Trace-metal covariation as a guide to water-mass conditions in ancient anoxic marine environments

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ABSTRACT

Patterns of sedimentary trace-metal variation can provide information not only about benthic redox conditions, but also about other water-mass properties in ancient marine depositional systems. Trace metals such as Mo, U, V, and Re display conservative concentration profiles in the global ocean but varying concentration profiles in modern anoxic silled basins (e.g., the Black Sea, Cariaco Basin, and Framvaren Fjord) as a consequence of enhanced sedimentary uptake, water-mass mixing, microbial cycling, and other processes. Because basin-specific patterns of aqueous trace-metal concentrations can be recorded by the sediment, chemostratigraphic studies of ancient anoxic marine facies have the potential to provide information about the degree of water-mass restriction as well as secular changes in aqueous chemistry and basin hydrography. In the Upper Pennsylvanian Hushpuckney and Stark shales of midcontinent North America, strong positive covariation among major trace metals supports extraction from a water mass of unmodified "normal" seawater chemistry with control of sedimentary trace-metal uptake primarily by benthic redox variation. This inference is consistent with unrestricted renewal of deep waters of the Late Pennsylvanian Midcontinent Sea via lateral advection of oxygen-deficient intermediate waters of the eastern tropical Panthalassic Ocean through a deep-water corridor in the Greater Permian Basin region. In contrast, trace metals in the Upper Devonian Ohio Shale of eastern North America exhibit divergent stratigraphic trends: relative to total organic carbon (TOC), V and Zn increase, Ni is constant, and Mo and U decrease upsection. This pattern records secular evolution of the aqueous chemistry of the silled Appalachian Basin in response to an increase in restriction of deep-water exchange. Basinal restriction intensified during the later stages of deposition of the Ohio Shale as a consequence of the onset of a major glacioeustatic regression that culminated at the Devonian-Carboniferous system boundary. Analysis of trace-metal patterns in other ancient anoxic marine systems has the potential to yield new insights regarding hydrographic variables such as rates of deep-water renewal and the degree of evolution of water-mass chemistry, in addition to information about paleoredox conditions.

INTRODUCTION

Enrichment of redox-sensitive trace metals in organic-rich facies has long been interpreted primarily in terms of benthic redox controls (e.g., Zheng et al., 2000), reflecting enhanced uptake by the sediment where dissolved H_2S has activated aqueous trace-metal complexes and/or host substrates (Helz et al., 1996; Vorlicek and Helz, 2002). It has been shown that trace-metal uptake by anoxic facies is also a function of the concentrations of both the aqueous species of interest and sedimentary organic matter, the latter being the primary host phase for many redox-sensitive trace metals (Algeo and Maynard, 2004; Algeo and Lyons, 2006). In restricted-marine settings such as silled basins, the aqueous concentrations of trace metals can become depleted through sedimentary uptake without adequate resupply, leading to a subsequent reduction in the quantity of trace metals per unit organic carbon of the sediment. These relationships provide a new analytical tool for paleoceanographic studies, potentially allowing assessment of aspects of the aqueous chemistry and basin hydrography of ancient anoxic marine systems. Here we examine patterns of aqueous trace-metal concentrations in the modern open ocean and three anoxic silled basins (the Black Sea, Cariaco Basin, and Framvaren Fjord) and consider the implications of these patterns for interpretation of sediment trace-metal concentration data from the Upper Pennsylvanian Hushpuckney and Stark shales (North American midcontinent) and Upper Devonian Ohio Shale (North American Appalachian Basin).

AQUEOUS TRACE-METAL DISTRIBUTIONS IN MODERN MARINE ENVIRONMENTS

In modern seawater, certain trace metals (e.g., Mo, U, V, and Re) exhibit nearly uniform vertical concentration profiles, reflecting conservative behavior within the water column (Fig. 1; Bruland, 1980, 1983). A second group of trace metals (e.g., Cu, Ni, and Zn) exhibits micronutrient behavior, in which surface waters are depleted relative to the deep ocean as a consequence of nutrient export linked to sinking organic matter. The depletion of surface waters relative to deep waters varies from approximately threefold to sixfold for Cu and Ni to approximately tenfold to twentyfold for Zn. Although a limited degree of interoceanic fractionation has been reported, especially with regard to the micronutrient elements (Bruland, 1983), trace-metal concentrations are relatively uniform in seawater globally.

Modern anoxic silled basins such as the Black Sea, Cariaco Basin, and Framvaren Fjord exhibit rather different vertical trace-metal concentration profiles from those of the open ocean as a consequence of their unique hydrographic and aqueous chemical histories. The Black Sea, with an area of 423,000 km[2] and abyssal plain depths of >2000 m, is the largest anoxic silled basin in the modern world. A chemocline (O_2-H_2S interface) at ~50–150 m separates an oxic surface layer with a salinity of 18‰–19‰ from an anoxic deep layer with a salinity of 22‰ and $[H_2S]_{aq}$ of 300–600 µmol L^{-1} (Brewer and Spencer, 1974). The deep Black Sea has been continuously anoxic since the Bosporus sill was transgressed ca. 7540 yr ago (Jones and Gagnon, 1994). The Cariaco Basin, an ~7000 km[2] tectonic depression
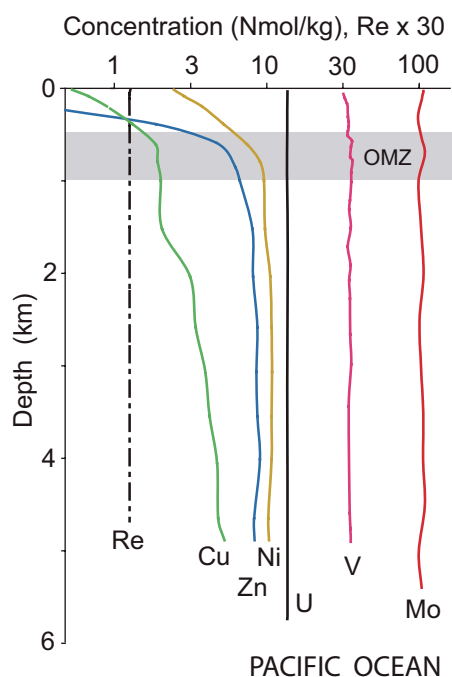
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Figure 1. Aqueous trace-metal concentration profiles for the modern open ocean. Gray background shading denotes the oxygen minimum zone (OMZ). Data sources: Bruland (1980, 1983), Collier (1984), Chen et al. (1986), Jeandel et al. (1987), Anbar et al. (1992), and Colodner et al. (1993). Profiles shown here are for the Pacific Ocean; trace-metal profiles for the Atlantic Ocean are nearly identical (e.g., Morris, 1975; Bruland and Franks, 1983).

on the Venezuelan continental shelf, is the second largest anoxic silled basin. It reaches a maximum depth of >1400 m and is surrounded by shallow (<150 m) sills that limit deep-water exchange, resulting in sulfidic conditions ($[H_2S]_{aq}$ of 30–40 µmol L^{-1}) below a chemocline that has deepened from ~250 m to ~375 m since the 1950s (Jacobs et al., 1987; Scranton et al., 1987). Cariaco Basin waters are fully marine, and water-column stratification is maintained by a thermocline. The deep water mass has been largely anoxic since 14.5 ka (Haug et al., 1998; Lyons et al., 2003), although various lines of evidence suggest that it may have undergone an oxic episode as recently as ~100 yr ago (Holmen and Rooth, 1990; Zhang and Millero, 1993). Framvaren is a small (5.8 km²) fjord in southern Norway with a maximum depth of 183 m. It is connected via a 2.5-m-deep, 500-m-long sill to adjacent fjords that are in communication with the Skaggerak and North Sea (Skei, 1983). The water column is stably stratified with an O_2-H_2S

interface at ~18 m; below a secondary pycnocline at ~80–100 m, $[H_2S]_{aq}$ rises rapidly from <2000 to 6000–8000 µmol L^{-1}. Framvaren was a meromictic lake with a chemocline at ~100 m until dredging of the sill ca. 1853 A.D. reconnected it to the sea and caused the chemocline to rise to its present level (Skei, 1983).

