AUTHIGENIC ILLITE AND ORGANIC MATTER: THE PRINCIPAL HOSTS OF VANADIUM IN THE MECCA QUARRY SHALE AT VELPEN, INDIANA

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Abstract—The Mecca Quarry Shale Member from Velpen, Indiana contains abundant vanadium which occurs in solid solution within illite-rich illite-smectite (I-S) having an average content of 1.65 wt. % V, and an overall composition of $K_{0.8}(Al_{2.8}Mg_{0.5}Fe_{0.4}V_{0.3})(Si_{7.2}Al_{0.8})O_{20}(OH)_4$, analogous to the V-rich dioctahedral mica, roscoelite. The illite contains more than twice as much V as the associated kerogen. Detrital mica has a composition typical of $2M_1$ muscovite and contains no vanadium. The V-rich illite has a structure and composition typical of formation during normal prograde diagenesis and probably is widespread in the Mecca Quarry Shale because the bed is enriched in V throughout the Midwest. The smectite-to-illite reaction can not be a result of passive burial metamorphism because the host strata were buried no deeper than ~0.5 km at Velpen. The formation of illite occurred in unlithified sediments at shallow depths under the influence of pervasive 80–110°C basinal brines, possibly the same fluids that were responsible for the Mississippi Valley-type lead-zinc mineralization common in the Midwest. The presence of two types of K-rich phyllosilicates may be part of the reason for the lack of correlation between bulk V concentrations and the intensities of X-ray diffraction peaks of illite reported by others.

Key Words—Black Shale, Illite, Mecca Quarry, Organic Matter, Vanadium.

INTRODUCTION

Black shales are characterized by abundant organic matter and commonly contain major amounts of heavy elements such as U, Mo, V, Se, Zn, and Fe. Although such shales have been widely studied by a variety of conventional methods, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), much remains to be learned about the distribution of metals among potential host phases. Besides detrital silicates, likely sites for heavy metals in shales include sulfides, authigenic clay minerals, oxides, phosphates, and organic matter (Coveney and Martin, 1983; Breit *et al.*, 1989; Desborough *et al.*, 1989; Ripley *et al.*, 1990).

A member of the Linton Formation (Middle Pennsylvanian, Westphalian D), the Mecca Quarry Shale was originally described by Zangerl and Richardson (1963) from Mecca, Parke Co., Indiana, ~150 km to the north of Velpen, Pike Co., Indiana, where the samples for the present study were collected from a stream cut at 38°21'27" N; 87°05'38" W (section 8, T2S, R6W). The Mecca Quarry Shale extends throughout the Midwest from Indiana and Kentucky to Nebraska and Oklahoma. Although there are considerable variations in the amounts of heavy metals, parts of the bed are characteristically metal-rich throughout the region (Coveney *et al.*, 1987a; Coveney and Glascock, 1989). Woodland (in Zangerl and Richardson, 1963) reported exceptionally enriched values for heavy metals, including greater than 1000–2000 ppm Mo, V, and Zn at the original Mecca Quarry site near Rockville, Indiana. Subsequently, using X-ray fluorescence, proton-induced X-ray emission, inductively-coupled plasma emission, and atomic absorption spectrometry, Coveney and Martin (1983) analyzed samples of the shale from 14 locations in Indiana and Illinois and found that unweathered exposures of the black shale portions of the Mecca Quarry and other Pennsylvanian black shales contain 1200–10,000 ppm V and ≤10,000 ppm Zn, 2500 ppm Mo, and 300 ppm uranium. Samples of bed "B" from Velpen contain 1660 ppm Mo, 2830 ppm Zn, 125 ppm U, and 2980 ppm V (Coveney and Glascock, 1989). Beds "A" and "D" are also metal-rich. Bed "C," which is very clayey and deficient in organic matter relative to other units, is usually less enriched in metals but commonly contains 600–2400 ppm V (Coveney and Martin, 1983).

