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Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems

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Abstract

The black shale submember of core shales of Pennsylvanian Kansas-type cyclothems is highly enriched in redox-sensitive trace elements (TEs) relative to the overlying gray shale submember as well as to many other modern and ancient organic-rich deposits. Controls on trace-element behavior in the black shale can be inferred from trace-element enrichment factors (EFs, relative to gray shale) and the relationship of TEs to total organic carbon (TOC). Most TEs conformed to one of two patterns: (1) Mo, U, V, Zn, and Pb exhibited moderate EFs and strong covariation with TOC in samples having <10 wt.% TOC but large EFs and weak covariation with TOC in samples having >10 wt.% TOC; and (2) Cu, Ni, Cr, and Co exhibited low EFs and moderate to strong covariation with TOC in all samples. These patterns are inferred to represent different responses to benthic redox conditions. The first pattern is characteristic of TEs of "strong euxinic affinity", i.e., those taken up in solid solution by Fe-sulfide or involved in other reactions catalyzed by free H₂S, and resident mainly in authigenic phases, whereas the second pattern is characteristic of TEs of "weak euxinic affinity", i.e., those not strongly influenced by the presence of free H₂S and resident mainly in the organic carbon or detrital fractions of the sediment. These inferences allowed development of a multiproxy technique for assessing redox facies in black shale samples: euxinic conditions were considered to have existed if at least two of four "redox-indicator" trace elements (Mo, U, V, Zn) showed euxinic levels of enrichment, and nonsulfidic anoxic conditions were inferred otherwise. The validity of the procedure is indicated by (1) agreement among all four "redox indicators" for a large majority of samples (69% of 185); (2) among samples yielding a mixed redox signal, a systematic sequence of TE enrichment (V \rightarrow Zn \rightarrow Mo \rightarrow U); and (3) for TEs of "weak euxinic affinity", reduced variance among samples representing each redox facies. Sequential enrichment may be a response to differential redox thresholds for accumulation (e.g., V) or postdepositional remobilization of trace elements (e.g., U) and may provide a basis for finer assessment of redox conditions in low-oxygen paleoenvironments than permitted by simple classification schemes. The multiproxy procedure for redox-facies analysis developed in this study is likely to be more reliable than widely used single-proxy indicators based on trace elements (e.g., Mo, authigenic U, or V/(V+Ni)) or C-S-Fe systematics (e.g., S/TOC or DOP). © 2004 Elsevier B.V. All rights reserved.

Keywords: Black shales; Organic carbon; Redox indicators; Anoxic; Euxinic; C-S-Fe systematics

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1. Introduction

Redox-sensitive trace element (TE) concentrations or ratios are among the most widely used indicators of redox conditions in modern and ancient sedimentary

systems (e.g., Calvert and Pedersen, 1993; Jones and Manning, 1994; Wignall, 1994; Crusius et al., 1996; Dean et al., 1997, 1999; Yarincik et al., 2000; Morford et al., 2001; Pailler et al., 2002). TEs commonly exhibit considerable enrichment in laminated, organic-rich facies, especially those deposited under euxinic conditions (Table 1) and, conversely, little if any enrichment in bioturbated, organic-poor facies. This pattern exists because (1) many TEs have multiple valence states, and the reduced forms that exist under low-oxygen conditions are more readily complexed with organic acids, taken into solid solution by authigenic sulfides, or precipitated as insoluble oxyhydroxides, and (2) all TEs are affected by processes that operate more strongly under low-oxygen conditions, e.g., Mn/Fe redox cycling, increased availability of organic carbon substrates, and presence of H₂S at sediment redox boundaries or in the water column under euxinic conditions (Pratt and Davis, 1992; Calvert and Pedersen, 1993: Morse and Luther, 1999). Because all of these processes are operative primarily or exclusively at dissolved oxygen levels low enough to exclude benthic organisms ($\sim < 0.2$ ml $O_2 l^{-1} H_2 O$), TE concentrations are one of only a few methods available to evaluate variation in redox conditions in laminated, organic-rich facies. The ability to assess minor fluctuations in O2 levels in such environments can be important, however, because even small quantities of benthic oxygen can influence

Table 1		
Trace-element	enrichment	factors ^a

the quantity and quality of preserved sedimentary organic matter (Canfield, 1994; Van Cappellen and Ingall, 1994; Tyson, 1995).

Core shales of Upper Pennsylvanian Kansas-type cyclothems offer favorable conditions for studying the geochemical signatures of redox facies in organic-rich sedimentary rocks. This is because (1) core shales are composed of a lower laminated black shale submember and an upper bioturbated gray shale submember, representing a range of redox conditions from mildly dysoxic to strongly anoxic and, possibly, euxinic; (2) the black shale submember contains intervals of both low and high TE concentrations, suggesting variation in type or intensity of redox controls on TE enrichment; (3) core shales represent depositional systems of relatively short duration ($\sim \le 10^5$ years; Heckel, 1986; Watney et al., 1989) in which few physicochemical factors other than benthic O₂ levels may have varied; and (4) general conditions in the Late Pennsylvanian Midcontinent Seaway are well studied (e.g., Heckel, 1977, 1991; Hatch and Leventhal, 1992; Hoffman et al., 1998). In this study, we investigated trace-element distributions in several core shales from Upper Pennsylvanian cyclothems of eastern Kansas with three objectives. First, we developed a multiproxy method for assessing redox facies in black shale samples based on a suite of TEs exhibiting large enrichment factors (EFs, relative to gray shale samples) and thus considered to have "strong euxinic

	Modern euxinic environments				Pennsylvanian core shales (present study)						
	Black Sea ^b	Cariaco Basin ^b	Saanich Inlet ^b	Framvaren Fjord ^b	Black shale versus average shale ^b	Euxinic versus dysoxic facies ^c	Euxinic versus anoxic facies ^c	Anoxic versus dysoxic facies ^c			
Мо	14.3	37.0	60.0	33.3	64.3	18.2	8.4	2.2			
U	8.2	5.5	3.5	20.2	25.1	221.5	8.1	27.4			
V	1.9	2.4	1.9	1.8	8.3	36.1	5.9	6.1			
Zn	1.1	1.5	3.3	100.0	26.7	63.2	10.0	6.3			
Pb	n/a	n/a	n/a	n/a	n/a	16.1	1.8	8.8			
Cu	1.4	1.0	2.4	7.3	2.8	2.9	1.9	1.5			
Ni	2.6	0.8	1.0	11.8	4.4	6.7	2.0	3.4			
Cr	2.8	1.3	1.5	0.8	6.6	9.9	1.6	6.0			
Со	n/a	n/a	n/a	n/a	1.5	2.0	1.4	1.4			
Mn	1.4	0.3	1.1	1.7	0.22	0.90	1.08	0.84			

^a Enrichment factors (EFs) calculated for Al-normalized concentrations.

^b Compared to average shale compositions from Taylor (1964) and Wedepohl (1971); data for modern environments from Calvert and Pedersen (1993).

^c Comparison between redox facies of the present study: dysoxic facies (n 48), nonsulfidic anoxic facies (n 89), and euxinic facies (n 96).

affinity" (Mo, U, V, and Zn). Second, we calculated the distribution of TEs among the detrital, organic, and sulfidic fractions of samples from both the nonsulfidic anoxic and euxinic facies. Third, we evaluated the processes controlling TE distributions in the study units on the basis of the foregoing results and by comparison with TE studies of modern marine environments and developed a general model for TE enrichment in core shales of Upper Pennsylvanian Kansas-type cyclothems.

2. Geologic setting

This study examined three core shales from the Kansas City Group (Missourian Stage, Upper Pennsylvanian) of eastern Kansas: (1) the Hushpuckney Shale Member of the Swope Formation, (2) the Stark Shale Member of the Dennis Formation, and (3) the Muncie Creek Shale Member of the Iola Formation (Fig. 1a,b). In this area, the Missourian succession consists mainly of interstratified marine shales and limestones deposited in 10- to 50-m-thick transgressive-regressive "Kansas-type" cyclothems produced by quasiperiodic global sea-level fluctuations resulting from waxing and waning of continental ice sheets during the Gondwanan Ice Age (Crowell, 1978; Heckel, 1986, 1994; West et al., 1997). "Core shales" are named for their central position within these cyclothems and represent transgressive to maximum highstand conditions (Heckel, 1977, 1991). During deposition of core shales, the Midcontinent Seaway was a stratified water mass, causing benthic O₂ depletion that facilitated accumulation of large quantities of sedimentary organic matter. Stratification may have been favored owing to paleoclimatic and paleogeographic factors: (1) the Midcontinent Seaway was located in the humid tropical climate belt ($\sim 5-$ 10°N; Scotese, 1994); (2) it was a semirestricted epicratonic sea surrounded by landmasses and, hence, probably received considerable runoff (Heckel, 1977); (3) it was subject to monsoonal precipitation (Crowley et al., 1989; Parrish, 1993); and (4) conditions were most humid during interglacial highstands, i.e., during core shale deposition (Cecil, 1990; West et al., 1997).

3. General character of core shales

In the study units, each core shale consists of a 40to 60-cm-thick black shale submember overlain by a 10- to 90-cm-thick gray shale submember (Fig. 1c).



Fig. 1. (a) Location map. Facies belts from Heckel (1977). (b) Missourian Stage stratigraphy of eastern Kansas. This study examines the Hushpuckney, Stark, and Muncie Creek shales, at the base of the Swope, Dennis, and Iola formations (or cyclothems), respectively. (c) Model core shale of Upper Pennsylvanian Kansas-type cyclothem showing lower black shale and upper gray shale submembers. Ichnofabric indices (ii) range from 1 (unbioturbated) to 6 (completely bioturbated; Droser and Bottjer, 1986).

The black shale generally is laminated, nonfossiliferous, moderately to strongly phosphatic, and high in TOC (>2.5 wt.%), whereas the gray shale is bioturbated, sparsely fossiliferous, weakly or nonphosphatic, and low in TOC (<2.5 wt.%). Internally, the black shale exhibits cm-scale compositional variation, alternating between dark-gray (Munsell 10 YR 6/1-5/1), organic-"poor" (<10 wt.% TOC) and black (Munsell 10 YR 3/1-2/1), organic-rich (>10 wt.% TOC) layers. The upper and lower contacts of the black shale tend to be sharp; the lower contact may be marked by a skeletal clast lag and corrosion of the top of the underlying transgressive limestone, whereas the upper contact generally is weakly penetrated by burrows from the overlying gray shale. Fineness of grain size, presence of phosphatic firmgrounds, absence of biota other than rare pelagic or epipelagic marine organisms, and ³⁴S-depletion of Fe-sulfides indicate slow, sediment-starved accumulation in a distal offshore setting (Heckel, 1977, 1991; Coveney and Shaffer, 1988; Schultz and Coveney, 1992). The overlying gray shale exhibits moderate to intense bioturbation, with discrete traces prevalent for ~ 10 to 30 cm above the black shale/gray shale contact and fully homogenized sediment above that point. The ichnogenera present belong to the Zoophycos assemblage, which commonly is developed in fine-grained sediments deposited in low-oxygen environments (Ekdale and Mason, 1988; Bromley, 1996; Savrda et al., 2001). These observations are consistent with uniformly anoxic conditions during deposition of the black shale submember and a rise in dissolved O2 levels above a critical threshold for benthic organisms at the black shale/gray shale contact (cf. Cruse and Lyons, 2000).