In order to facilitate comparisons among basins, trace-metal concentrations are reported here as a ratio of the observed value to the concentration predicted based on conservative behavior in the source water mass ($[X]_{obs}/[X]_{pred}$; Fig. 2), calculated per the method of Anderson et al. (1989). For each basin, the predicted concentration of a given trace metal is a salinity-weighted function of its concentrations in the low-salinity (ls) and high-salinity (hs) source-water fluxes to the basin under consideration:

$$[X]_{pred} = [X]_{ls} + [X]_{hs} \times (S_{obs} - S_{ls})/(S_{hs} - S_{ls}), \quad (1)$$

where S denotes salinity and [X] is the concentration of the trace metal of interest. The source waters used in this calculation are Bosporus surface water and Aegean deep water for the Black Sea (S = 17.5‰ and 38.5‰, respectively; Anderson et al., 1989), local riverwater and Skaggerak seawater for Framvaren Fjord (S = 0‰ and 33‰, respectively; Levitus, 1982; Skei, 1986), and unmixed Central Atlantic seawater for the Cariaco Basin (S = 35‰; Levitus, 1982). Salinity profiles for the Black Sea, Cariaco Basin, and Framvaren Fjord were taken from Brewer and Spencer (1974), Scranton et al. (1987), and Skei (1986), respectively.

In the surface waters of modern anoxic silled basins, observed concentrations are often close to 100% of predicted values, e.g., as in the Cariaco Basin, where surface waters are fully marine (Fig. 2). In Black Sea and Framvaren Fjord surface waters, some trace metals (e.g., Mo) consistently exhibit lower than predicted concentrations, a consequence of mixing of surface waters with trace-metal–depleted deep waters and of the long aqueous residence times of these elements relative to rates of vertical mixing (Figs. 2A, 2C; Table 1). One feature common to all three silled basins is the strong variability of trace-metal concentrations in surface waters. The causes of this variability are not fully understood, but may include (1) unaccounted-for variations in the trace-metal content of the low-salinity end member in water masses with multiple source fluxes, (2) depth-specific salinity variations due to localized incursions of low-salinity waters (e.g., via the interleaving process of Stigebrandt and Molvaer, 1988), and (3) depth-specific redox variations caused by localized resupply or consumption of dissolved oxygen, and attendant effects

upon trace-metal scavenging by particulates in the water column.

Below the chemocline, the trace-metal profiles of modern anoxic silled basins commonly exhibit sharp concentration decreases, with lower and comparatively stable concentrations reached at depths of a few meters (Framvaren Fjord) to a few hundred meters (Black Sea) below the chemocline (Fig. 2). The degree of drawdown of deep-water trace-metal concentrations varies somewhat among basins, generally being stronger for the Black Sea and Framvaren Fjord than for the Cariaco Basin. These patterns are in accord with dominant control by elevated rates of aqueous trace-metal removal to the sediment without compensating rates of resupply (Emerson and Huested, 1991; Algeo and Lyons, 2006). Differences between basins are superficially correlated with differences in deep-water sulfide concentrations, although sulfide activity is not thought to control rates of trace-metal removal to the sediment (Emerson and Huested, 1991), provided that a relatively low threshold concentration is exceeded (Helz et al., 1996; Zheng et al., 2000). However, deep-water sulfide concentrations are related to deep-water renewal ages (Algeo and Lyons, 2006), and those ages may be an important control on the degree of aqueous trace-metal depletion. Deep waters of the Cariaco Basin have been continuously anoxic probably for no more than ~100 yr (Holmen and Rooth, 1990; Zhang and Millero, 1993), versus several thousand years for the Black Sea and Framvaren Fjord (Skei, 1983; Jones and Gagnon, 1994), which may have allowed insufficient time for large-scale removal of trace metals to the sediment in a basin with a volume as large as that of the Cariaco Basin. This hypothesis is consistent with the pattern of trace-metal depletion observed in the deep Cariaco Basin, in which trace metals having comparatively short seawater residence times (e.g., Cu and V) are removed more quickly than trace metals having longer residence times (e.g., Mo and U; Table 1).

Most trace metals exhibit similar concentration profiles in the deep waters of all three basins, e.g., Cu and Zn are uniformly strongly depleted, U is weakly depleted, and Ni is weakly enriched (Fig. 2; note that there are insufficient Re data for interbasinal comparison). This observation is significant because it implies the operation of similar processes at comparable rates in each basin. Although Mo is depleted to a lesser degree in the Cariaco Basin than in the Black Sea and Framvaren Fjord, this pattern can be explained in terms of differences in water-mass volume and redox history (as described above), suggesting no fundamental differences
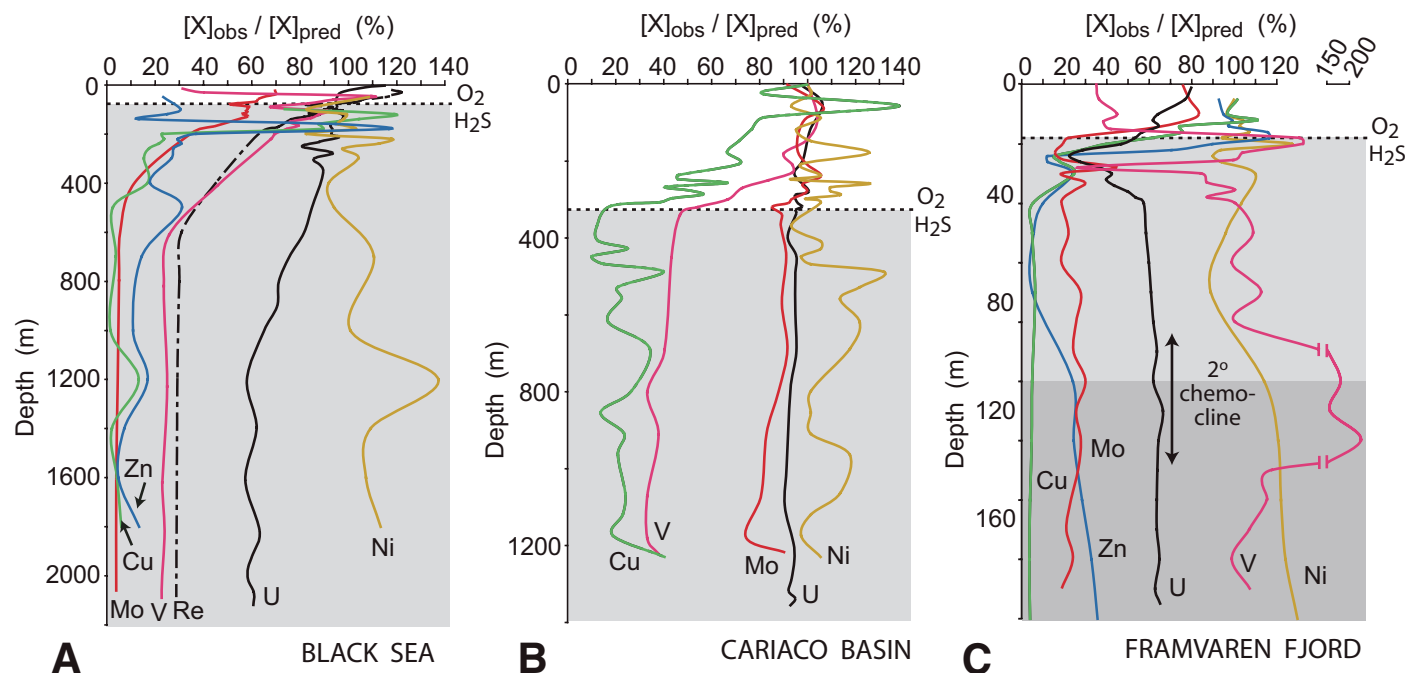
Figure 2. Aqueous trace-metal concentration profiles for modern silled-basin environments. (A) Black Sea. (B) Cariaco Basin. (C) Framvaren Fjord. Depth of chemocline (O_2/H_2S) is shown for each basin. The ratio of observed to predicted concentrations ($[X]_{obs}/[X]_{pred}$) is calculated per the method of Anderson et al. (1989). Zn and Re data for the Cariaco Basin and Re data for Framvaren Fjord are not available; Re data, also unavailable for the Devonian and Pennsylvanian study units (Figs. 5–8), are shown for the Black Sea and the Pacific Ocean (Fig. 1) owing to their potential as a conservative tracer in paleoceanographic studies. Gray background shading denotes the sulfidic subpycnoclinal water mass. Data sources: Anderson (1987), Jacobs et al. (1987), Haraldsson and Westerlund (1988), Todd et al. (1988), Anderson et al. (1989), Emerson and Huested (1991), Colodner et al. (1995), and Swarzenski et al. (1999a).