Vanadium commonly substitutes in the octahedral sites of 2:1 clay minerals as V^{3+} in the mica roscoelite (Gaines *et al.*, 1997), smectite, illite-smectite, illite, and muscovite (Zhang *et al.*, 1987; Meunier 1994). Breit and Wanty (1991) showed that V is common in organic material as V^{4+} that originated in marine waters by absorption on sedimentary particles. Vanadium can also occur in sulfides, in the mineral patronite, VS_4 (Gaines *et al.*, 1997). The Mecca Quarry Shale contains numerous potential hosts for V, including sulfides, organic matter, and 2:1 phyllosilicates. On the basis of energy dispersive spectroscopic (EDS) data, Coveney *et al.* (1987a) reported that most V in the Mecca Quarry Shale occurs in illite. However, Desborough *et al.* (1989) inferred from correlation coefficients, based upon bulk geochemical data, that V, as well as Mo, U, and Ni, occur mainly in organic matter. The present study was designed in part to resolve these divergent findings.
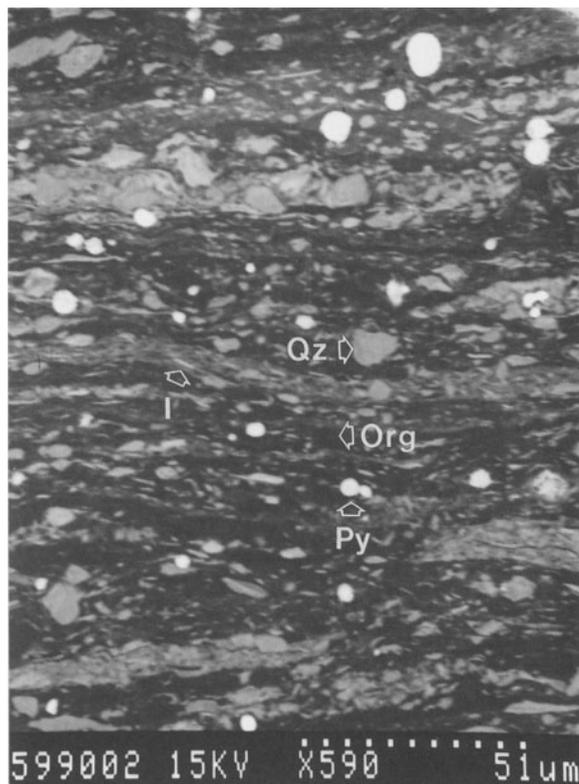
Figure 1. Low-magnification BSE image of an ion-milled thin section of Mecca Quarry Shale. Bright round objects are pyrite (Py) framboids, black material is kerogen (Org) with an elongated shape inferred to result from plastic deformation under load stress. Most material of intermediate contrast is detrital quartz (Qz).

Figure 2. Low-magnification TEM image showing the textural relations among kerogen (Org; light gray), and clay minerals, chiefly authigenic V-rich illite.

MATERIALS AND EXPERIMENTAL METHODS

Our study utilized XRD, SEM, and transmission electron microscopy (TEM) with EDS to characterize the distribution of V and other elements and to determine their origins. Samples were collected from bed "B", an organic-rich portion of the Mecca Quarry Shale, representing 15 cm of the unit's total thickness of 55 cm at Velpen. Four samples were chosen as representative of the occurrence of V and Mo in the Mecca Quarry Shale as determined by previous studies. Two sets of thin sections were prepared for each sample. One was treated with L R White resin to prevent collapse of smectite layers during sample preparation and observation (Kim *et al.*, 1995) by TEM and analytical electron microscopy (AEM). The other set was not treated and was subsequently used for AEM analyses of organic material.

A Philips automated diffractometer with graphite monochromator and CuKα radiation was used for XRD. Thin sections were ion-milled to provide for optimum resolution and clarity of optical, SEM, and TEM images taken with a Hitachi S-570 SEM and a Philips CM-12 TEM at the University of Michigan.