The major components of the study units were determined by petrographic, mineralogic (XRD), and geochemical (XRF, LECO) methods to be: (1) organic matter, (2) Fe-sulfide (mainly pyrite), (3) phosphate, and (4) siliciclastic minerals (illite, mixed-layer I/S, quartz, and chlorite; Algeo and Maynard, 1997; Hoffman et al., 1998). The dominant elemental affinities of these components, as determined by cluster analysis, are: (1) organic matter: TOC, Ni, Cu, U, Mo, and V; (2) Fe-sulfide: Zn; (3) phosphate: TIC, Ca, P, Sr, Y, and U; and (4) siliciclastics: Si, Zr, Nb, Ti, Mg, Al, K, Rb, Na, Ba, Fe, and Mn. The organic fraction consists of vitrinite (including vitridetrinite and desmocollinite), inertinite (including fusinite and semifusinite),

alginite, and bituminite (cf. Wenger and Baker, 1986). The vitrinitic macerals occur in thin, elongate bands $(<1.5 \times 2-80 \mu)$ that are internally structureless and commonly contain embedded grains of clay, pyrite framboids, and inertinite; much of it represents bacterially degraded woody plant debris of terrigenous origin. The inertinitic macerals occur both in association with and independently of vitrinite as small, very bright, angular grains; much of it may be charcoal derived from woody plant tissue (Susan Rimmer, U. of Kentucky, personal communication, 2003). The organic matter in the study units is of relatively low maturation rank ($R_0 \sim 0.57$; Wenger and Baker, 1986), so loss of organic carbon due to thermal alteration is not a concern in this study.

4. Methods

The three core shales of this study were investigated as follows: the Hushpuckney Shale in the Edmonds, Ermal, and Mitchellson cores, the Stark Shale in the Edmonds, Ermal, Womel, and Heilman cores, and the Muncie Creek Shale in the Edmonds core (Fig. 1b). Each study unit was examined by standard transmitted- and reflected-light petrographic, and X-radiographic techniques (Algeo and Maynard, 1997; Hoffman et al., 1998). In each unit, samples were collected from 5- to 10-cm-thick intervals in the lower, middle, and upper parts of the black shale submember as well as from the lower part of the overlying gray shale submember. Each sample corresponded to a layer of nearly uniform composition, as determined by petrographic and X-radiographic character, and sampled layers were of subequal thickness, averaging ~ 1 cm. Samples were ground in an agate ball mill and refrigerated to prevent oxidation of organic carbon and sulfides prior to analysis.

Trace-element concentrations were determined by XRF using a wavelength-dispersive Rigaku 3040 XRF spectrometer at the University of Cincinnati. Samples were calibrated with both USGS (SDO-1, Sco-1, SGR-1) and internal black shale standards (analyzed by XRAL). Analytical precision based on replicate analyses was better than \pm 3.2% for Mn and \pm 5% for other trace elements. Detection limits for trace elements were 2 ppm for Mo and Pb, 5 ppm for Zn, Cu, Ni, and Co, and 10 ppm for Cr, V, and U.

Total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC; by difference), and total sulfur (TS) were determined by LECO analysis using a LECO CS-244 analyzer at Indiana University. Samples were calibrated with laboratory standards; analytical precision (2σ) based on replicate analyses was $\pm 2.0\%$ and $\pm 7.6\%$ of measured values for C and S, respectively. A total of 234 samples were analyzed by XRF and LECO for this study: 49 from the gray shale submember and 185 from the black shale submember. Geochemical analyses were performed on samples representing ~ 50% of the total stratigraphic thickness of the black shale facies in the eight study units.

Trace-element concentrations commonly are normalized to Al to correct for variable dilution by organic matter and authigenic minerals (e.g., Arthur et al., 1990; Calvert and Pedersen, 1993; Morford et al., 2001). We follow this convention, reporting all trace-element concentrations as Al-normalized values having units of 10^{-4} . This normalization procedure is valid if Al resides primarily in siliciclastic phases and was immobile in the diagenetic environment, both of which appear to be true of the study units. Traceelement concentrations occasionally are reported on a non-detrital basis, by subtracting a calculated detrital component; for example, Wignall (1994) and Pailler et al. (2002) determined "authigenic U" concentrations on the basis of Th/U ratios. In this paper, we report whole-rock trace-element concentrations and estimate the proportion of each trace element resident in the detrital fraction of black shale samples from its concentration in gray shale samples of the same study unit. The data are available from the corresponding author upon request.

5. Results

5.1. TOC-TE covariation

All of the redox-sensitive trace elements (TEs) examined in this study except Mn exhibit low and nearly invariant concentrations in gray shale samples, and higher concentrations with some degree of positive covariation with TOC in black shale samples (Figs. 2–5). Two distinct patterns of TOC–TE covariation are evident. One pattern is manifested by TEs with large enrichment factors, i.e., Mo, V, Zn

(max. EFs ~ 50-100), and U (max. EF >1000; Figs. 2b and 3a-c). Such large EFs are characteristic only of samples with >10 wt.% TOC, and these samples show comparatively weak TOC-TE covariation; conversely, samples with <10 wt.% TOC are characterized by modest TE enrichment but stronger TOC-TE covariation. These TEs generally exhibit large EFs in modern euxinic marine environments (Table 1; Brumsack, 1986, 1989; Jacobs et al., 1987; Emerson and Huested, 1991; Crusius et al., 1996; Dean et al., 1999; Yarincik et al., 2000; Morford et al., 2001), suggesting a temporally invariant association with euxinic conditions. We regard this group of TEs as displaying "strong euxinic affinity". (Pb may also belong to this group despite modest EFs because virtually all samples with >10 wt.% TOC show enrichment relative to low-TOC samples; Fig. 3d).

A second pattern of TOC-TE covariation is exhibited by a group of trace elements with smaller levels of enrichment, i.e., Cu, Ni, Cr, and Co (max. EFs <20; Fig. 4a–d). These TEs are enriched to only a limited degree in black shale samples with >10 wt.% TOC relative to those with <10 wt.% TOC, contributing to strong positive TOC-TE covariation for samples at all TOC values (except for Co, which exhibits little TOC dependence). Thus, unlike TEs in the first group, those of the second group (Cu, Ni, Cr, and Co) do not show a distinct change in behavior at a TOC threshold of 10 wt.% but, rather, merely a modest increase in variance among high-TOC samples relative to low-TOC samples. This modest increase in variance might have gone unnoticed, and its significance unrecognized, if not for the results of a redox-facies analysis based on the TEs of strong euxinic affinity. This analysis (explained below) resulted in the redox-facies assignments shown in Fig. 4a-d, from which it is apparent that the increase in variance among samples with >10 wt.% TOC is due to divergent trends for sample populations representing nonsulfidic anoxic and euxinic facies. These TEs exhibit small EFs in modern euxinic environments (Table 1), evidence of the generally limited influence of free H₂S on their accumulation. We regard the second group of TEs as displaying "weak euxinic affinity".

Mn displays a pattern of TOC covariation different from that of the other TEs considered in this study. First, it exhibits little systematic variation with TOC



and, hence, no relationship to the redox facies that subsequently will be defined (Fig. 5a). Second, virtually all samples yielded concentrations that are low relative to average crustal values ($\sim 96 \times 10^{-4}$; Taylor, 1964; Wedepohl, 1971), suggesting some degree of Mn depletion in both the gray shale and black shale submembers of all study units. The only exceptions were two samples taken from weakly cemented carbonate nodules in a gray shale: these yielded values of $320-430 \times 10^{-4}$, which are enriched by more than an order-of-magnitude relative to black shale and noncalcareous gray shale samples of this study, as well as by a factor of 3-4 relative to average crustal values.

5.2. Evaluating redox facies

Early work on redox facies focused on the effects of low oxygen levels on benthic biotas, leading to recognition of aerobic, dysaerobic, and anaerobic biofacies (Rhoads and Morse, 1971). The dysaerobic biofacies is characterized by skeletal or trace-fossil assemblages reflecting reduced benthic O2 levels, and the anaerobic biofacies by an absence of benthic organisms (Rhoads et al., 1991; Wignall, 1994). The corresponding redox classification of sedimentary environments includes oxic, dysoxic (or suboxic), and anoxic facies, and the last one can be divided into nonsulfidic and sulfidic (euxinic) subfacies (Fig. 6a). Estimates of the oxygen tensions associated with these environments come from studies of modern benthic environments: >2.0, 2.0-0.2, and <0.2 ml $O_2 l^{-1} H_2O$ for oxic, suboxic, and anoxic environments, respectively, with euxinic conditions marked by 0 ml $O_2 l^{-1} H_2O$ and measurable quantities of free H₂S in the water column (Edwards, 1985; Tyson and Pearson, 1991); for comparison, oxygen-saturated surface waters contain 4.5 to 8.0 ml O_2 l⁻¹ H₂O (Wright and Colling, 1995). Although this redox classification system has been amended to include a variety of special situations, e.g., episodic benthic

anoxia (poikiloaerobia; Oschmann, 1991) and stabilization of the oxic/anoxic boundary at the sediment– water interface (exaerobia; Savrda and Bottjer, 1991), it is still fundamentally a simple three- or four-part scheme.

In the study units, samples from the black shale and gray shale submembers are easily distinguished on the basis of color, organic carbon content (>2.5 wt.% versus <2.5 wt.%), and ichnofabric (laminated versus bioturbated). Several additional observations suggest that the two submembers were deposited under markedly different redox conditions: (1) the black shale/gray shale contact is a sharply demarcated surface in most study units, and (2) burrows in the black shale are generally restricted to the uppermost 2 to 5 cm and penetrate downward from the overlying gray shale. These observations suggest that benthic conditions during black shale deposition were sufficiently O₂-depleted as to exclude benthic organisms (i.e., anoxic/euxinic), and that a possibly sharp rise in dissolved O_2 levels coincided with the onset of gray shale deposition, crossing a critical threshold to dysoxic levels that allowed benthic colonization. Also noteworthy is that the gray shale submember is TEpoor and exhibits no TOC-TE covariation (Fig. 2a), suggesting TE residence primarily in the siliciclastic detrital fraction; this inference is supported by comparison with TE data for average shales (e.g., Taylor, 1964; Wedepohl, 1971). On the other hand, black shale samples exhibit elevated TE concentrations relative to gray shales (Table 1) and positive TOC-TE covariation (Figs. 2-4), indicating enrichment by processes associated with low-oxygen environments. We consider gray shale samples of the study units to represent dysoxic facies and black shale samples to represent nonsulfidic anoxic or euxinic facies, with ~ 2.5 wt.% TOC representing the threshold for anoxic conditions ("anoxic threshold"; Fig. 6a).

Is it possible to distinguish black shale samples of the study units deposited under nonsulfidic anoxic versus euxinic conditions on the basis of trace-ele-

Fig. 2. TOC-TE relationships with Mo as an example: (a) $\log -\log \operatorname{crossplot}$, (b) $\operatorname{linear-linear crossplot}$. Mo concentrations are Al-normalized ($\times 10^{-4}$); n=233. EF is the "enrichment factor" of black shale samples, i.e., relative to the average gray shale sample. Redox-facies assignments are explained in the text. (c) Theoretical model of TE enrichment: gray shale samples exhibit low and invariant TE concentrations owing to TE residence primarily in detrital phases; black shale samples deposited under nonsulfidic anoxic conditions exhibit modest TE enrichment and strong TOC-TE covariation owing to TE residence primarily in organic phases; and black shale samples deposited under euxinic conditions exhibit strong TE enrichment and, at most, weak TOC-TE covariation owing to TE residence primarily in authigenic sulfide or oxyhydroxide phases.