in Mo behavior between basins. In contrast, V exhibits markedly different concentration profiles between basins, i.e., depleted in the Black Sea and Cariaco Basin, but enriched in Framvaren Fjord (Fig. 2). The causes of interbasinal differences in V profiles, although poorly understood, must be related to differences in V behavior. Emerson and Huested (1991) postulated that V may accumulate in the deep-water layer owing to the presence of unusually large quantities of dissolved organic carbon and the

affinity of the reduced form of vanadium (the vanadyl ion, VO^{2+}) for organic ligands (Wehrli and Stumm, 1989). However, aqueous [V] is elevated only between ~80 m and 120 m (i.e., within the secondary pycnocline), whereas dissolved organic carbon is elevated throughout the deep water mass (Skei, 1986), suggesting that the mechanism proposed by Emerson and Huested (1991) requires an additional feature, e.g., scavenging of V-bearing organic ligands by particulates below ~120 m (cf. Skei et al.,

1996). As shown by Mo and V, differences in aqueous trace-metal concentrations can develop in restricted marine systems as a consequence of basin-specific processes.

Patterns of variation in aqueous trace-metal concentrations in modern marine systems provide a guide for interpretation of trace-metal data from ancient marine facies. In marine paleoenvironments in which deep waters were exchanged freely with the open ocean, aqueous trace-metal concentrations should have been similar to those of contemporaneous open-marine seawater (Fig. 1). In such settings, variation in sediment trace-metal concentrations would have been controlled largely by benthic redox conditions (Zheng et al., 2000; Vorlicek and Helz, 2002), resulting in similar responses among trace metals to environmental redox fluctuations (e.g., Algeo et al., 2004). The chemostratigraphic record of a system responding primarily to redox controls is expected to exhibit strong positive covariation among trace metals, although the degree of covariation potentially may be influenced by other factors, e.g., element-specific differences in uptake mechanisms and redox activation thresholds (Helz et al., 1996; Algeo and Maynard, 2004) and differences in susceptibility

TABLE 1. TRACE-METAL RESIDENCE TIMES IN SEAWATER

Trace metal	Mass M^* (10^{12} kg)	Source flux $f_Q^\dagger$ (10^6 kg yr^{-1})	Residence time $t^\S$ (10^3 yr)
Re	0.011	0.014	750
Mo	13.3	18.2	731
U	4.40	10.9	402
Ni	0.63	3.0	213
V	2.69	56.0	48
Zn	0.69	25.0	28
Cu	0.13	42.6	3.1

*Data from Emerson and Huested (1991), Colodner et al. (1993), and Wright and Colling (1995); based on seawater mass of 1.322 x 10^{21} kg.
†Estimated premodern fluxes; anthropogenic inputs not included.
§Calculated as M/f_Q (mass/source flux), assuming present-day equilibrium.

to postdepositional remobilization (Zheng et al., 2002).

On the other hand, in marine paleoenvironments in which deep-water exchange was restricted, the concentrations of trace metals in the subchemoclinal water mass are likely to have differed from those in contemporaneous "normal" seawater (i.e., having aqueous trace-metal concentrations similar to those in the global ocean; cf. Figs. 1 and 2). Because aqueous trace-metal chemistry influences sediment trace-metal chemistry (Algeo and Lyons, 2006), it is reasonable to infer that unique aqueous trace-metal signatures (as found in modern anoxic silled basins; Fig. 2) can be exported to the sediment. An additional feature of restricted marine paleoenvironments is that the relative concentrations of trace metals have the potential to evolve through time in response to a number of processes, including differential removal rates to the sediment, changes in source fluxes, and variations in bacterial cycling of trace metals within the water column (Anderson et al., 1989; Emerson and Huested, 1991; McKee and Todd, 1993; Skei et al., 1996; Swarzenski et al., 1999a, 1999b; Algeo, 2004). Patterns of chemical evolution are likely to be basin specific, resulting in unique chemostratigraphic trends within each ancient marine system. These processes may operate independently of, or in addition to, sediment trace-metal concentration changes resulting from benthic redox fluctuations. Thus, analyses of patterns of chemostratigraphic covariation among trace metals have the potential to provide insights regarding the general hydrographic character of marine paleoenvironments (open versus restricted) as well as a variety of chemical and physical processes operating therein, although application of these principles to the pre-Phanerozoic, when the redox chemistry of the global ocean was fundamentally different than that of the modern world (Canfield, 1998; Anbar and Knoll, 2002), must be undertaken with caution.

GEOLOGIC SETTING OF PENNSYLVANIAN AND DEVONIAN–MISSISSIPPIAN STUDY UNITS

Black (organic rich) shales are deposited under a wide range of environmental conditions and in diverse depositional settings (Arthur and Sageman, 1994). Trace metals are generally present in elevated concentrations in black shales, although the degree and pattern of trace-metal enrichment can vary considerably among different formations for reasons that generally remain poorly understood. In this study we examined patterns of trace-metal covariation in two sets of black shale units: (1) Upper Pennsyl-

vanian cyclothemic "core shales" (deep-water facies) of midcontinent North America, and (2) Devonian–Mississippian shales of the Central Appalachian Basin. These units accumulated in markedly different depositional settings, the former in a broad, shallow epicontinental sea in good communication with the global ocean, and the latter in a deep, silled intracratonic basin with a restricted deep water mass (Heckel, 1977, 1991; Potter et al., 1982; Ettensohn et al., 1988; Algeo et al., 2007, 2008a). Examination of trace-element patterns in these two depositional systems reveals differences both in secular trends at a broad (formation) stratigraphic scale and in high-frequency patterns at a fine (centimeter) stratigraphic scale. Such differences in trace-metal patterns may provide significant new insights regarding the hydrographic and environmental characteristics, as well as the sequence stratigraphic histories, of these paleomarine systems. The insights gained from our analysis are not compromised by inequalities in the duration of benthic anoxia in the depositional systems of interest (~50–100 k.y. for individual core shales of midcontinent cyclothems versus ~15 m.y. for the Ohio Shale; Algeo et al., 2004, 2007). This difference is irrelevant because deep-water renewal, even in highly restricted marine basins such as the Black Sea and Framvaren Fiord, is on the order of a few hundred to a few thousand years (Murray et al., 1991; Dyrssen et al., 1996), as a consequence of which the aqueous chemistry of such systems is in dynamic equilibrium with that of other water masses with which communication exists, including the global ocean.