RESULTS

XRD and SEM data for bulk samples

XRD patterns showed the presence of quartz, chlorite, kaolinite, illite, apatite, sphalerite, and pyrite in all bulk samples. Asymmetry in the 10-Å peak of illite implied the presence of a small proportion of smectite mixed layers, whereas the half-height peak width was 0.9 °2θ. These characteristics correspond to a late diagenetic grade (*e.g.*, Merriman and Peacor, 1999).

Domains of darkest contrast in back-scattered electron (BSE) images (Figure 1) consist primarily of kerogen as verified by EDS analysis. Domains with light contrast consist mainly of detrital quartz, chlorite, illite, and authigenic illite as verified by direct EDS analysis. The elongation of kerogen particles and silicates, which are commonly crenulated, implies compaction and distortion during diagenesis. Pyrite is ubiquitous as framboids. About 0.2–1.0% sphalerite is also visible in nearly each polished rock section, along with traces of other sulfides and selenides (Coveney and Martin, 1983).

Description of dioctahedral phyllosilicates

Phyllosilicate grains occur in packets of 10-Å layers which are typically a few tens of layers in thickness and commonly curved, kinked, or splayed, probably because of compaction (Figures 2 and 3). Layer terminations are common. Some high-resolution images show wispy 10-Å units that are as thin as one or two
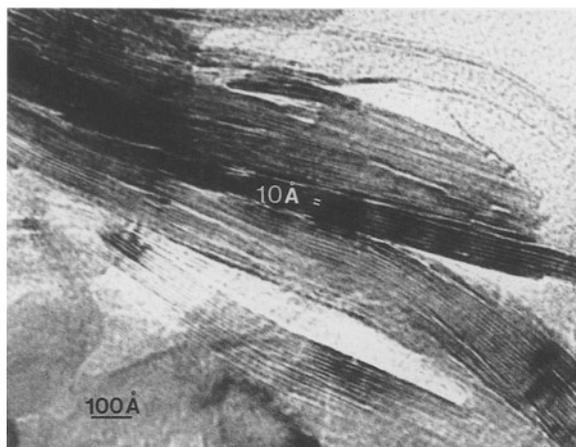
Figure 3. High-resolution TEM lattice-fringe image of typical authigenic V-rich illite. Mottled areas without 10-Å fringes correspond to kerogen.
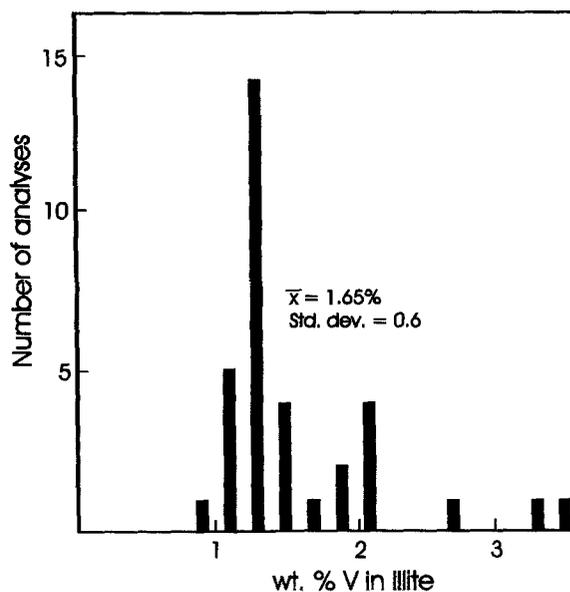

Figure 4. Vanadium contents of authigenic illite. The figure displays the results of 35 quantitative analyses of illite from bed "B" of the Mecca Quarry Shale, Velpen, Indiana. $\bar{X}$, the mean value, is 1.65 wt. %.

layers. Illite gives selected area electron diffraction (SAED) patterns with broad but regularly spaced 00l reflections, and non-00l reflections which are diffuse and weak. SAED patterns are typical of illite or illite-smectite (I-S) where stacks involve interfaces of coherent and incoherent (turbostratically related) domains. These phases are 1M_d illite or I-S (Dong and Peacor, 1996). Some lattice fringes show contrast differences and two-layer spacings (21 Å) which are typical of (Reichweite, R = 1) I-S. The spacing is a result in part of the treatment with LR White resin. However, most of the particles are illite, with spacings of ~10Å. The asymmetry in the 10-Å peak of the XRD pattern is presumably a result of the random intercalation of (R = 1) I-S layers.