Fig. 3. Trace elements of "strong euxinic affinity": (a) U; (b) V; (c) Zn; and (d) Pb; this group also includes Mo (Fig. 2). All trace-element concentrations are Al-normalized ($\times 10^{-4}$); n=233 for U, V, and Zn; 71 for Pb. EF is the "enrichment factor" of black shale samples, i.e., relative to the average gray shale sample. Redox-facies assignments are explained in the text.

ment data? Euxinic conditions generally favor higher concentrations of organic carbon, total sulfur (if the system is not Fe-limited), and TEs (Leventhal, 1983; Arthur and Sageman, 1994; Wignall, 1994). Benthic oxygen levels have been assessed frequently on the basis of redox-sensitive TEs, especially multivalence elements in which the reduced species either complexes readily with organic matter or forms an insoluble chemical precipitate, e.g., Mo (e.g., Coveney et al., 1991; Emerson and Huested, 1991; Crusius et al., 1996; Dean et al., 1997, 1999; Adelson et al., 2001), U (e.g., Wignall and Myers, 1988; Wignall and Maynard, 1993), and V (e.g., Lewan, 1984; Lewan and Maynard, 1982; Hatch and Leventhal, 1992; Morford and Emerson, 1999). Some of the samples of the present study are so TE-enriched that euxinic conditions almost certainly existed during their accumulation. However, the challenge is to find a systematic method of evaluating redox facies for all black shale samples of the study units (n = 185).

Our approach to redox-facies analysis is based on TOC-TE relationships. Although black shale samples generally plot along an unbroken continuum in log-log crossplots (e.g., Fig. 2a), a distinct change is apparent at roughly the midpoint of this continuum for TEs of "strong euxinic affinity", i.e., Mo, U, V, Zn, and Pb: (1) a sharp increase in TE enrichment factors, and (2) a decrease in the strength of TOC-TE covariation. These relationships are also apparent in linear-linear crossplots (e.g., Fig. 2b), which manifest two important features more clearly: (1) the sharp rise in TE enrichment factors corresponds to a TOC threshold of ~ 10 wt.%, which we will term the "euxinic threshold", and (2) the strong positive



Fig. 4. Trace elements of "weak euxinic affinity": (a) Cu; (b) Ni; (c) Cr; and (d) Co. All trace-element concentrations are Al-normalized $(\times 10^{-4})$; n=233 for Cu, Ni, Cr, and Mn; 182 for Co. EF is the "enrichment factor" of black shale samples, i.e., relative to the average gray shale sample. Redox-facies assignments are explained in the text.

TOC-TE covariation apparent for low-TOC (<10 wt.%) samples extends into the high-TOC field as a dense linear array of relatively TE-poor samples (Fig. 2b,c). This cluster of samples can be delimited by a $\pm 2\sigma$ variance envelope calculated from the correlation parameters for samples with <10 wt.% TOC (Table 2) and represents what we will refer to as an "anoxic trend". Similar patterns of linear covariation of TOC with TE concentrations in black shales have been encountered in other studies (e.g., Holland, 1984; Robl and Barron, 1987).

These observations are of little utility without a theory to account for them, so we will offer a hypothesis and test it against subsequent results. We propose that the observed TOC-TE relationships are due to changes in the dominant controls on TE accumulation with increasing TOC (Fig. 2c). Under

dysoxic conditions, TEs are deposited mainly in association with the detrital fraction of the sediment, resulting in no covariation with TOC. Under nonsulfidic anoxic conditions, TEs are deposited largely in the form of organometallic complexes with more limited diffusion into the sediment and precipitation as authigenic phases at redox boundaries (Pratt and Davis, 1992). These conditions can result in variable TOC values (often much in excess of 10 wt.%) but favor strong TOC-TE correlations at all TOC concentrations because the uptake of TEs is limited by the availability of suitable organic substrates. Under euxinic conditions, in which free H₂S is present and TEs are reduced to their lowest valence state, insoluble metal sulfides and oxyhydroxides can precipitate in quantity directly from the water column or at the sediment-water interface (Morse and Luther, 1999).



Fig. 5. Mn concentrations by (a) redox facies, and (b) host core shale. Mn exhibits only weakly significant differences between redox facies ($\alpha < 10\%$) but large and highly significant differences between core shales ($\alpha \ll 1\%$). Mn concentrations are Al-normalized ($\times 10^{-4}$); n=233. EF is the "enrichment factor" of black shale samples, i.e., relative to the average gray shale sample. Redox-facies assignments are explained in the text.

These conditions result in strong TE enrichment and weak TOC–TE correlations because TEs reside mainly in authigenic minerals rather than organic carbon. The association of strong TE enrichment with a specific TOC threshold ($\sim 10 \text{ wt.\%}$) exists because generally higher fluxes of organic carbon to the sediment are required in order to deplete bottom waters of all dissolved O₂ and to allow the zone of sulfate reduction to rise into the water column (Canfield, 1994).

How can these observations be applied to the determination of sample redox facies? First, we consider samples falling *within* an "anoxic trend" to represent nonsulfidic anoxic conditions, owing to lack of TE enrichment above that which can be accommo-

dated by the organic fraction of the sediment (Fig. 2c). This assumes that the positive covariation of TE and TOC concentrations manifested by "anoxic trends" is a consequence of organic matter in the black shales being "saturated", or nearly so, with respect to TEs. Second, we consider samples plotting above the "anoxic trend" to represent euxinic conditions, in which strong TE enrichment occurred in response to free H₂S in the water column and was more-or-less independent of TOC accumulation rates (Fig. 2c). Only TEs of "strong euxinic affinity" (i.e., Mo, U, V, Zn, and Pb) exhibit a well-defined "anoxic trend" and a population of strongly TE-enriched samples that plot above it (Figs. 2 and 3); TEs of "weak euxinic affinity" (i.e., Cu, Ni, Cr, and Co) display more ambiguous TOC-TE relationships in the absence of a priori information regarding sample redox facies (Fig. 4). For this reason, redox-facies analysis of black shale samples was based exclusively on TEs of "strong euxinic affinity," specifically, Mo, U, V, and Zn (n.b., Pb was excluded owing to a lack of data for many samples). The procedure we used consisted of (1) determining whether each "redox-indicator" trace element fell within or above its respective "anoxic trend" in a given sample and rating it as indicative of nonsulfidic anoxic or euxinic conditions, respectively; (2) assigning a sample to the euxinic facies if two or more "redox indicators" were rated euxinic or, conversely, to the nonsulfidic anoxic facies if no more than one "redox indicator" was rated euxinic (n.b., this threshold is arbitrary but practical, and the results deriving from it have some interesting implications that are discussed below). Of the 185 black shale samples analyzed in this study, 128 exhibited complete agreement between all four "redox indicators", including 74 assigned to the nonsulfidic anoxic facies and 54 to the euxinic facies. Of the remaining 57 samples yielding conflicting redox signals, 15 were assigned to the nonsulfidic anoxic facies and 42 to the euxinic facies.

How confident are redox-facies assignments for individual samples? Several lines of evidence suggest that the procedure above has meaningfully separated samples into populations representing nonsulfidic anoxic versus euxinic facies. First, a large majority of the samples (69%, or 128 out of 185) exhibit complete agreement among the four "redox indicators" (Mo, U, V, and Zn). Second, and more



Fig. 6. (a) Redox threshold scale for TE enrichment. The "anoxic threshold" (~ 2.5 wt.% TOC) corresponds to limited enrichment of TEs other than Co, the "subanoxic threshold" (~ 7 wt.% TOC) to modest V enrichment, and the "euxinic threshold" (~ 10 wt.% TOC) to strong enrichment of Mo, U, V, Zn, and Pb, and modest increases in other TEs except Cr. Downward arrows indicate loss of (1) Mn in all low-oxygen facies through Mn–Fe redox cycling, (2) Cr in euxinic facies through bacterial remineralization of organic-bound Cr, probably at the sediment– water interface, and lack of subsequent uptake by authigenic sulfides, and (3) U in euxinic facies through postdepositional remobilization under conditions of weakly increasing or fluctuating benthic O₂ levels. Benthic O₂ levels increase to the left and H₂S values to the right of the 0 ml l⁻¹ H₂O baseline; values are approximate. (b) Process model for TE enrichment in core shales of Upper Pennsylvanian Kansas-type cyclothems. See text for discussion.

importantly, the redox-facies assignments based on TEs of "strong euxinic affinity" explain much of the variance in the concentrations of TEs of "weak euxinic affinity" (i.e., Cu, Ni, Cr, and Co; Fig. 4). Each of the latter trace elements exhibits moderate to strong, positive covariation with TOC across the full range of sample TOC values (2–40 wt.%) with only minor enrichment and a small increase in variance for samples with >10 wt.% TOC. None of these TEs displayed two distinct sample populations among the high-TOC samples prior to redox-facies assignment. However, when samples are

coded by redox facies based on the procedure above, it becomes clear that increases in variance at >10 wt.% TOC for TEs of "weak euxinic affinity" are due to diverging trends for sample populations representing the nonsulfidic anoxic and euxinic facies, with the latter typically exhibiting very slight TE enrichment relative to the former (e.g., Fig. 4a). Because this increase in variance could not be explained prior to redox-facies analysis, the procedure developed above has demonstrated "predictive value". This is a strong argument that the redox-facies assignments for the study

Table 2				
Correlation	coefficients	for	elemental	pairs ^a

		Nonsulfidic anoxic facies ^b										
		TOC	Mo	U	V	Zn	Pb	Cu	Ni	Cr	Со	Mn
Euxinic facies ^c	TOC	_	0.61	0.64	0.64	0.73	0.57	0.69	0.92	0.93	0.46	- 0.28
	Mo	0.30	_	0.46	0.68	0.44	0.45	0.63	0.51	0.56	0.03	- 0.13
	U	0.14	0.36	_	0.40	0.67	0.44	0.56	0.76	0.75	0.52	- 0.32
	V	0.47	0.76	0.50	_	0.45	0.72	0.44	0.50	0.56	0.17	-0.14
	Zn	0.25	0.38	0.49	0.58	_	0.61	0.65	0.77	0.78	0.37	- 0.30
	Pb	0.19	0.77	0.46	0.73	0.52	_	0.61	0.43	0.58	-0.09	-0.40
	Cu	0.45	0.52	0.58	0.58	0.58	0.24	_	0.67	0.71	0.18	-0.41
	Ni	0.45	0.50	0.57	0.56	0.59	0.33	0.59	_	0.93	0.63	- 0.32
	Cr	0.40	0.03	0.21	0.15	0.18	0.02	0.58	0.47	-	0.51	-0.40
	Со	0.27	0.24	0.55	0.48	0.45	-0.21	0.29	0.61	0.13	_	- 0.19
	Mn	0.51	0.29	0.29	0.45	0.41	0.41	0.22	0.44	0.08	0.39	_
	TS	0.04	0.33	0.15	0.18	0.14	0.24	0.14	0.05	-0.01	-0.05	-0.06
"Anoxic trend"d	т	_	0.17	0.16	1.80	3.60	0.21	0.25	1.33	3.73	0.04	- 0.30
	b	_	1.41	0.03	3.67	0.33	3.18	5.08	5.56	3.35	1.10	24.4

^a Spearman's r values; calculated from Al-normalized TE concentrations; correlation coefficients in bold are significant at $\alpha < 1\%$ level.

^b Based on total TE concentrations of samples assigned to the nonsulfidic anoxic facies.

^c Based on "sulfidic" fraction TE concentrations of samples assigned to the euxinic facies.

samples are generally correct. The redox-facies analysis failed to separate samples into statistically distinct clusters for only one element, Mn (Fig. 5a; Table 2).

One additional consideration supports the validity of our procedure for redox-facies analysis: a consistent pattern of TE behavior among the 57 samples yielding a mixed redox signal (Table 3). For samples in which only one "redox indicator" was rated euxinic (n 15), this was invariably V (n 7) or Zn (n 8). For samples in which two "redox indicators" were rated euxinic and two anoxic (i.e., the most ambiguous case; n 11), V was most likely to be rated euxinic, Zn and Mo were intermediate, and U was most likely to be rated anoxic. For samples in which all but one "redox indicator" was rated euxinic (n 20), the exception was almost invariably U (n 16). This pattern appears to reflect a gradient of sensitivity to declining benthic O_2 levels and/or rising H_2S levels such that V enrichment commenced first and, as reducing conditions intensified, Mo and Zn and finally U accumulated in higher concentrations. An alternative possibility is that the sequence reflects the sensitivity of TEs to postdepositional remobilization as a consequence of rising or fluctuating O_2 levels; in this case, U was the most easily and V the least easily remobilized. Whatever, the nature of the controls on these TEs, the fact that such a systematic pattern exists tends to validate the redox-facies analysis procedure developed in this study.