The Upper Pennsylvanian Hushpuckney and Stark shales represent core shales (deep-water facies) of midcontinent North American cyclothems (Figs. 3A, 3B; Heckel, 1977). During the middle Pennsylvanian to Early Permian, the interior region of North America was repeatedly flooded when Southern Hemisphere Gondwanan ice sheets melted and eustatic elevations rose by 60–150 m (Heckel, 1986; Soreghan and Giles, 1999; Joachimski et al., 2006), producing an interior sea (the Late Pennsylvanian Midcontinent Sea) that covered an area up to ~2.1 × 10^6 km^2 (Fig. 4A; Algeo and Heckel, 2008; Algeo et al., 2008a). Each successive eustatic highstand resulted in widespread deposition of a thin (<1 m) organic-rich black shale characterized by abundant phosphatic granule layers, lack of biota other than nektic and pelagic organisms, and strongly ^{34}S-depleted authigenic sulfides, reflecting sedimentation in a clastic-starved, distal offshore setting with oxygen-depleted and at least intermittently sulfidic bottom waters (Heckel, 1977, 1991; Coveney and Shaffer, 1988; Hoffman et al., 1998; Algeo et al., 2004). Although the accumulation of organic-rich

sediments is generally associated with either high rates of primary productivity or deep-water restriction, midcontinent Pennsylvanian core shales exhibit little evidence that either of these features existed in the Late Pennsylvanian Midcontinent Sea. Primary productivity rates are thought to have been lower than in modern epicratonic marine systems (≤21 g C m^{-2} yr^{-1}), and paleogeographic reconstructions provide no evidence for a marginal sill that could have restricted deep-water exchange with the contemporaneous global ocean (Algeo and Heckel, 2008; Algeo et al., 2008a). Rather, a key factor in the development of widespread bottom-water anoxia in the Late Pennsylvanian Midcontinent Sea was an unusual paleogeographic circumstance: the location of the outlet of the sea to the global ocean in a portion of the eastern tropical Panthalassic Ocean, in which extreme shallowing of the oxygen-minimum zone (OMZ) occurred (comparable to OMZ) shallowing in the modern eastern tropical Pacific; Levitus, 1982; Thunell and Kepple, 2004), allowing lateral advection of oxygen-poor, denitrified waters into the Late Pennsylvanian Midcontinent Sea through a ~1000-km-long deep-water channel in the Greater Permian Basin region (Algeo and Heckel, 2008; Algeo et al., 2008a, 2008b).

In contrast to the Late Pennsylvanian Midcontinent Sea, the Devonian–Mississippian Appalachian Sea was a silled marine basin in which deep-water exchange with the contemporaneous open ocean was strongly restricted (Potter et al., 1982; Ettensohn et al., 1988; Algeo et al., 2007) and in which primary productivity rates may have been significantly elevated (Algeo et al., 1995, 2001). It formed during the Middle Devonian, when a major eustatic transgression flooded the interior of the North American craton (Johnson et al., 1985; Schieber, 1998a). The Devonian–Mississippian Appalachian Sea occupied an elongate basin extending from New York southwestward to central Tennessee that was actively subsiding in response to crustal flexure and sediment loading associated with the Acadian orogeny (Fig. 4B; Ettensohn et al., 1988). Although proximal portions of the basin to the northeast were dominated by the shallow-marine Catskill Delta system, the basin deepened axially to the southwest to depths of perhaps several hundred meters (Potter et al., 1982). The basin was bounded by structural sills on its western and southern margins with the Illinois and Black Warrior Basins, respectively, representing sites of active uplift (forebulges) localized by preexisting basement features (Ettensohn et al., 1988; Schieber, 1998a). Sill depths were at least intermittently sufficiently shallow (perhaps <50 m) as to allow penetration of storm energy and extensive sediment
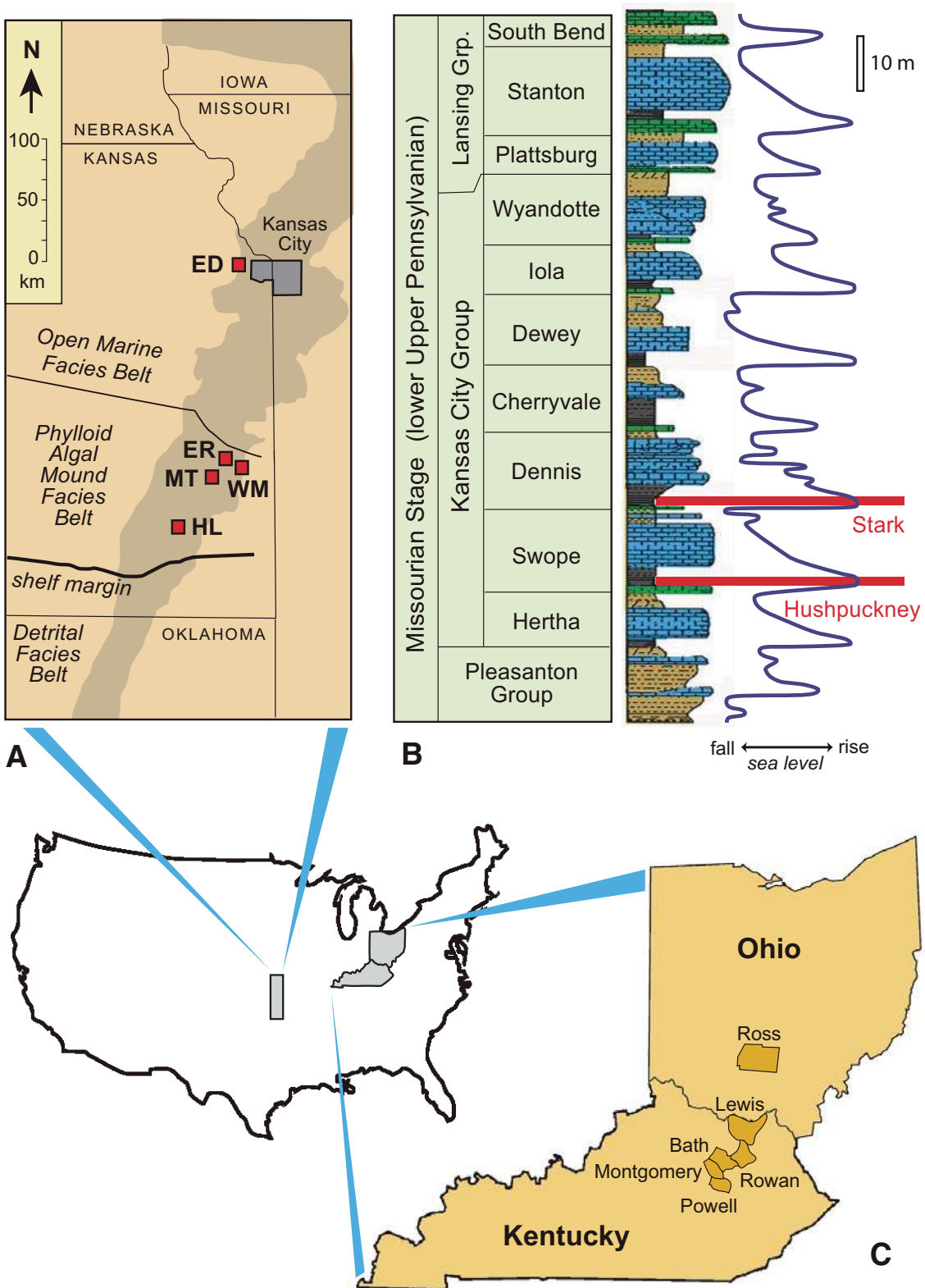
Figure 3. Orientation data for study units. (A) Location map for Upper Pennsylvanian Hushpuckney and Stark shale drill cores. (B) Stratigraphic column for Missourian Stage (lower Upper Pennsylvanian) of midcontinent North America. (C) Location map for Devonian–Mississippian black shale drill cores of Central Appalachian Basin. See Table 2 for additional location information. Drill core abbreviations: ED—Edmonds #1A; ER—Ermal #1; HL—Heilman #1; MT—Mitchellson #1; WM—Womelsdorf #1.
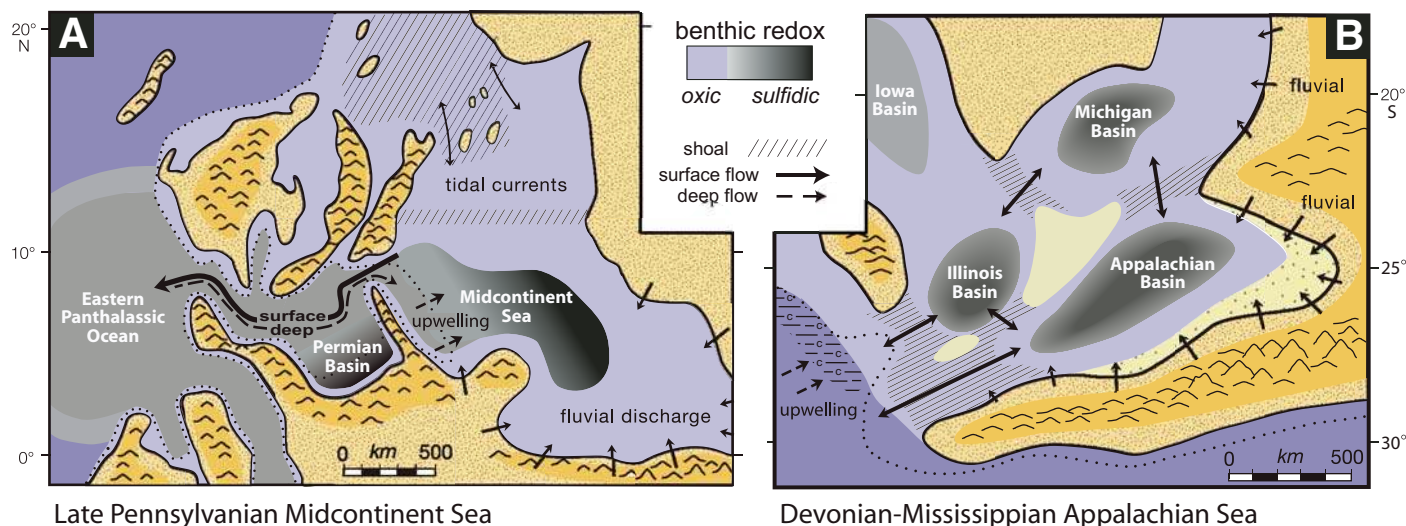
Figure 4. Paleogeography and paleohydrography of (A) the Late Pennsylvanian Midcontinent Sea, and (B) the Devonian–Mississippian Appalachian Sea and adjacent areas. Generalized patterns of benthic redox conditions and large-scale circulation are shown; spatial variation in redox conditions is based on redox proxies in Robl et al. (1984), Robl and Barron (1988), Algeo and Maynard (1997), Jaminski (1997), Jaminski et al. (1998), Hoffman et al. (1998), Algeo et al. (2004), and Cruse and Lyons (2004). For modern geographic reference frames, see Algeo et al. (2004, 2008a) for the Late Pennsylvanian Midcontinent Sea, and Algeo et al. (2007) for the Devonian–Mississippian Appalachian Sea.

