 ppm (as previously discussed) in an aqueous solution (Nikolić 1993). This diagram is essentially identical to that of Wanty & Goldhaber (1992) but, for the sake of simplicity, we present only a part of the diagram (Fig. 6) for which
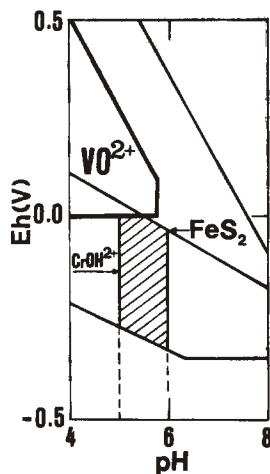

Fig. 6. Eh–pH diagram for VO^{2+} and its associated humic/fulvic acid complexes in the presence of molecular (FeS_2) and ionic ($CrOH^{2+}$) species in the Pennsylvanian W. KY swamp. Hatched area represents approximate stability field for interstitial water within the swamp/peat-forming system.

physicochemical conditions attributed to a peat-forming system are close to natural conditions i.e. those defined by Baas-Becking et al. (1960). We may further restrict the Eh values by the existence of FeS_2 in natural marine (aqueous) environments which should be in the region +0.1 V to −0.2 V for the pH range given above. Thermodynamic data used for the FeS_2 field are those reported by Wagman et al. (1982). The total dissolved element concentrations in the construction of the FeS_2 stability field are: 280 ppm of Fe (an arithmetic mean value for the swamp waters of the Okefenokee system); and 90 ppm of inorganic S (found in the average seawater) (Goldberg 1961). Although this diagram has been prepared for arbitrarily selected values for V, Fe and S, the critical boundary between the VO^{2+} and FeS_2 fields is not significantly affected by modifying these values ten-fold in either direction. Thus this diagram may be used to estimate possible physicochemical conditions of the swamp/peat-forming system at the time when the Pennsylvanian W. KY peat is formed.

It is apparent from Fig. 6 that VO^{2+} species are stable thermodynamically only at high Eh conditions (>0 V). Therefore, natural solutions with Eh lower than 0 V would not be expected to contain VO^{2+} or its complexes thereof. Nevertheless, such solutions may contain VO^{2+} (down to −0.2 V) because of the formation of stable

complexes between VO^{2+} and organic acid ligands (such as salycylate) (Breit & Wanty 1991). It is quite certain that we may expect similar enlargment of the VO^{2+} stability field for VO^{2+}-humic/fulvic acid complexes in the W. KY Pennsylvanian swamp/peat water (Fig. 6).

Wilson & Weber (1979) observed that the VO^{2+} concentration in the reaction solution containing a ten-fold molar excess of (soil) fulvic acid (under strictly anaerobic conditions) is rather low due to the formation of minor (diamagnetic) (VOOH) and major solid $VO(OH)_2$ above $c.$ pH 4.5. In fact, their data fitted exactly the Francavilla & Chasteen (1975) experimental curve obtained for VO^{2+} in aqueous solution in the absence of air O_2. Although there are some differences in the chemical behaviour/structure between soil fulvic acid and the corresponding peat component, these results clearly indicate that the peat is probably the most effective for the VO^{2+} complexation at pHs < 6.

Bacterial H_2S production is pH dependent and one of the main sulphate reducing bacteria is *Desulfovibrio desulfuricans*. These organisms are predominantly active at pH 6.5–8.0 (Alexander 1967), though there are a few cases where they grow at pH 5.5. The marine peat-forming milieu has a pH near neutrality (7), while the freshwater swamp/peat is at pH 4. Thus higher pH (5–6) may be the cause of high H_2S production in the ancient W. KY swamp/peat basin and of the consequent higher FeS_2 production.

Under the deduced physicochemical conditions of deposition of W. KY No. 9 coal (Fig. 6) the bulk of Cr present in the Pennsylvanian swamp water should be present as $CrOH^{2+}$ ions. The Okefenokee swamp waters contain <60 ppb Cr (Casagrande & Erchull 1977). If the Pennsylvanian swamp water of W. KY was enriched with Cr by a mediation of the Des Moinesian volcanic ash (likewise V) than it is quite reasonable to assume that Cr of this water exceeded >60 ppb. On the other hand, much of the stability field of Cr is occupied by insoluble Cr_2O_3. This species dissolves to form $CrOH^{2+}$ below pH 5 for the Cr concentrations >1 ppb (Brookins 1988). Hence, physicochemical conditions of the W. KY Pennsylvanian swamp interstitial water within the upper part of the Des Moinesian peat are probably best represented by a shaded area (Fig. 6). It is worth emphasizing that on Earth there are at present no such enormous forest swamps like those during Carboniferous time (subsequently leading to the formation of the largest coalfields); whose geomorphological and climatic conditions seem to be rather incompatible with these at present. It is

therefore difficult to reconstruct the physico-chemical conditions of sedimentation in the Pennsylvanian swamp of the W. KY Basin when the geomorphology and climate were quite different.

Conclusions

1. VO^{2+}-non-P in a thin coal band (rich in V) of the Western KY No. 9 bed are detected by ESR.

2. The ESR spectral parameters of VO^{2+}-non-P indicate that this ion is bound to oxygen ligand donor atoms, possibly carboxylate/phenolate groups.

3. The vanadylation occurred during the peat-forming stage of coal formation in the Middle Pennsylvanian swamp of W. KY.

4. The V enrichment in the top benches relative to lower benches of the W. KY No. 9 coalbed is caused by abrupt and high influx of V into the Pennsylvanian swamp of W. KY. It is suggested that the main source of the metal was from volcanic ash on the land by weathering/leaching which remove V from the ash to the ancient swamp.

5. From the chemistry of VO^{2+}, FeS_2 and $CrOH^{2+}$, it is deduced that the oxidation potential Eh and pH of the ancient peat interstitial water was approximately -0.2 to -0.3 V and 5 to 6, respectively during the W. KY No. 9 coal formation.

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