5.3. TE concentrations in detrital/organic/sulfidic fractions

The distribution of TEs between the various components of a sample is of interest in understanding the

 Table 3

 Samples yielding mixed redox facies signals (n 57)

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Sample assignment	No. of euxinic redox indicators	Anomalous redox indicators	V	Zn	Mo	U	Total no. of samples
Nonsulfidic anoxic facies	1	Single euxinic TE	7	8	0	0	15
Euxinic facies	2	Two euxinic TEs Two anoxic TEs	10 1	4 7	6 5	2 9	22
	3	Single anoxic TE	0	1	3	16	20

processes responsible for trace-element enrichment. In the study units, the quantities of TEs resident in the detrital, "organic", and "sulfidic" fractions of a sample can be estimated on the basis of the TOC– TE relationships documented above (Figs. 2–5). The detrital TE concentration is determined from "background" values in the gray shale submember, in which TEs exhibit low, relatively uniform, Al-normalized concentrations with no apparent relationship to TOC (Fig. 2a). This pattern is widely accepted as evidence of TE residence primarily in detrital minerals (e.g., Dean et al., 1997, 1999; Adelson et al., 2001). For samples from the black shale submember, the detrital TE concentration is calculated as:

$$X_{\text{detr}} = X / \text{Al}_{\text{back}} * \text{Al} \tag{1}$$

where X_{detr} is the detrital concentration of trace element X (ppm); X/Al_{back} is the average Al-normalized "background" concentration of trace element X in the gray shale facies (×10⁻⁴); and Al is the Al concentration of the sample (wt.%).

The "organic" TE concentration of a sample can be estimated on the basis of the "anoxic trend" for the trace element of interest, i.e., its correlation with TOC for samples with <10 wt.% TOC (Fig. 2c; Table 2). Most TEs in this study exhibit a very strong relationship with TOC in this range of TOC values ($\alpha \ll 1\%$; Table 2), suggesting residence primarily in the organic carbon fraction. The "or-

Table 4

Distribution of redox-sensitive trace elements between sample fraction
--

Nonsulfidic anoxic facies samples Euxinic facies samples "Organic" "Sulfidic" "Sulfidic" Detrital Detrital "Organic" fraction (%) fraction (%) fraction (%) fraction (%) fraction (%) fraction (%) TEs of strong Mo 57 25 18 9 8 83 euxinic affinity U 5 33 79 62 1 20 V 20 48 32 5 18 77 3 79 Zn 21 61 18 18 Pb 8 37 55 3 20 77 9 59 TEs of weak Cu 83 8 8 33 euxinic affinity 8 Ni 37 55 25 53 22 2 Cr 22 76 18 78 4 Co 83 0 17 58 -244

^a By definition, the detrital fraction represents 100% of the TE content of dysoxic facies samples.

ganic" TE concentration of a sample is calculated as:

$$X_{\rm org} = [b_{\rm at} + m_{\rm at} \times \text{TOC}] \times \text{Al} - X_{\rm detr}$$
(2)

where X_{org} and X_{detr} are the "organic" and detrital concentrations of element X (ppm); TOC and Al are the TOC and Al concentrations of the sample (wt.%); and b_{at} and m_{at} are the y-intercept and slope of the "anoxic trend" of element X (Table 2). Once the detrital and "organic" concentrations are determined, the TE concentration in the "sulfidic" fraction of a sample is determined by difference:

$$X_{\text{sulf}} = X_{\text{tot}} - (X_{\text{org}} + X_{\text{detr}}) \tag{3}$$

where X_{sulf} and X_{tot} are the "sulfidic" and total concentrations of element X (ppm). On the basis of the detrital, "organic," and "sulfidic" concentrations of each sample, the proportion of TEs resident in each fraction was then calculated for the study units as a whole (Table 4).

The simplest interpretation of the "organic" and "sulfidic" fractions calculated above is that TE enrichment in the nonsulfidic anoxic facies is primarily due to the greater availability of organic matter as a substrate for TE uptake, and that further TE enrichment in the euxinic facies is primarily due to the presence of free H_2S in the water column or at the sediment–water interface, allowing TE uptake by authigenic sulfides. Because this scenario is unquestionably oversimplified, we denote the "organic" and "sulfidic" fractions parenthetically. In each redox facies, multiple processes can operate simultaneously to produce TE enrichment, and the relative intensities of these processes may vary nonlinearly with changes in bottom water O2 levels (e.g., Pratt and Davis, 1992). For example, decreasing O₂ levels commonly result in greater organic carbon preservation and, hence, greater export of TEs to the sediment in association with the organic flux. At the same time, decreasing O_2 levels also generally cause the $O_2/$ SO_4^2 - redox boundary to rise toward the sedimentwater interface, reducing the depth to which dissolved TEs must diffuse in order to be taken up by Fe-sulfide precipitation and further enrich the sediment in TEs. For this reason, some portion of the TEs assigned to the "organic" fraction may actually be resident in Fesulfides; however, this share is likely to be small in view of the strong correlations between TOC and TEs in nonsulfidic anoxic facies samples (Table 2), which suggests residence of TEs primarily in organic matter. The same general consideration applies to the euxinic facies. Although the presence of free H₂S certainly increases the export flux of TEs to the sediment via authigenic sulfide precipitation (Huerta-Diaz and Morse, 1992), it may also increase the rate of formation of some insoluble oxyhydroxides (e.g., Cr(OH)₃) and affect the quality of organic matter in a manner that influences TE uptake by this fraction (Francois, 1988; Pratt and Davis, 1992). Thus, although we infer that the bulk of the "organic" and "sulfidic" TE fractions are hosted by organic carbon and Fe-sulfides, respectively, it is likely that in each case small but indeterminate amounts are associated with other fractions of the host sample.

The distribution of TEs between the detrital, "organic", and "sulfidic" fractions of anoxic and euxinic samples of the study units exhibits some noteworthy patterns (Table 4). First, as hosts of TEs, the detrital and "organic" fractions are relatively more important in the nonsulfidic anoxic facies, and the "sulfidic" fraction more so in the euxinic facies. Second, the groups of TEs of strong and weak euxinic affinity exhibit distinctly different patterns of TE enrichment. TEs of "strong euxinic affinity" are hosted primarily by the "organic" fraction under nonsulfidic anoxic conditions, but overwhelmingly by the "sulfidic" fraction under euxinic conditions. In contrast, TEs of "weak euxinic affinity" exhibit less control by redox facies: for both nonsulfidic anoxic and euxinic conditions, Ni and Cr are hosted primarily by the "organic" fraction with secondary concentration in the detrital fraction, and Cu and Co are hosted primarily by the detrital fraction with secondary concentration in the "sulfidic" fraction. Some of these relationships are unsurprising considering that sample assignment to the nonsulfidic anoxic facies was based on strong TOC–TE covariation; however, quantifying TE distribution among the various host sample fractions will be useful in the context of discussing controls on TE behavior and may facilitate estimates of TE mass fluxes to the sediment.

5.4. Elemental correlations by redox facies

Insight regarding the behavior of TEs in each redox facies may be gained by examining patterns of covariation with TOC and other TEs. Conceptually, each redox facies should be characterized by a specific set of conditions, and TEs that respond to the same physicochemical properties or substrate-type availability within a given facies should covary the most strongly. Many earlier studies of black shales have reported correlations between TOC and various TEs without regard to redox facies (e.g., Vine and Tourtelot, 1970; Holland, 1984; Robl and Barron, 1987). However, the complex relations between TOC and TEs apparent in this study (Figs. 2-5) suggest that multiple controls influence TE accumulation, and that the relative importance of these controls vary from one redox facies to the next. We investigated the nature of these controls in the study units through calculation of pairwise correlation coefficients for TOC and each TE (Table 2). Further, we performed this calculation independently for each redox facies in order to isolate facies-specific controls. For euxinic facies samples, we first subtracted the "organic" and detrital fractions from total TE concentrations in order to avoid any spurious correlations with TOC (i.e., unrelated to conditions in the euxinic facies); thus, these correlation coefficients reflect elemental relationships among TEs hosted in the "sulfidic" fraction of the euxinic facies.

The results of this correlation analysis provide insights into controls on TE behavior in the study units. For anoxic facies samples, several observations are relevant. First, correlations for most trace-element pairs are statistically significant at $\alpha < 1\%$; the only nonsignificant correlations involve Co and Mn (Table 2). Second, all TEs except Mn exhibit strong positive covariation with TOC, with most *r* values >0.60. Third, correlations among almost all TE pairs (except those involving Co and Mn) have *r* values >0.40; thus, all TEs are responding to similar controls although perhaps indirectly, through an association with organic carbon. Fourth, U, Zn, Pb, Cu, Ni, and Cr form a group in which almost all *r* values exceed 0.60, suggesting a somewhat stronger relationship among these TEs than with Mo and V. Finally, Mo and V exhibit moderately strong covariation between themselves (*r* 0.68).

Elemental relationships in the "sulfidic" fraction of the euxinic facies differ considerably from those identified in the anoxic facies (Table 2). First, a smaller percentage (but >50%) of the pairwise correlations are statistically significant at $\alpha < 1\%$. Second, correlations of TEs with TOC are much weaker (r < 0.50, except for Mn). Second, correlations of TEs with total sulfur (TS) are weak (r < 0.35) and, with the exception of Mo, statistically insignificant. Third, the strongest correlations among TE pairs involve Mo, V, and Pb, with r values >0.70. Fourth, Cu, Ni, Zn, and U form a group with r values >0.55(except the U-Zn pair), and some of these TEs exhibit correlations of similar r values with trace elements of the Mo-V-Pb group. Fifth, Cr exhibits a modest correlation to Cu and Ni (r>0.45), and Co a modest correlation to Ni, U, V, and Zn (r>0.45), but these two trace elements do not "fit" neatly into the groups identified above. Rather, Cr, Co, and Mn generally exhibit weak relationships to other TEs in euxinic facies samples, suggesting independent controls on their behavior, whereas the Mo-V-Pb and Cu-Ni-Zn-U groups exhibit strong internal covariation that can be interpreted in terms of known processes of trace-element enrichment in low-oxygen environments.

6. Discussion

6.1. Redox controls on TE behavior

The behavior of redox-sensitive trace elements (TEs) has been extensively investigated in modern

marine environments under a wide range of benthic oxygen levels. In this section, we will review some of this work and discuss it implications for TE enrichment patterns in the study units.