winnowing (Schieber, 1994, 1998b; Schieber and Riciputi, 2004). The silled nature of the basin resulted in semirestricted exchange of deep waters, which are estimated to have had a renewal time (~100–500 yr) intermediate between those of modern Cariaco Basin and Black Sea deep waters (Algeo and Lyons, 2006; Algeo et al., 2007). As a consequence of the restricted character of the basin, deep waters of the Devonian–Mississippian Appalachian Sea were oxygen depleted through most of the ~15 m.y. Late Devonian interval, resulting in accumulation of a wedge of black shales that thins from hundreds of meters in New York to 50–90 m in northeastern Kentucky (Fig. 3C;

Potter et al., 1982). Preservation of organic matter was enhanced by a stably stratified water column, with introduction of only small quantities of dissolved oxygen episodically into the deep basin through turbiditic interflows from the north and east (Jaminski, 1997; Jaminski et al., 1998) (interflows are intrusions of turbid water at a specific density level within a density-stratified water column; see Wilson and Roberts, 1995). In addition, there is evidence for generally elevated fluxes of nutrients from terrestrial environments during the Late Devonian as a consequence of enhanced pedogenic weathering in response to the rapid spread of vascular land plants (Algeo et al., 1995, 2001).

METHODS

Source Materials

The Upper Pennsylvanian (lower Missourian Stage) Hushpuckney and Stark shales were studied in five drill cores from eastern Kansas (Figs. 3A, 3B; Table 2). Each study unit consists of a laminated black shale facies (total organic carbon, TOC >2.5%) and an overlying bioturbated gray shale facies (TOC <2.5%). The black shale facies can generally be subdivided into lower and upper members that exhibit pronounced differences in the type and quantity of organic matter and the concentrations of

TABLE 2. LOCATION INFORMATION FOR STUDY DRILL CORES

Drill core	County, State	Location*	Units Sampled[†]	Curation Site
Edmonds #1A	Leavenworth, KS	Sec 35, Twp 9S, Rng 22E	Hushpuckney, Stark	Kansas Geol. Survey
Ermal #1	Bourbon, KS	Sec 7, Twp 24S, Rng 22E	Hushpuckney, Stark	Kansas Geol. Survey
Mitchellson #1	Bourbon, KS	Sec 18, Twp 25S, Rng 21E	Hushpuckney	Kansas Geol. Survey
Womelsdorf #1	Bourbon, KS	Sec 17, Twp 24S, Rng 23E	Stark	Kansas Geol. Survey
Heilman #1	Neosho, KS	Sec 36, Twp 28S, Rng 18E	Stark	Kansas Geol. Survey
D-2, D-3	Powell, KY	n/a	Ohio-Sunbury shales	Kentucky Geol. Survey
D-4, D-5	Montgomery, KY	n/a	Ohio-Sunbury shales	Kentucky Geol. Survey
D-6, D-7, D-8	Bath, KY	n/a	Ohio-Sunbury shales	Kentucky Geol. Survey
D-9, D-10, D-11	Rowan, KY	n/a	Ohio-Sunbury shales	Kentucky Geol. Survey
K-3	Lewis, KY	Sec 2W73, 3250 FSL,1150 FEL	Sunbury Shale	Kentucky Geol. Survey
K-6	Fleming, KY	Sec 21W71, 5400 FSL, 225 FEL	Ohio-Sunbury shales	Kentucky Geol. Survey
OHRS-5	Ross, OH	458,600 Ft N & 1,836,900 Ft E	Ohio Shale, Cleveland	Ohio Geol. Survey

Note: KS—Kansas; KY—Kentucky; OH—Ohio; Geol.—Geological.
*Sec—Section; Twp—Township; Rng—Range; FSL—feet from south line; FEL—feet from east line; Ft—feet; n/a—not available.
[†]Hushpuckney, Stark shales.

trace metals, reflecting environmental differences between the transgressive and regressive stages of glacioeustatic cycles in the Late Pennsylvanian Midcontinent Sea (Algeo et al., 2004). Samples were collected at high stratigraphic resolution in each study unit: the black shale facies was sampled in toto with individual samples averaging ~1 cm in thickness taken from layers of relatively uniform composition, as determined by petrographic and X-ray radiographic techniques (Algeo et al. 1994; Algeo and Maynard, 1997), whereas the gray shale facies was sampled discontinuously at intervals of 2–5 cm owing to its more limited compositional variation.