EDS spectra are typical of illite or (R = 1) I-S. The spectra indicate that this phase is Si-rich and K-poor relative to muscovite. The most striking feature of the EDS spectra, however, is the presence of a strong peak from V which constitutes ~0.9–3.5 wt. % of the illite, judging from 35 quantitative analyses (Figure 4) supplemented by ~65 semi-quantitative analyses. A typical formula, derived from EDS data on the basis of normalization to 12 tetrahedral and octahedral cations (*i.e.*, assuming an ideal dioctahedral structure) is $K_{0.8}$ $(Al_{2.8}Mg_{0.5}Fe_{0.4}V_{0.3}(Si_{7.2}Al_{0.8})O_{20}(OH)_4$. Authigenic illite, which constitutes ~10% of the shale as judged from XRD data, contains a mean content of 1.65 wt. % V (Figure 4). This accounts for ~65% of the 0.27% V indicated by whole-rock analyses of bed "B" (Coveney *et al.*, 1987a).

TEM images obtained from another white mica (not shown) shows large, anhedral grains greater than a micrometer in thickness. These images contain straight lattice fringes, no dislocations, and uniform contrast. SAED patterns are sharp with non-00l reflections showing 20-Å periodicity typical of 2M_1 polytypes.

EDS analyses of these grains are typical of muscovite in that they are K-rich and Si-poor relative to illite. This material is muscovite of detrital origin and contains no vanadium.