6.1.1. Molybdenum

Mo is present in seawater as Mo(VI), primarily as molybdate (MoO_4^2), at relatively high abundance $(\sim 10 \text{ ppb})$ for a trace metal. Mo may become concentrated in organic-rich sediments through a series of reactions. Transfer of MoO_4^2 to the sediment-water interface may be promoted through adsorption onto humic substances (Brumsack, 1989; Helz et al., 1996) or particulate Mn-Fe-oxyhydroxides, in the latter case being associated with redox cycling of Mn and Fe (Magyar et al., 1993; Adelson et al., 2001). In anoxic sediment porewaters, MoO_4^2 may be released from organic matter through decay by sulfate-reducing bacteria and reduced to Mo(V) (e.g., MoO_2^+) or Mo(IV) species (e.g., thiomolybdate, $MoO_xS_{4-x}^{2-}$; Calvert and Pedersen, 1993; Zheng et al., 2000). The latter species may be deposited as organic thiomolybdates or, after further reduction to MoS_4^2 , in solid solution with Fe-sulfides (Huerta-Diaz and Morse, 1992; Helz et al., 1996; Morse and Luther, 1999; Adelson et al., 2001). Under noneuxinic conditions, slow downward diffusion of Mo along a concentration gradient limits its uptake by authigenic sulfides forming below the sediment-water interface, but under euxinic conditions, more rapid uptake by authigenic sulfides forming from free H₂S in the water column may be possible (Huerta-Diaz and Morse, 1992; Morse and Luther, 1999; Adelson et al., 2001). Accumulation of Mo under euxinic conditions may depend less on reduction of Mo(VI) to Mo (IV) than on conversion of Mo to a particle-reactive element at elevated HS⁻ activities ($a_{\rm HS} \rightarrow \sim 10^{-4}$; Helz et al., 1996).

In the study units, samples of the nonsulfidic anoxic facies contain Mo in small (relative to the detrital fraction) and subequal amounts in the "organic" and "sulfidic" fractions (Fig. 2b; Table 4), suggesting limited Mo uptake by both organic carbon and Fe-sulfides (Fig. 6b). In euxinic facies samples, Mo resides predominantly in the "sulfidic" fraction (Table 4) and exhibits a strong relationship with V and Pb (Table 2); both Mo and Pb (but not V) were probably taken up strongly in solid solution by Fe-sulfides. Mo enrichment appears to require lower benthic O_2 levels or higher H₂S levels than V enrichment (Table 3; Fig. 6a), possibly because precipitation of V-oxyhydroxides commences in the semireduced state (e.g., V(IV)) or because free H₂S is required for complete reduction of thiomolybdates to MOS_4^2 prior to uptake by authigenic Fe-sulfides. The fact that Mo is the only TE to exhibit a significant correlation with total sulfur in the "sulfidic" fraction of the euxinic facies (Table 2) may support the hypothesis that it was taken up directly from solution by authigenic pyrite forming in the water column or at the sediment–water interface (Fig. 6b).

6.1.2. Uranium

Under oxic-suboxic conditions, U is present mainly as soluble U(VI) in the form of uranyl carbonate complexes $(UO_2(CO_3)_3^4)$, which are chemically unreactive (Langmuir, 1978; Klinkhammer and Palmer, 1991; Calvert and Pedersen, 1993). U enrichment is limited in oxic environments: modern continental margin sediments typically contain only 1-10 ppm. Under anoxic conditions, U is reduced to U(IV), forming the highly soluble uranyl ion UO²⁺ or less soluble uranous fluoride complexes. In the reduced state, removal of U to the sediment may be accelerated by: (1) formation of organic-metal ligands in humic acids, and (2) diffusion across the sediment-water interface and precipitation as crystalline uraninite (UO_2) or a metastable precursor to it (Klinkhammer and Palmer, 1991; Zheng et al., 2002). The latter process may be promoted by the presence of HS⁻ and, hence, can be accelerated by active sulfate reduction (Langmuir, 1978; Klinkhammer and Palmer, 1991), although more recent work suggests that U(VI) reduction occurs at the Fe(II)-Fe(III) redox boundary and, hence, may be controlled by Fe redox reactions (Zheng et al., 2002). Reduction of U(VI) does not seem to occur in the water column under any conditions; indeed, it has not been observed in any modern euxinic environments (Anderson et al., 1989). This suggests that the reduction process is not a simple inorganic reaction. Rather, U(VI) reduction may require particle surfaces for catalysis or specific enzymes produced by iron and sulfate-reducing bacteria in the sediment (Barnes and Cochran, 1990; Zheng et al., 2002). U is not influenced by Mn and Fe redox cycling in the water column.

In the study units, little U is present in the detrital fraction (Table 4), resulting in large enrichment factors in the black shale relative to background levels in the gray shale (Table 1). In the nonsulfidic anoxic facies, U is present mostly in the "organic" fraction (Table 4) and exhibits a strong correlation with TOC (Fig. 3a; Table 2); it is almost certainly complexed with organic carbon (Fig. 6b). In the euxinic facies, U is present mostly in the "sulfidic" fraction (Table 4) and exhibits an association with Cu, Ni, and Zn (Table 2). However, unlike these latter TEs, U is not taken up in any appreciable quantity by authigenic sulfides. The most likely explanation for its behavior under euxinic conditions is that it was precipitated as a nonsulfide authigenic phase $(UO_2?)$ in close association with microenvironments of active sulfate reduction and authigenic pyrite formation within the sediment (Fig. 6b). This is consistent with the suggestion that U precipitation is catalyzed by reactions at sediment redox boundaries (Langmuir, 1978; Klinkhammer and Palmer, 1991; Zheng et al., 2002). The fact that U exhibits a moderately strong correlation with Cu, Ni, and Zn in the "sulfidic" fraction of the euxinic facies and that it can have precipitated only in the sediment may indicate that most Cu-Ni-Zn enrichment in the euxinic facies also took place in the sediment rather than in the water column (see also discussion of Cu). In contrast, the relatively weak correlation of Mo with the Cu-Ni-Zn-U group in the euxinic facies (Table 2) may be consistent with the inference that Mo was taken up by syngenetic Fe-sulfides (i.e., formed in the water column).

Were there factors other than benthic anoxia that influenced authigenic U concentrations in the study units? Wignall (1994) identified two additional controls on U: (1) availability of host mineral or organic substrates, and (2) sedimentation rates. It has been suggested that humic-rich organic matter in more acidic, nearshore waters is particularly prone to uptake of certain TEs, including U and Mo (Coveney et al., 1991; Wignall and Maynard, 1993). We note that *all* TEs increase proximally in the present study units (Algeo and Maynard, 1997; Hoffman et al., 1998), favoring control dominantly by redox conditions rather than organic matter type. This issue may be resolvable by extraction and analysis of various organic fractions (i.e., terrestrial versus marine) in these shales, but such work has not been carried out to date. The other proposed control, sedimentation rates, is influential because U accumulation in anoxic/euxinic systems occurs only within the sediment and not in the water column (Anderson et al., 1989; Zheng et al., 2002); hence, slower sedimentation rates allow more time for diffusion of uranyl ions into the sediment and for precipitation of uraninite (UO_2) or a metastable precursor to it. This relationship may make authigenic U a useful proxy for sedimentation rate changes. In the study units, U concentrations exhibit moderate positive covariation with total P, a proxy for authigenic phosphate (Hoffman et al., 1998, their Fig. 7); this may be consistent with a sedimentation rate control in that growth of phosphate nodules also is favored by slow sedimentation rates.

6.1.3. Vanadium

In oxic environments, V exists as V(V) in vanadate ionic species such as HVO_4^2 and $H_2VO_4^-$ (Sadiq, 1988; Wehrli and Stumm, 1989). Under mildly reducing conditions, V(V) converts to V(IV) and forms the vanadyl ion (VO²⁺), related hydroxyl species (e.g., $VO(OH)_3^{-}$), or an insoluble hydroxide (e.g., VO(OH)₂; Van der Sloot et al., 1985). Reduction to vanadate to vanadyl is facilitated by the presence of humic and fulvic acids (Wilson and Weber, 1979; Templeton and Chasteen, 1980). The V(IV) ionic species may be removed to the sediment by surface adsorption processes or by formation of organometallic ligands (Emerson and Huested, 1991; Morford and Emerson, 1999). Under more strongly reducing conditions, the presence of free H₂S causes V to be further reduced to V(III), which may be taken up by geoporphyrins or be precipitated as a solid oxide (V_2O_3) or hydroxide $(V(OH)_3)$ phase (Breit and Wanty, 1991; Wanty and Goldhaber, 1992). The two-step reduction process exhibited by V may result in formation of separate V-bearing phases with differential solubilities under nonsulfidic anoxic versus euxinic conditions (Breit and Wanty, 1991; Calvert and Pedersen, 1993).

In the study units, samples from the nonsulfidic anoxic facies contain V in the "organic" fraction and, in lesser amounts, the "sulfidic" fraction (Table 4). V exhibits a strong correlation with TOC (Fig. 3b), which is consistent with V being resident mainly in organic matter (Fig. 6b). In the euxinic facies, V resides predominantly in the "sulfidic" fraction (Table 4) and exhibits a strong relationship with Mo and Pb (Table 2). Unlike Mo and Pb, however, V probably was not taken up in solid solution by Fe-sulfides. The reason for the strong association of these elements is uncertain, but possibly the burial flux of V increased under euxinic conditions, when free H₂S in the water caused reduction of V(IV) to V(III) and its subsequent rainout as an insoluble oxyhydroxide (Fig. 6b); higher benthic H₂S levels also would be expected to result in an increased rainout of Mo- and Pb-bearing pyrite framboids.

Several features of its distribution set V apart from other TEs of "strong euxinic affinity": (1) V exhibits stepwise increases at $\sim 7 \text{ wt.}\%$ and $\sim 10 \text{ wt.}\%$ TOC (Fig. 3b; versus a single threshold at ~ 10 wt.% TOC for Mo, U, Zn, and Pb; Figs. 2b and 3a,c-d; (2) a large number of samples assigned to the nonsulfidic anoxic facies plot above the "anoxic trend" for V (Fig. 3b); and (3) V enrichment precedes that of Mo, U, and Zn in samples yielding mixed "redox indicators" and, for many samples assigned to the nonsulfidic anoxic facies, V is the only "redox indicator" rated as euxinic (Table 3; n.b., these observations have interrelated causes). Given the small number of samples responsible for these anomalies (<20), a stochastic effect might be inferred. However, it is also possible that V enrichment began under somewhat less reducing conditions than required for Mo-U-Zn-Pb enrichment, i.e., at a "subanoxic threshold" corresponding to ~7 wt.% TOC (Fig. 6a). This could be accounted for by the two-step reduction of V, e.g., formation of sparingly soluble V(IV) compounds under mildly reducing conditions, and formation of insoluble V(III) compounds under more strongly reducing conditions (Fig. 6b; cf. Calvert and Pedersen, 1993). One additional observation supports this inference: stratigraphically, the majority of samples with V-only enrichment are located at the tops of thick high-TOC intervals within black shale submembers of the study units, above the point at which Mo-U-Zn-Pb enrichment has fallen below euxinic levels; this is consistent with a gradual increase in benthic oxygen levels upsection (Algeo et al., 2004). We conclude that V concentrations, when evaluated in combination with other reliable redox indicators (as in this study), have the potential to provide information about more subtle changes in

benthic oxygen levels within ancient black shales than heretofore recognized (Fig. 6a).

6.1.4. Zinc

In oxic environments, Zn may exist as Zn^{2+} or ZnCl⁺ (Calvert and Pedersen, 1993), although most Zn probably complexes with humic and fulvic acids (Achterberg et al., 1997). In anoxic waters, dissolved Zn is rapidly precipitated as ZnS, in solid solution in pyrite or sometimes as an independent authigenic sphalerite phase (Brumsack, 1980; Morse and Luther, 1999). However, the degree-of-trace-metal-pyritization (DTMP) of Zn typically is low in submodern sediments (Huerta-Diaz and Morse, 1992), implying slow reaction kinetics and residence primarily in nonsulfide mineral or organic phases. Decay of organic matter by sulfate-reducing bacteria may liberate Zn from organic-metal complexes within the zone of sulfate reduction, facilitating subsequent uptake of Zn by authigenic Fe-sulfides formed in the burial environment.