A geochemical survey of the Devonian–Mississippian black shale succession in Kentucky was undertaken by Thomas Robl of the University of Kentucky as part of the U.S. Department of Energy–funded Eastern Gas Shales Project during the early 1980s (for further information, see Robl et al., 1984; Robl and Barron, 1988). We have analyzed elemental concentration data from a total of 496 samples in 10 drill cores (the D series) from this study, in which samples represent homogenized 0.6-m-thick drill core intervals collected at a uniform spacing of ~1.6 m (Fig. 3C; Table 2). For presentation, chemostratigraphic data were normalized to a common depth scale (that of the K-6 drill core). Subsequently, we undertook high-resolution (centimeter scale) analysis of several dozen short (20 cm thick) stratigraphic intervals of the Cleveland and Sunbury Shales from drill cores in northeastern Kentucky and southern and central Ohio in order to examine high-frequency chemostratigraphic patterns (Jaminski, 1997; Jaminski et al., 1998; Kuhn, 1999); we report a subset of these (to date largely unpublished) results here.

Geochemical Analyses

Samples processed at the University of Cincinnati were ground in an agate ball mill and refrigerated prior to analysis. Trace-element concentrations were determined using a wavelength-dispersive Rigaku 3040 X-ray fluorescence (XRF) spectrometer, and results were calibrated with both U.S. Geological Survey (USGS) (SDO-1, SCO-1, SGR-1) and internal black shale standards (analyzed by XRAL Incorporated). Analytical precision based on replicate analyses was better than ±5% for all trace elements, and detection limits were ~2 ppm for trace metals. Carbon and sulfur concentrations were determined using an Eltra CS-2000 elemental analyzer. Total carbon (TC) and total sulfur (TS) were determined from whole-rock samples, and TOC was determined by acidifying

a sample split with dilute HCl at ~50 °C for 4 h prior to analysis. Analyses were calibrated with the USGS Devonian black shale standard SDO-1; analytical precision (2σ) based on replicate analyses was ±2.0% and ±7.6% of measured values for C and S, respectively. Elemental data (except for U) from the Kentucky Geological Survey's D-series drill cores were generated using similar XRF and C-S pyrolysis procedures (for details, see Robl et al., 1984; Robl and Barron, 1988). The U concentration data were generated at the University of Cincinnati using a Core Lab spectral gamma core logger with an NaI detector and 256 channel spectral analyzer. Output was calibrated using Core Lab standard gamma verifier tubes, and reproducibility was optimized by operating the instrument at ultralow belt speeds (0.002 m min⁻¹ for spectral gamma) so as to achieve higher counts per unit core length.

Degree of pyritization (DOP) is a paleoredox proxy based on the ratio of pyrite Fe to total reactive Fe in a sample (Raiswell et al., 1988). DOP_T, the ratio of pyrite Fe (based on total S) to total Fe, can be used in place of true DOP, if pyrite S composes the bulk of total S and reactive Fe composes the bulk of total Fe (true of many black shale formations including the study units; Kuhn, 1999). The advantage of DOP_T is that values can be generated rapidly for large numbers of samples using XRF and C-S elemental analyses. In this study, DOP_T was calibrated to true DOP using sample sets from the study units for which both proxies were determined. DOP-DOP_T relationships were established for the midcontinent Pennsylvanian core shales using data in Cruse and Lyons (2004), which yielded a second-order polynomial correlation ($y = 0.65x^2 + 0.29x + 0.016$) with $r^2 = 0.96$ and mean $\Delta(DOP - DOP_T) = 0.03$, and for the Appalachian Basin Devonian black shales using data in Kuhn (1999) and Werne et al. (2002), which yielded a correlation ($y = 1.21x^2 - 0.45x + 0.33$) with $r^2 = 0.87$ and mean $\Delta(DOP - DOP_T) = 0.04$. For both study units, DOP_T is a reliable estimator of true DOP; in Figures 5–8, DOP_{est} is a true DOP scale based on the correlation equations above. Fe_T/Al is also useful as a paleoredox proxy (Lyons and Severmann, 2006), and, because total Fe appears in the numerator rather than in the denominator of the equation, it is independent of DOP_T values.

Data Presentation

Trace-metal concentration data are presented in three different ways in this study, with the choice of method dictated by specific goals. In Figures 5 and 6, trace-metal concentrations are normalized to the mean concentration of each

metal in an interval of the study unit characterized by low and relatively uniform concentrations. This transformation serves two purposes: (1) it rescales trace metals having very different absolute concentrations to a more limited range of values, and (2) it allows secular (stratigraphic) trends among trace metals to be more readily observed. The weighted running averages shown in these figures serve to emphasize the secular (long-term) trends in the data sets at the expense of high-frequency (sample to sample) variation. TOC is included in these plots because its relationship to trace-metal concentrations provides information about paleoredox conditions: a similar degree of enrichment of TOC and trace metals implies relatively less reducing conditions (e.g., suboxic to weakly sulfidic conditions, where metal uptake by the sediment tends to be limited by the availability of organic host phases), whereas substantially greater enrichment of trace metals relative to TOC implies strongly sulfidic conditions (under which aqueous trace-metal complexes have become activated; Helz et al., 1996). In Figures 7 and 8, trace-metal concentrations are shown on both a log scale (column E) and a Z scale (column F). The Z scale, in which elemental concentrations are normalized to a mean (μ) of 0 and a standard deviation (σ) of 1.0, facilitates interelemental comparisons by equalizing the total variance for each element. Relative to the normalization procedure above, these methods tend to emphasize variation at the low end of the concentration scale, providing greater insight into the pattern of sample to sample variation throughout each study unit. The different methods used to plot chemostratigraphic data in Figures 5–6 and 7–8 are thus complementary and intended to reveal different aspects of trace-metal covariation in the study units. There is no "best" way to present trace-metal concentration data, and each method has its specific utility.