Kerogen

At the Velpen location, bed "B" of the Mecca Quarry Shale contains 0.3% carbonate C and 37% organic C in organic matter that is largely of terrestrial origin (Coveney *et al.*, 1987a). Most of the organic material displays rather uniform contrast during observation by SEM, and EDS spectra show dominant carbon, with small amounts of V, Mo, Fe, and sulfur. Analyses of kerogen could not be precisely quantified because of the large errors associated with carbon and interference by carbon that was used to coat the samples, but we estimate the organic matter to contain ~5 wt. % total metal. Figure 5 illustrates typical wispy illite packets in organic material. As indicated above, the majority of the V in the shale is contained in authigenic illite. No V was detected in any other phase except for the organic matter. Therefore, the organic matter is assumed to contain the 25% vanadium not accounted for by that in illite, as noted above. Nevertheless, because the rock consists of 37 wt. % organic carbon, corresponding to >50% organic matter, the amount of organically bound V cannot exceed ~0.2%, which is only 15% of the amount contained by a comparable amount of V-rich illite. As shown in Figure 6, the organic matter contains 50–100-Å diameter round objects, which are probably spherical in
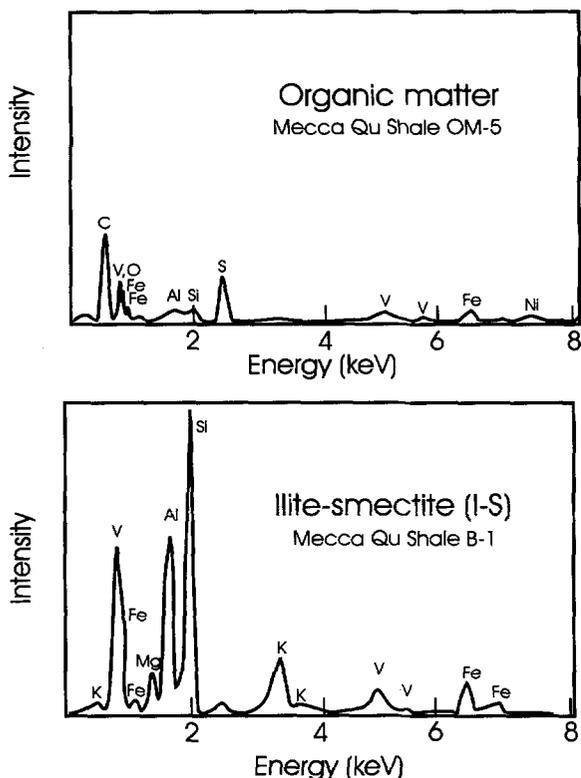
Figure 5.   Typical AEM spectra of organic matter (top) and authigenic illite (bottom). The V is concentrated mainly in the illite. Lesser amounts of V occur in organic matter, but none could be detected in either pyrite or apatite.
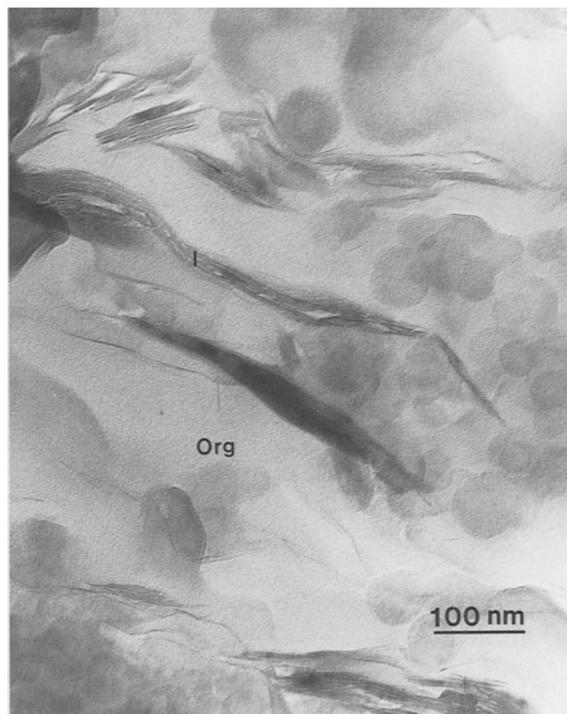

Figure 6.   Medium-resolution TEM image dominated by organic material with light-gray contrast, but with darker, rounded areas which are also comprised largely of carbon. Wispy, distorted illite packets as thin as 20–30 Å are inferred to result from plastic deformation of the kerogen matrix.

three dimensions. These objects have a composition that is similar to the surrounding kerogen. The organic material is partially ordered, as SAED patterns consist of two broad, diffuse rings. Euhedral crystals of apatite ~100 μm in diameter, similar to those observed by Ohr *et al.* (1991) in Gulf Coast sediments, dispersed in kerogen, contain no vanadium.

DISCUSSION

The TEM-EDS data indicate the presence of both V and Mo in the organic matter. Extended X-ray absorption fine structure (EXAFS) data of Helz *et al.* (1996) indicate two kinds of bonding sites for molybdenum. One has Mo-S and Mo-Fe interatomic distances typical of a cubane-type compound, whereas the other is an organic complex having Mo-O double bonds. The possibility exists that the rounded particles with unique contrast described above consist of locally ordered cubane-type units. EXAFS data show the presence of local ordering, however, which is not necessarily associated with a crystalline material producing a diffraction pattern. Semiquantitative EDS analyses illustrate uniform distributions of Mo, V, Fe, and S in the kerogen. These elements may occur in randomly

distributed, and locally ordered molecular units, one of which probably has a cubane-like structure. The existence of V and S in molecular units in kerogen is well established elsewhere (Breit and Wanty, 1991).