In the study units, Zn resides mainly in the "organic" fraction of the nonsulfidic anoxic facies and mainly in the "sulfidic" fraction of the euxinic facies (Table 4). Zn exhibits a very strong association with TOC in the nonsulfidic anoxic facies, and a moderately strong association with Cu, Ni, and U in the euxinic facies (Fig. 3c; Table 2). In terms of its "sensitivity" to redox changes, Zn is intermediate between V and U (Table 3). The simplest interpretation of these observations is that Zn is predominantly bound in organic complexes in samples from the nonsulfidic anoxic facies and is present in solid solution with Fe-sulfides in euxinic facies samples (Fig. 6b). As noted above, the fact that Zn covaries with U in the "sulfidic" fraction of the euxinic facies, and that U enrichment must have taken place in the sediment rather than in the water column, strongly suggests that Zn enrichment also took place in the sediment. This would be consistent with Zn release through remineralization of organic matter by sulfatereducing bacteria and transfer of Zn to an Fe-sulfide phase under euxinic conditions.

6.1.5. Lead

In oxic environments, Pb may exist as a cation (Pb^+) at low pH or as a soluble Pb-carbonate compound $(PbCO_3)$ at high pH (Drever, 1997). In anoxic

waters, it is removed rapidly as insoluble PbS, commonly as an independent sulfide phase rather than in solid solution in pyrite (Morse and Luther, 1999).

In the study units, Pb resides predominantly in the "sulfidic" fractions of both the nonsulfidic anoxic and euxinic facies, with a relative increase in the latter (Table 4). In the nonsulfidic anoxic facies, the correlation of Pb to TOC is moderate (r 0.57) but weaker than that of most other TEs (Fig. 3d; Table 2), consistent with a greater proportion being resident in a nonorganic phase (e.g., Fe-sulfides). In the euxinic facies, Pb exhibits a strong relationship with Mo and V (Table 2), possibly because Mo and Pb were taken up in solid solution by authigenic pyrite formed in the water column, and V was co-precipitated as an insoluble oxyhydroxide (Fig. 6b; see discussion of Mo and V).

6.1.6. Copper

In oxic environments, Cu is present mainly in organic-metal ligands and, to a lesser degree, in solution as CuCl⁺ (Calvert and Pedersen, 1993; Achterberg et al., 1997). Removal of Cu to the sediment may be accelerated by: (1) formation of organic-metal ligands in humic acids, and (2) adsorption onto particulate Fe-Mn-oxyhydroxides and settling to the sediment-water interface. Release of Cu through remineralization of organic matter by sulfate-reducing bacteria or reductive dissolution of Fe-Mn-oxyhydroxides may liberate Cu within the sediment or at the sediment-water interface. Under anoxic conditions, it may be reduced from Cu(II) to Cu(I) with subsequent precipitation as an independent sulfide phase (CuS or Cu₂S) or uptake by Fe-sulfides in solid solution (Huerta-Diaz and Morse, 1992; Achterberg et al., 1997; Morse and Luther, 1999).

In the study units, Cu is mainly of detrital origin with small and subequal amounts in the "organic" and "sulfidic" fractions of nonsulfidic anoxic facies samples, and larger relative amounts in the "sulfidic" fraction of euxinic facies samples (Fig. 4a; Table 4). Cu exhibits a strong association with TOC in the nonsulfidic anoxic facies and a moderately strong association with Ni, Zn, and U in the euxinic facies (Table 2). Cu was presumably transported to the sediment–water interface in organic complexes and, possibly, adsorbed to Fe–Mn-oxyhydroxides (Fig. 6b). Its relative enrichment in the "sulfidic" fraction of the euxinic facies may be due to the release and reduction of Cu at or below the sediment-water interface and its subsequent uptake in solid solution by authigenic pyrite. As noted above, the fact that Cu covaries with U in the "sulfidic" fraction of the euxinic facies, and that U enrichment must have taken place in the sediment rather than in the water column, suggests that Cu enrichment also took place in the sediment.

6.1.7. Nickel

In oxic environments, Ni may exist as Ni^{2+} or $NiCl^+$ ions (Calvert and Pedersen, 1993), although most Ni is present in solution as a Ni-carbonate complex (NiCO₃) or adsorbed on humic and fulvic acids (Achterberg et al., 1997). Removal of Ni to the sediment may be accelerated by complexing and sedimentation with organic matter, and remineralization of the latter at or below the sediment–water interface may liberate Ni to sediment porewaters. Under anoxic conditions, Ni forms an insoluble sulfide (NiS) that can be taken up in solid solution by authigenic pyrite (Huerta-Diaz and Morse, 1992). However, Ni uptake is kinetically slow, tending to limit its concentration in authigenic sulfides (Morse and Luther, 1999).

In the study units, Ni resides mainly in the "organic" fraction and secondarily in the detrital fraction of both the nonsulfidic anoxic and euxinic facies (Fig. 4b; Table 4); however, euxinic facies samples exhibit a sharp increase in the relative proportion resident in the "sulfidic" fraction. Ni covaries strongly with TOC in nonsulfidic anoxic facies samples and with Cu, Zn, and U in the "sulfidic" fraction of euxinic facies samples (Table 2). Controls on its behavior were probably similar to those of Cu: transport to the sediment-water interface in organic complexes, release through remineralization of organic matter, and subsequent uptake in solid solution by authigenic pyrite (Fig. 6b). The strong association of Ni with TOC may support the hypothesis of Lewan and Maynard (1982) that Ni is taken up mainly by tetrapyrrole complexes, preservation of significant quantities of which occurs only in anoxic/euxinic facies. As noted, the fact that Ni covaries with U in the "sulfidic" fraction of the euxinic facies, and that U enrichment must have taken place in the sediment

rather than in the water column, suggests that Ni enrichment also took place in the sediment.

6.1.8. Chromium

In oxic environments, Cr is present mainly as Cr(VI) in the chromate anion (CrO_4^2) and to a lesser extent (~ 5%) as Cr(III) in aquahydroxyl cations, e.g., $Cr(H_2O)_4(OH)_2^+$ (Cranston and Murray, 1978; Calvert and Pedersen, 1993). The chromate anion is not strongly absorbed at pH>7 and, hence, remains mobile in seawater (Drever, 1997). Under anoxic conditions, Cr(VI) is reduced to Cr(III), forming aquahydroxyl or hydroxyl cations (e.g., $Cr(OH)_2^+$) that can be precipitated as insoluble Cr(OH)₃ or Cr₂O₃ at high pH (Elderfield, 1970; Emerson et al., 1979; Drever, 1997). At low pH, $Cr(OH)_2^+$ is thought to readily complex with humic and fulvic acids and to be adsorbed by Fe- and Mn-oxyhydroxides, which may provide transport vectors for increased Cr export to the sediment under anoxic conditions (Achterberg et al., 1997). In modern marine environments, Cr is commonly associated with organic matter, although most Cr uptake occurs in the sediment rather than in the water column (Francois, 1988). Cr(III) uptake by authigenic Fe-sulfides is very limited owing to structural and electronic incompatibilities with pyrite crystals (Huerta-Diaz and Morse, 1992; Morse and Luther, 1999).

In the study units, Cr resides primarily in the "organic" fraction and secondarily in the detrital fraction of both the nonsulfidic anoxic and euxinic facies (Fig. 4c; Table 4). Cr exhibits strong covariation with TOC in the nonsulfidic anoxic facies and no systematic association with other TEs in the euxinic facies (Table 2). Little Cr is associated with the "sulfidic" fraction of either facies (Table 4), and for the TOC range in which samples of the nonsulfidic anoxic and euxinic facies overlap ($\sim 10-20$ wt.%) Cr is perceptibly depleted in samples of the latter facies relative to the former (Fig. 4c). We infer that (1) Cr is hosted mainly by organic and detrital phases, possibly with some accumulation as an independent Cr-oxyhydroxide phase; and (2) the small loss of Cr in samples of the euxinic facies relative to those of the nonsulfidic anoxic facies (at equivalent TOC values) is due to Cr release upon remineralization of organic matter by sulfate-reducing bacteria, with little or no subsequent uptake of dissolved Cr by authigenic sulfides (Fig. 6b; cf. Morse and Luther, 1999). This may account for the absence of covariation between Cr and TEs that go into solid solution in pyrite (e.g., Mo, Pb, Cu, Ni, Zn), and it is consistent with the fact that Cr is not known to form an insoluble sulfide. Cr released in this manner probably was lost to the overlying water column by diffusion or advection associated with sediment compaction.

6.1.9. Cobalt

In oxic environments, Co is present as a dissolved cation (Co^{2+}) or complexed with humic and fulvic acids (Achterberg et al., 1997). In anoxic waters, Co forms an insoluble sulfide (CoS) that can be taken up in solid solution by authigenic Fe-sulfides (Huerta-Diaz and Morse, 1992). However, Co uptake is kinetically slow, tending to limit its concentration in authigenic sulfides (Morse and Luther, 1999). The degree to which Co is influenced by Fe–Mn redox cycling is uncertain.

In the study units, Co resides primarily in the detrital fraction with secondary concentration in the "sulfidic" fraction of both the nonsulfidic anoxic and euxinic facies; no Co appears to reside in the "organic" fraction of either facies (Fig. 4d; Table 4). Co exhibits a modest correlation with TOC, U, Ni, and Cr in the nonsulfidic anoxic facies and with U, V, Zn, and Ni in the euxinic facies (Table 2), which is broadly consistent with residence of non-detrital Co in authigenic sulfides (Fig. 6b).

6.1.10. Manganese

In oxic environments, Mn forms highly insoluble Mn(III) or Mn(IV) hydroxides or oxides (e.g., MnO₂) that are rapidly deposited in particulate form (Sholkovitz et al., 1992; Calvert and Pedersen, 1993). Under anoxic conditions, Mn is reduced to Mn(II) and forms soluble Mn²⁺ or MnCl⁺ cations. Because dissolved Mn is not readily taken up by any organic or mineral phase (although trace quantities may be present in pyrite; Huerta-Diaz and Morse, 1992), it diffuses upward out of the sediment or from the sedimentwater interface into the water column in anoxic systems. Owing to kinetic sluggishness, Mn(II) is slow to precipitate under oxic conditions, and Mnoxyhydroxides are slow to remineralize under anoxic conditions. Consequently, Mn is intensely recycled through anoxic water columns, with rainout of particulate Mn-oxyhydroxides from the pycnocline to the sediment-water interface and upward advection of aqueous Mn(II) following remineralization (Fig. 6b; n.b., Fe engages in this cycling process as well).

Mn-Fe redox cycling is important for TE enrichment in anoxic systems because it can accelerate export of TEs from seawater to the sediment-water interface. TEs subject to uptake by particulate Mn-Fe-oxyhydroxides include cations of chalcophilic elements (Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺, and Co²⁺) and ionic species of certain oxides and hydroxides (e.g., MoO_4^{2-} , $Cr(OH)_2^+$, and possibly VO^{2+} ; Fig. 6b). The tendency for various TEs to adsorb onto Mn-Fe-oxyhydroxides varies as a function of pH although all adsorb strongly at pH>6 (Dzombak and Morel, 1990), i.e., conditions characteristic of oxic seawater (pH 8.2) as well as slightly reducing porewaters in organic-rich facies (pH>6.8; Van Cappellen and Wang, 1996). TEs that are exported to the sediment in this manner are released upon reductive dissolution of Mn-Fe-oxyhydroxides at the sediment-water interface and are then available to participate in other reactions, e.g., uptake in solid solution by authigenic sulfides or precipitation of insoluble metal oxyhydroxides (Fig. 6b). These reactions proceed most vigorously in the presence of free H₂S (i.e., in euxinic facies), resulting in substantial enrichment of authigenic pyrite framboids in certain TEs (e.g., Davison et al., 1992). Mn is exported only slowly from anoxic systems, mostly through incorporation in Mn(II)-bearing carbonates deposited at the intersection of the pycnocline and the seafloor, producing a "bathtub ring" in basins with stable pycnoclines (e.g., Okita and Shanks, 1992) or interstratified black shale and Mn-carbonate layers in basins with fluctuating pycnoclines (e.g., Jenkyns et al., 1991).