TRACE-METAL PATTERNS IN THE LATE PENNSYLVANIAN MIDCONTINENT SEA

Secular Trends

Although midcontinent Pennsylvanian core shales exhibit generally high trace-metal concentrations, variation within and between different units can be considerable (Fig. 5D). Chemostratigraphic trends are similar in the Hushpuckney and Stark shales: the highest trace-metal concentrations are associated with the lower black shale facies, yet the upper black shale facies nonetheless exhibits strong enrichment above the detrital background levels that characterize the gray shale facies. Relative to
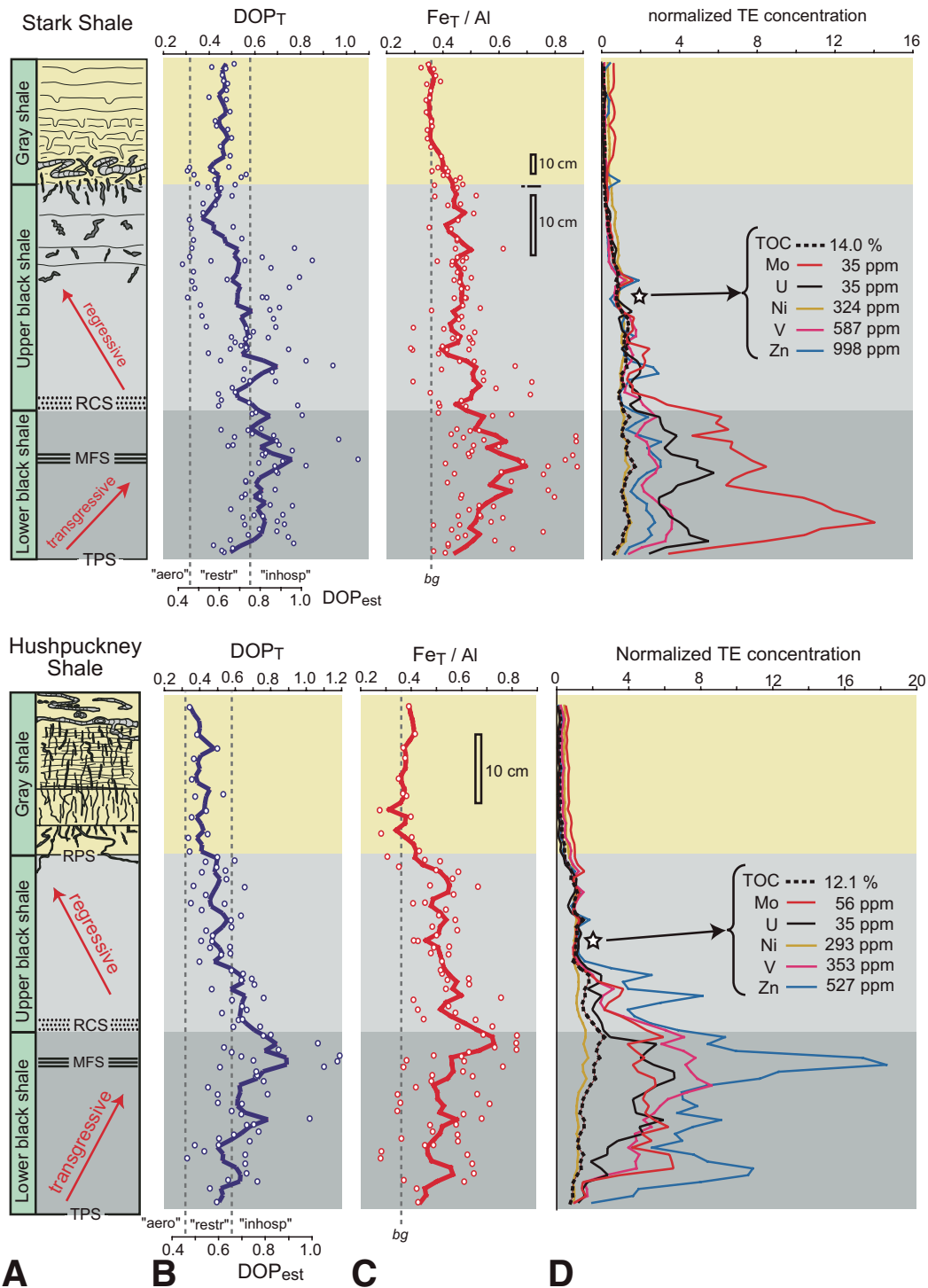
Figure 5. Chemostratigraphy of Upper Pennsylvanian Hushpuckney and Stark shales from midcontinent North America. (A) Stratigraphic column. TPS—transgressive pycnoclinal surface; RPS—regressive pycnoclinal surface; MFS—maximum flooding surface; RCS—regressive condensation surface (see Algeo et al., 2004, for discussion). (B) Degree of pyritization (DOP$_T$) and (C) Fe$_T$/Al are paleoredox proxies; DOP$_{est}$ is a true DOP scale (see Methods discussion). For reference, the aerobic (aero), restricted (restr), and inhospitable (inhosp) redox fields of Raiswell et al. (1988) and the background (bg) Fe$_T$/Al ratio are shown. (D) Total organic carbon (TOC) and trace-metal concentrations, normalized to a value of 1.0 for the middle interval of the upper black shale facies (star); actual concentrations equivalent to a normalized concentration of 1.0 are shown to the right. TE—trace element. For all proxies in B–D, the solid lines represent an inverse-distance-weighted running mean. Shaded background fields represent the division of core shales into a lower black shale, upper black shale, and gray shale facies; note change in vertical scale for the Stark at black shale–gray shale contact.
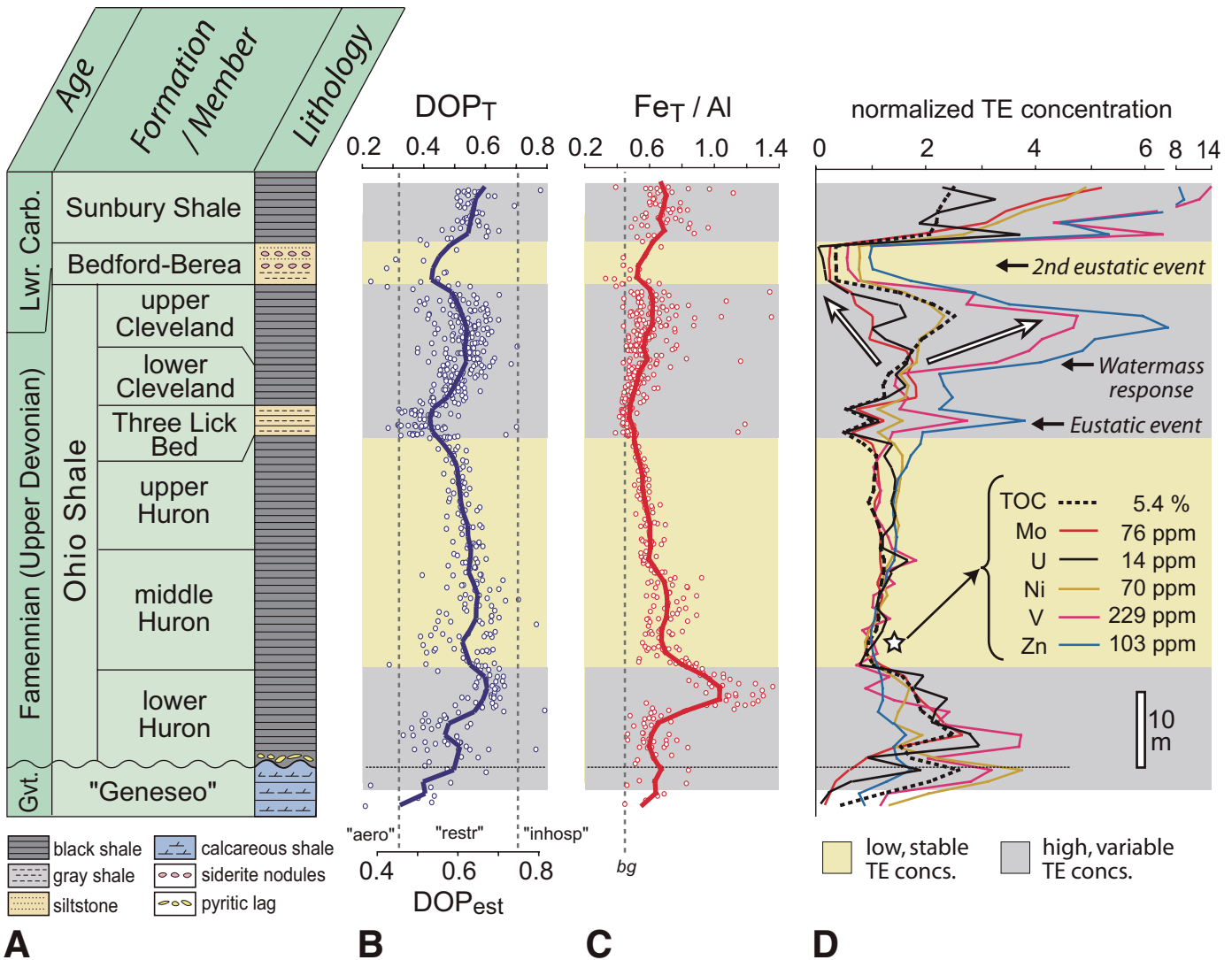
Figure 6. Chemostratigraphy of Upper Devonian–Lower Mississippian black shale succession of Central Appalachian Basin. (A) Stratigraphic column. (B) Degree of pyritization (DOP_T). (C) Fe_T/Al (aero—aerobic, restr—restricted, inhosp—inhospitable; see Fig. 5 caption for more information). (D) Trace-metal concentration profiles, normalized to a value of 1.0 near the base of the middle Huron Member of the Ohio Shale (star); actual concentrations equivalent to a normalized concentration of 1.0 are shown to the right. For all proxies in B–D, the solid lines represent an inverse-distance-weighted running mean. Trace-metal concentration trends shown by arrows are discussed in the text. Shaded background fields delineate intervals of similar trace-metal character; see key in lower right. TOC—total organic carbon; TE—trace element.

the upper black shale facies (the midpoint of which is the reference point for normalization of concentration data in Fig. 5D), the lower black shale facies is enriched by factors of 1.5× to >10× for Mo (in the Stark) and Zn (in the Hushpuckney). Trace-metal enrichment generally correlates well with variation in the paleoredox proxies, DOP_T and Fe_T/Al (Figs. 5B, 5C). Values of DOP_{est} that exceed 0.75 (the "inhospitable" zone of Raiswell et al., 1988) are closely associated with strong trace-metal enrichment in both study units. The paleoredox proxies make

clear that conditions were generally more reducing during deposition of the lower black shale facies (i.e., strongly sulfidic) compared with the upper black shale facies (i.e., mostly weakly sulfidic, but increasingly suboxic toward the black shale–gray shale contact).