Most V occurs uniformly distributed in solid solution in illite-rich I-S clay. Previous electron-microprobe data for the Mecca Quarry Shale indicated that K and V occurred in the same host phase, identified as illite (Coveney *et al.,* 1987a). However, the earlier results did not distinguish between authigenic illite and detrital muscovite, nor were they quantified. The occurrence of V in illite is consistent with data from other metal-rich shales (*e.g.,* Zhang *et al.,* 1987) and with other observations of V in 2:1 phyllosilicates (*e.g.,* Meunier, 1994). Note, however, that roscoelite occurs almost exclusively in mineral deposits affected by hydrothermal fluids (Gaines *et al.,* 1997). Even the V-rich illite observed by Meunier (1994) occurs only locally in U deposits of hydrothermal origin.

In the Mecca Quarry Shale, by contrast, V occurs rather uniformly distributed in I-S with features common to prograde sedimentary diagenesis. With respect to its SAED pattern, packet thickness, dislocations, orientation, and composition, the clay closely resembles the illite formed during late diagenesis with smectite as a reactant (Merriman and Peacor, 1999). Such

features are characteristic, for example, of illite in Gulf Coast mudstones derived from the completion of the smectite-to-illite reaction during passive burial diagenesis in an environment not affected by tectonically induced change (Merriman and Peacor, 1999). The relatively uniform distribution of V in both authigenic illite and kerogen implies that V did not substitute into the illite or I-S after its formation. Prior to illitization, most of the V may have been largely hosted by organic matter, judging from the correlation between V and organic C reported by Desborough *et al.* (1989).

It is commonly assumed that metals are mainly introduced into black shales, such as the Mecca Quarry, during sedimentation (*e.g.*, Heckel, 1977; Holland, 1979; Piper, 1994). As Vine and Tourtelot (1970) stressed, however, metals can be introduced into shales at various stages in their history. Post-sedimentary introduction of heavy metals is especially likely for beds, such as the Mecca Quarry Shale, that are thin and sufficiently jointed to create high permeability for circulating pore fluids (Coveney and Glascock, 1989). Migration of such fluids through the shale bed may have been enhanced by the appreciable porosity that can exist in precursor mud prior to the completion of clay transitions.

The Mecca Quarry Shale occurs in a cratonic environment and was not buried deeper than ~0.5 km at Velpen (Sloss, 1988; Collinson *et al.*, 1988). Judging from the diagenetic history of Gulf Coast sediments where the I-S reaction is completed at depths of ~1800 m below which no further changes occur in the proportions of illite to smectite (Merriman and Peacor, 1999), the transition could not have occurred at such shallow depths under normal passive, burial-diagenetic conditions. Independent data show, however, that circulating Mississippi Valley-type brines with temperatures to ~100°C pervasively invaded the Illinois basin during the Paleozoic (and perhaps later) (Hatch *et al.*, 1976; Coveney *et al.*, 1987b). These fluids are likely agents for the prograde diagenetic reactions that formed the V-rich illite.

The available data suggest that V was introduced into the Mecca Quarry Shale during or shortly after sedimentation and was subsequently redistributed during diagenesis aided by invasive hydrothermal brines at depths of <500 m. The invading fluids may have been an important source of metals for the shales, including some of the V contained within the organic constituents. Mississippi Valley-type brines are known to have contained Mo and other metals which are not commonly thought of as being associated with Pb-Zn deposits (Erickson *et al.*, 1981; Saunders and Savrda, 1993).

In any case, our detailed TEM-EDS and XRD studies show that illite hosts ~65% of the V contained by the Mecca Quarry Shale at Velpen, Indiana. The remaining 35% of the V occurs in association with or-

ganic matter. General correlations between V and organic carbon previously reported for the Mecca Quarry Shale and other metalliferous marine Pennsylvanian shales of the Midwest may reflect a strong association of V with organic matter in the precursor sediments but the correlation has no direct significance about the main host phase at present. The practice of inferring host phases for V from correlation coefficients based on bulk chemical analyses should be avoided whenever possible. Direct analytical techniques, such as those reported here, provide the surest means of identifying the host phases of metals in shales.

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