Mn concentration patterns in the study units are different from those of all other TEs. First, Mn exhibits no systematic relationship to redox facies (Fig. 5a), a marginally significant negative correlation with TOC in the nonsulfidic anoxic facies, and an anomalous positive correlation with TOC in the euxinic facies (Table 2). Second, the largest variance in Mn concentrations is between core shales, with the Stark Shale yielding the lowest and the Muncie Creek Shale the highest concentrations regardless of redox facies (Fig. 5b). This is consistent with an earlier analysis of degree-of-anoxia indicators in the study units that showed the Stark Shale to have been deposited under the most intensely anoxic and the Muncie Creek Shale under the least intensely anoxic conditions (Hoffman et al., 1998). The differences between core shales also account for the anomalous positive correlation of Mn with TOC in the euxinic facies: it is a spurious product of euxinic facies samples of the Stark Shale having lower TOC values $(\sim 10-25 \text{ wt.}\%)$ than many nonsulfidic anoxic facies samples of the Muncie Creek and Hushpuckney shales (~ 25-40 wt.%). Third, all samples in this study-from both the gray and black shale submembers-exhibit low Mn concentrations relative to average crustal values ($\sim 15-30 \times 10^{-4}$ versus ~ 96×10^{-4} ; Taylor, 1964) with the exception of two samples from gray-shale carbonate nodules $(320-430 \times 10^{-4})$ that represent more-or-less fully oxic benthic conditions. In summary, we conclude that (1) Mn was lost from virtually all samples in the study units, probably as a consequence of reductive dissolution of Mn–Fe-oxyhydroxides on the floor of the Midcontinent Seaway; (2) Mn loss commenced under weakly dysoxic conditions and intensified only marginally, if at all, with onset of anoxic conditions (Fig. 6a,b); and (3) the response of Mn to redox conditions in the study units was temporally "integrative", i.e., Mn exhibits little bed-scale variation in response to small-scale redox fluctuations in a single core shale, but it shows substantial variation in average concentrations from one core shale to the next, reflecting differences in the long-term mean redox conditions of these formations (Fig. 5b).

6.2. General controls on TE accumulation

Removal of dissolved TEs to the sediment can be effectuated by either biogenic or nonbiogenic processes. Biogenic processes involve uptake of TEs that serve as minor bionutrients by plankton. TEs that exhibit concentration patterns in the modern open ocean indicative of biogenic uptake include Zn, Cu, and Ni, all of which are depleted in surface waters by a factor of five or more relative to deep waters (Bruland, 1980; Brumsack, 1986; Piper, 1994). The potential significance of this process is that it may accelerate export of TEs to deep waters under conditions of elevated primary productivity. Many other TEs, including Mo, U, V, and Cr, are conservative in oxic seawater and show no evidence of a bionutrient role in modern marine systems (Calvert and Pedersen, 1993; Morford and Emerson, 1999). A few TEs, including Co and Pb, exhibit depleted concentrations in deep waters relative to surface waters owing to high rates of particle scavenging (Brumsack, 1986).

Although intensified primary productivity has been inferred for some TE-enriched black shales on the basis of C-P systematics (e.g., Murphy et al., 2000), the high rates of sedimentation typical of upwelling zones with suboxic bottom waters are not generally conducive to TE enrichment (e.g., Brumsack, 1986). Rather, such enrichment more likely is favored by a combination of slow sedimentation rates and intense anoxia (Lewan and Maynard, 1982; Brumsack, 1986). We consider the latter factors to have been more important in the present study units, which are unlikely to have been associated with elevated primary productivity owing to (1) very slow sedimentation rates (~ 1 cm 10^3 y⁻¹; Watney et al., 1989), and (2) the terrigenous origin of much of the organic matter (Algeo and Maynard, 1997; Hoffman et al., 1998; Algeo et al., 2004; cf. Wenger and Baker, 1986).

Nonbiogenic processes operative under reducing conditions include adsorption of ionic species onto organic or lithogenic substrates, formation of organometallic ligands, uptake of TEs in solid solution by Fe-sulfides, and precipitation of TE-bearing authigenic sulfides or oxyhydroxides; these processes were discussed in some detail in the preceding section. In oxic/suboxic environments, accumulation of TEs is more limited, but some enrichment may occur through diffusion of dissolved TEs from the water column into the sediment. This is commonly manifested in modern marine systems as downhole concentration gradients maintained by fixation of TEs at subsurface redox boundaries (e.g., Brumsack, 1986; Emerson and Huested, 1991; Calvert and Pedersen, 1993; Crusius et al., 1996). Such diffusive uptake of TEs appears not to have been important in the study units, as dysoxic facies samples exhibit no measurable enrichment relative to average shale values (Taylor, 1964; Wedepohl, 1971) and no relationship to TOC concentrations (e.g., Fig. 2a).

A final consideration is whether TE distributions in the study units have been set or altered by diagenetic processes. Some earlier studies inferred a large role for basinal brines in concentrating trace metals in the core shales of Pennsylvanian cyclothems (e.g., Coveney and Glascock, 1989). However, the results of this study demonstrate patterns of TE enrichment that are clearly consistent with trace metals being mainly or exclusively of depositional-and then largely of hydrogenous-origin (cf. Piper, 1994). Further, the study units display no evidence of geochemical alteration of the type associated with meteorically influenced core shales of Middle Pennsylvanian age (Hatch and Leventhal, 1997). Whether a limited diagenetic redistribution of certain TEs has occurred in the study units is open to further investigation. Remobilization of TEs as a consequence of rising benthic O₂ levels is common in modern marine environments (e.g., Thomson et al., 1995, 1998), but there is little evidence for translocation of TEs under continuously anoxic conditions, such as those prevailing during deposition of the black shale submembers of the study units. Remobilization of certain trace elements in the burial environment is possible (e.g., Breit and Wanty, 1991), but any such redistribution of TEs in the study units must have occurred at a relatively fine scale (probably < 1 cm). We base this inference on the preservation of (1) highly significant and easily interpretable relationships among TEs and TOC (Figs. 2-4; Table 2), and (2) substantial sampleto-sample (i.e., cm-scale) variation in TE concentrations in the stratigraphic dimension (Algeo et al., 2004).

6.3. Evaluating small-scale redox changes in lowoxygen environments

Do redox-sensitive trace elements (TEs) show differences in behavior that might allow for a more sensitive assessment of paleoredox conditions than achieved using a simple binary classification scheme (i.e., nonsulfidic anoxic versus euxinic conditions)? Potentially useful in this regard is any systematic pattern of differential TE enrichment in a series or suite of samples. Differential enrichment might reflect an "accumulation control", e.g., sequential crossing of redox thresholds favoring accumulation of different TEs as benthic O_2 levels decreased or H_2S levels increased, or a "remobilization control", e.g., variable rates of remobilization and loss of TEs as a consequence of a postdepositional rise in benthic O_2 levels. Both controls have been documented in modern marine environments, and such heuristic observations may prove useful in assessing controls on TE behavior in the study units.

Sequential enrichment of TEs occurs as the available oxidants in the sediment are consumed and specific redox thresholds are crossed (Pailler et al., 2002). For example, reduction of V occurs in two steps under a wide range of Eh-pH states, with reduction to V(IV) generally commencing under nonsulfidic anoxic conditions, and reduction to V(III) favored in the presence of dissolved H₂S (Breit and Wanty, 1991; Wanty and Goldhaber, 1992). Mo accumulation also increases sharply in the zone of sulfate reduction (Crusius et al., 1996; Zheng et al., 2000; Crusius and Thomson, 2000). On the other hand, precipitation of authigenic U commences somewhat earlier in the redox series, at the potential of Fe(III) reduction (Klinkhammer and Palmer, 1991; Chaillou et al., 2002; Zheng et al., 2002). However, the limited thicknesses of the zones of Fe(III), Mn(IV), and NO_3^- reduction may make recognition of sequential TE enrichment difficult in ancient marine sediments.

Sequential loss of TEs occurs when sediments at or just below the sediment-water interface are exposed to increased benthic O_2 levels. U in particular appears to be prone to remobilization: exposure to even low O2 concentrations for brief periods causes a marked increase in the rate of U regeneration and loss to the overlying water column (Anderson et al., 1989; Colley et al., 1989; Thomson et al., 1995). In controlled studies, 15 μ mol O₂ (0.48 ml l⁻¹ H₂O) was sufficient to cause release of 1/3 to 2/3 of authigenic U in sediments, whereas no measurable quantity of U was released at $<3 \ \mu mol O_2$ ($<0.10 \ ml \ l^{-1} H_2O$; Zheng et al., 2002). Release of U in oxidizing porewaters may be a consequence of its residence primarily in highly soluble uraninite crystals, rather than in more refractory Fe-sulfides (Klinkhammer and Palmer, 1991; Zheng et al., 2002). In contrast, other TEs are remobilized only slowly, particularly those resident in Fe-sulfides, which are kinetically slow to dissolve at low O_2 concentrations (Yu et al., 2001).

Fluctuations in benthic O₂ levels are common in low-oxygen facies of modern marine environments. Transient increases occur in association with turbidity currents and longer term increases may result from climatic forcing of deep-ocean ventilation (Thomson et al., 1995; Pailler et al., 2002). Studies of turbidites from modern abyssal settings have documented downward migrating oxidation fronts characterized by sharp concentration peaks for a variety of TEs just below the oxic/"post-oxic" boundary (Thomson et al., 1998). Whether the duration of benthic oxygenation events affects TE remobilization patterns is open to question, but the possibility should be examined as it may be possible to distinguish static anoxic facies, i.e., those subject to continuously low but nonzero benthic O_2 levels, from dynamic anoxic facies; i.e., those subject to wide redox fluctuations at seasonal or other time scales (e.g., poikiloaerobic facies; Wignall, 1994, Fisher and Wignall, 2001).

Systematic differences in TE concentrations are indeed observed in the study units. First, V enrichment is apparent at ~ 7 wt.% TOC ("subanoxic threshold") with further enrichment at $\sim 10 \text{ wt.\%}$ TOC ("euxinic threshold"), the latter a threshold also for elevated Mo, U, and Zn concentrations (Figs. 2b, 3a-c and 6a). Second, for samples exhibiting less than 100% agreement among "redox-indicator" trace elements, V was the one most commonly enriched to euxinic levels, Zn and Mo were next, and U was the least commonly enriched (Table 3). Finally, the stratigraphic distribution of TEs is particularly revealing: thick (>10 cm) intervals of uniformly euxinic character generally contain high concentrations of all four "redox indicators" (including U), whereas euxinic layers from intervals of fluctuating redox character are commonly rich in Mo, V, and Zn but poor in U (Algeo et al., this issue; cf. Fisher and Wignall, 2001). These patterns suggest that (1) greater relative enrichment of V in the study units is due to an "accumulation control", probably related to semireduction of V(V) to V(IV) at benthic O_2 levels insufficiently low for rapid accumulation of other TEs; and (2) lesser relative enrichment of U in the study units is due to a "remobilization control", in which small quantities of dissolved O₂ present within nonsulfidic anoxic facies were sufficient to cause partial postdepositional loss of U from sediments previously deposited under euxinic conditions (but to a depth of no more than a few centimeters below the sediment-water interface). We discount the possibility that U concentrations reflect an "accumulation control" (i.e., that accumulation of U required lower O2 or higher H2S concentrations than for Mo or Zn) because (1) U values rise at the same TOC threshold ($\sim 10 \text{ wt.\%}$) as Mo and Zn values, suggesting onset of enrichment under similar redox conditions; and (2) in modern marine sediments, U enrichment has been shown to occur at a higher redox potential than for Mo (Crusius and Thomson, 2000; Zheng et al., 2000, 2002; Chaillou et al., 2002).

6.4. Comparison with C-S-Fe systematics

C-S-Fe systematics have been used extensively to assess paleoredox conditions in marine systems. In TOC-S crossplots, a "normal marine trend" with a slope of 0.4 was identified for modern oxic-suboxic environments by Berner and Raiswell (1983, 1984) and a parallel "Black Sea trend" with a positive Yintercept (~ 1.0-1.5 wt.% S) was identified for euxinic environments by Leventhal (1983, 1987; Fig. 7a); the latter reflects an elevated S burial flux resulting from precipitation of syngenetic Fe-sulfides. Subsequently, it was recognized that both patterns represent C-limited systems, in which the amount of H₂S produced by sulfate-reducing bacteria covaries with the amount of labile organic carbon present, and the retention of sulfide S is not limited by the availability of reactive Fe. It also was discovered that many organic-rich facies represent Fe-limited systems, in which the retention of sulfide S depends on the availability of reactive Fe, mainly in the form of Fe-oxyhydroxides. These facies typically exhibit little systematic TOC-S covariation but relatively constant S/Fe ratios (e.g., Raiswell and Berner, 1985; Dean and Arthur, 1989). Degree-of-pyritization (DOP), i.e., the ratio of sulfide-hosted Fe to total reactive Fe in a sample, was subsequently proposed as a more reliable indicator of redox conditions in organic-rich facies than TOC/S ratios (Raiswell et al., 1988); DOP values of <0.45, 0.45-0.75, and >0.75 correspond approximately to oxic, dysoxic, and anoxic environments, respectively (Canfield et al., 1996; Raiswell et al., 2001). To distinguish between nonsulfidic and sulfidic anoxic facies, Raiswell et al. (2001) proposed a method based on extractable fractions of Fe called "indicator of anoxicity", with values >0.5 suggesting the formation of syngenetic pyrite.

TOC-S relationships among black shale samples of the study units are typical of organic-rich sedi-



Fig. 7. C–S–Fe systematics. (a) TOC–S (total sulfur). Trend line for oxic–suboxic marine shales from Berner and Raiswell (1983). (b) Fe–S (total sulfur). DOP_{tot} values of 0.25, 0.5, 0.75, and 1.0 are shown as diagonal lines; the 1.0 line is equivalent to the composition of stoichiometric pyrite (S/Fe=1.15 weight ratio). In both panels, the large outer ovals are standard deviation ellipses $(\pm 1\sigma)$ about the mean, and the small inner ovals are standard mean error ellipses $(\pm 1\sigma)$ for individual redox facies; n=233. Redoxfacies assignments are explained in the text.

ments deposited under Fe-limited, anoxic conditions: samples plot well below the "normal marine trend" for oxic-suboxic environments and exhibit little systematic TOC-S covariation (Fig. 7a; n.b., we use total sulfur (TS) as a proxy for sulfide S, which comprises ~ 60-90% of total sulfur in similar facies; cf. Mossmann et al., 1991; Schimmelmann and Kastner, 1993). Average TOC and S values increase along the dysoxic-anoxic-euxinic continuum, although the increase in TOC is much greater than that in S. Dysoxic facies samples (from the gray shale submembers of the study units) occupy a discrete field, but there is broad overlap among anoxic/euxinic facies samples (from the black shale submembers). One feature merits further comment: the distribution of most dysoxic facies samples above the "normal marine trend" (Fig. 7a). While the TOC values are typical of gray shales in general (0-2 wt.%), these samples appear to be anomalously enriched in S relative to many modern and ancient organic-poor mudstones (e.g., Beier and Hayes, 1989; Dean and Arthur, 1989; cf. Cruse and Lyons, 2000, their Fig. 8). The low thermal rank of the study units ($R_0 \sim 0.57$; Wenger and Baker, 1986) makes it unlikely that significant quantities of organic carbon have been lost, and low TOC values make it unlikely that the "excess" S resides in the organic fraction. The most likely explanation for the anomalous S enrichment of the dysoxic facies is that H₂S fluxed upward out of the underlying black shales, in which sulfate reduction continued even as organic-poor muds were being deposited above them. The stratigraphic distribution of high- and low-S samples in the study units is consistent with this hypothesis: (1) all high-S samples were taken from within $\sim 10-20$ cm of the black shale/gray shale contact, and (2) samples from stratigraphically higher intervals exhibit uniformly low S concentrations (<1 wt.%) and plot near the "normal marine trend" (Fig. 7a). This hypothesis also could be tested with sulfide S isotopic analysis, but this work has not been undertaken to date.

Fe-S relationships in the study units offer even less power to discriminate among redox facies: average Fe values decrease as S values increase along the dysoxic-anoxic-euxinic continuum, but the overlap between redox facies is considerable (Fig. 7b). Although Fe and S show little covariation when plotted by redox facies, strong covariation was observed for individual core shales at specific locales (Hoffman et al., 1998; their Fig. 9), which is consistent with Fe-limitation of sulfide S accumulation. Although calculation of DOP values requires determination of acid-soluble Fe and sulfide S concentrations via the chromium reduction method (Canfield et al., 1986), we can make a rough assessment using DOP_{tot} values based on total Fe and S concentrations. In the study units, DOPtot values average ~ 0.35 for the dysoxic facies, ~ 0.50 for the anoxic facies, and ~ 0.65 for the euxinic facies (Fig. 7b). These values are low compared to the DOP values assigned corresponding redox facies by Raiswell et al. (1988) but similar to the DOP values reported for Pennsylvanian core shales by Hatch and Leventhal (1992) and Cruse and Lyons (2000). Further, differences in DOP_{tot} values between redox facies of the study units are consistent with their inferred relative paleo-oxygen levels (i.e., higher DOP_{tot} values under more reducing conditions). These DOP_{tot} values may be low because of the presence of large amounts of unreactive Fe in the study units, possibly resident in Fe-chlorite from which Fe is not readily liberated (Canfield et al., 1992; cf. Desborough et al., 1991). We do not have the data necessary to evaluate Raiswell et al.'s (2001) "indicator of anoxicity" in the study units.

From the considerations above, we infer that the C–S–Fe systematics of the study units are consistent with nonsulfidic anoxic to euxinic conditions as well as with generally Fe-limited conditions of authigenic sulfide formation. However, C-S-Fe relationships appear to have poor discriminatory power for resolving redox facies: although individual facies are statistically significant at the $\alpha < 1\%$ confidence level in TOC-S and Fe-S crossplots, broad overlap of facies ranges would have precluded reliable redox-facies assignments without a priori information based on TOC-TE relationships (Fig. 7a,b). We tentatively conclude that the redox analysis procedure developed in this study is more reliable because (1) it is based on trace elements of strong euxinic affinity, i.e., those exhibiting substantial enrichment under euxinic conditions and, hence, offering maximum discriminatory power, and (2) the use of multiple proxies allows tests of the internal consistency of results (cf. Jones and Manning, 1994; Yarincik et al., 2000; Morford et al., 2001). Independent corroboration of our redox facies assignments may be possible based on (1) pyrite framboid size distributions (e.g., Wilkin and Arthur, 2001; Wilkin and Barnes, 1997; Wilkin et al., 1997; Wignall and Newton, 1998), (2) sulfide Δ^{34} S values (e.g., Coveney and Shaffer, 1988; Beier and Hayes, 1989; Saelen et al., 1993), or (3) bacterial biomarkers indicative of photic-zone euxinia (e.g., Repeta, 1993; Koopmans et al., 1996; Behrens et al., 2000; Roehl et al., 2001), although such tests have not been carried out to date.

7. Conclusions

- (1) Core shales of Upper Pennsylvanian Kansas-type cyclothems represent a promising system for paleoredox analysis: they record a wide range of redox conditions (from mildly dysoxic to strongly euxinic), exhibit a fairly monotonic stratigraphic trend toward increasing oxygenation upward, and were of sufficiently short duration ($<10^5$ y) that the influence of other physicochemical factors was minimized.
- (2) The gray and black shale submembers of core shales are easily distinguishable on the basis of color, TOC content, ichnofabric index, and redox-sensitive trace element (TE) concentrations, and represent dysoxic and anoxic conditions, respectively.
- (3) In the black shale submember, all TEs exhibit modest enrichment factors (EFs, relative to gray shales) and pronounced TOC-TE covariation in low-TOC (<10 wt.%) samples. In high-TOC (>10 wt.%) samples, TEs exhibit two different patterns: Mo, U, V, Zn, and Pb are strongly enriched but only weakly covariant with TOC, whereas Cu, Ni, Cr, and Co are weakly enriched but strongly covariant with TOC.
- (4) A theoretical basis for these TOC-TE relationships is that (i) under dysoxic conditions, TE concentrations were low and nearly invariant owing to residence primarily in detrital phases; (ii) under nonsulfidic anoxic conditions, modest TE enrichment and strong covariation with TOC was a consequence of residence primarily in organic phases, and of "saturation" of the organic fraction with respect to TEs; and (iii) under euxinic conditions, strong TE enrichment and weak covariation with TOC was due to formation of authigenic, TE-bearing sulfide or oxyhydroxide phases that exhibit little TOC dependence. A TOC threshold of ~ 2.5 wt.% was required to reduce dissolved O2 below the level at which benthic colonization was possible, and a TOC threshold of ~ 10 wt.% was necessary for complete depletion of benthic O₂ and accumulation of free H_2S in the water column.
- (5) Black shale samples can be assigned to the nonsulfidic anoxic versus euxinic redox facies on the basis of TOC-TE relationships among

trace elements of "strong euxinic affinity", i.e., Mo, U, V, and Zn. These assignments are considered to be reliable because (i) a large majority of samples (69%) exhibited full agreement among these four redox proxies, (ii) in samples yielding mixed redox signals, a systematic sequence of TE enrichment was observed ($V \rightarrow Zn \rightarrow Mo \rightarrow U$), suggesting a response to minor redox variations, and (iii) redoxfacies assignments made on the basis of TEs of strong euxinic affinity accounted for patterns of variance in trace elements of weak euxinic affinity (i.e., Cu, Ni, Cr, and Co), demonstrating "predictive" value.

- (6) The proportions of TEs resident in the detrital, organic, and sulfidic fractions of samples can be estimated on the basis of patterns of TOC-TE covariation. For samples assigned to the non-sulfidic anoxic facies, ~ 2/3 of authigenic Mo, U, V, and Zn resides in the "organic" fraction and ~ 1/3 in the "sulfidic" fraction. For samples assigned to the euxinic facies, these proportions change to ~ 1/5 in the "organic" fraction and ~ 4/5 in the "sulfidic" fraction. This suggests TE uptake under euxinic conditions mainly by authigenic precipitates rather than by organic matter, e.g., Mo and Zn in Fe-sulfides, and U and V in independent oxyhydroxide phases.
- (7) Mn behaves differently from other TEs in the study units in that (1) it becomes more depleted with increasing benthic anoxia; (2) depletion commences under dysoxic, rather than anoxic, conditions; and (3) depletion is "time integrative", resulting in significant differences between core shales but no systematic variation between redox facies of a single core shale. These patterns are consistent with redox cycling of Mn through the water column and kinetically sluggish redox reactions involving Mn.
- (8) C-S-Fe systematics in the study units are consistent with TE-based redox-facies assignments but are largely unreliable as independent indicators of nonsulfidic anoxic versus euxinic conditions. The TE-based redox-facies procedure developed in this study provides a more reliable assessment of paleoredox conditions because it (i) has a strong theoretical basis, (ii) is limited to a suite of TEs of "strong euxinic affinity", i.e., those exhibiting the greatest enrichment under

euxinic conditions and, hence, offering maximum discriminatory power, and (iii) makes use of multiple proxies that allow tests of the internal consistency of results.

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