High-Frequency Patterns

The study units exhibit strong covariation among trace metals at a fine (centimeter) stratigraphic scale (Fig. 7E). Such covariation is par-

ticularly pronounced because each trace metal individually exhibits a large (1–2 order of magnitude) concentration range. When converted to a Z scale (so that the total variance in each concentration record is the same), it becomes apparent that the sample to sample patterns of variation are nearly identical for all trace metals (Fig. 7F). Absent is any evidence of independent behavior, i.e., variation unique to a specific trace metal and unrelated to variation in other trace metals. Such a strong pattern of covariation suggests that trace-metal concentrations in
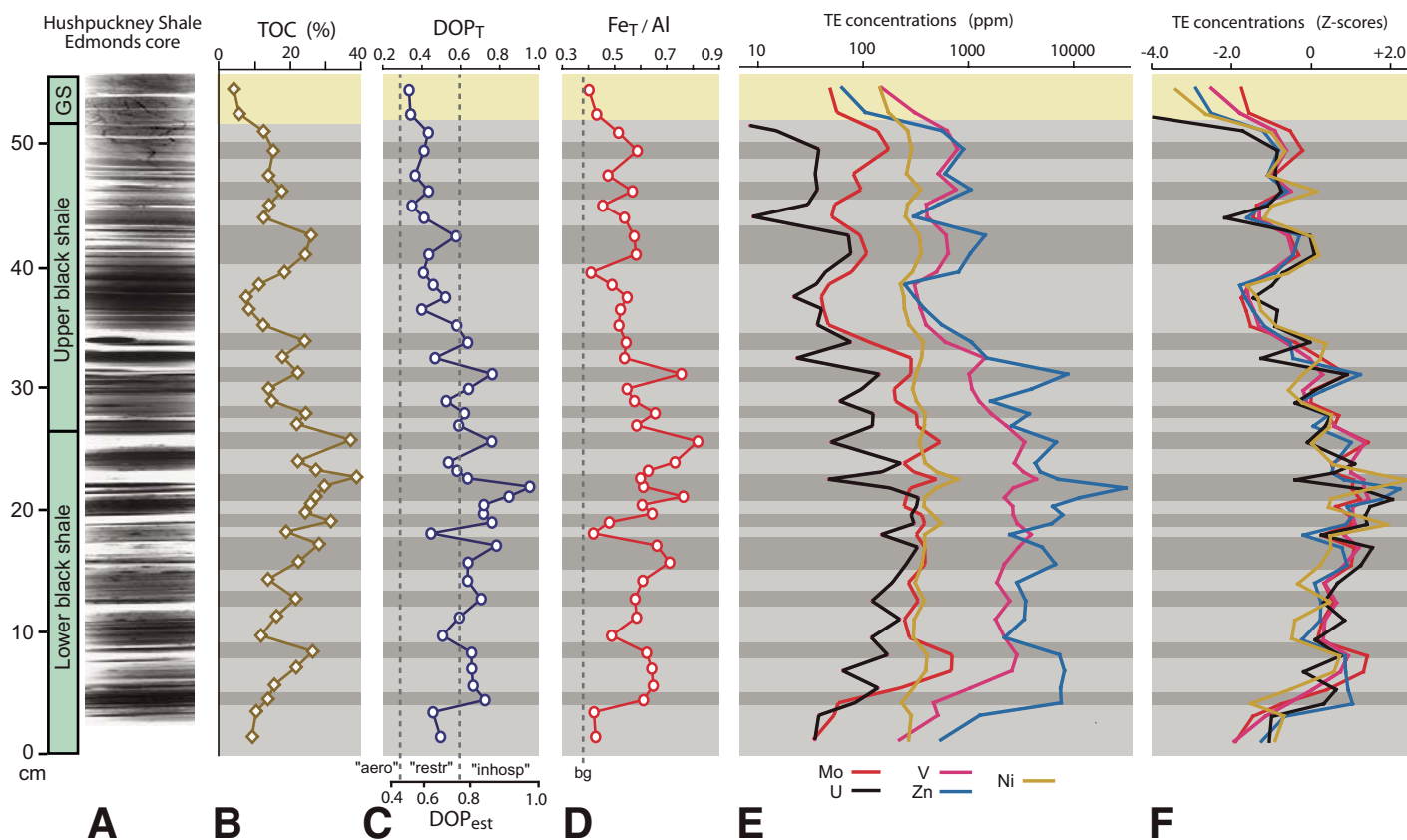
Figure 7. Detailed chemostratigraphic variation of the Hushpuckney Shale in the Edmonds drill core. (A) X-ray radiograph. (B) Total organic carbon (TOC). (C) Degree of pyritization (DOP_T) (aero—aerobic, restr—restricted, inhosp—inhospitable; see Fig. 5). (D) Fe_T/Al. (E) Trace-metal concentrations (log scale). (F) Trace-metal concentrations (Z scores; see Methods discussion). In the X-ray radiograph image, lighter and darker hues represent less and more dense areas of the study core, respectively; note the strong centimeter-scale stratigraphic variation in sample density, which is controlled largely by organic carbon content. Background shaded fields represent intervals of more oxidizing (lighter color) and more reducing (darker color) redox conditions, relative to adjacent parts of the study section. GS—gray shale; TE—trace element.

the source water mass did not vary measurably relative to each other (i.e., aqueous trace-metal concentration ratios were roughly constant). This condition is characteristic of water masses in good communication with the global ocean, in which the inventory of dissolved trace metals is sufficiently large as to preclude changes in aqueous concentrations at time scales shorter than the seawater residence time of a given metal (Table 1). Furthermore, centimeter-scale patterns of variation in trace-metal abundances are matched almost exactly by those in the TOC, DOP_T, and Fe_T/Al records (Figs. 7B–7D). The close correspondence among all of these records is evidence that trace-metal concentrations in the midcontinent Pennsylvanian core shales were controlled primarily by paleoredox variation. The fundamental length scale of compositional variation in midcontinent Pennsylvanian core shales is revealed by X-ray radiography to be a few centimeters (Fig. 7A), implying strong variation in benthic redox conditions at time scales

of approximately a few thousand years (Algeo et al., 2004). Given the extreme compositional contrasts between successive centimeter-thick layers, benthic redox and other environmental factors in the Late Pennsylvanian Midcontinent Sea depositional system must have fluctuated dramatically at this time scale.

Paleoceanographic Implications

The trace-metal chemostratigraphy of the study units can be used to address aspects of the hydrology of the Late Pennsylvanian Midcontinent Sea, specifically, whether its deep waters exchanged freely with the global ocean (Algeo et al., 2008a). This issue is of interest with regard to the overall salinity balance of the Late Pennsylvanian Midcontinent Sea (fully marine or brackish?) as well as with regard to controls on primary productivity and benthic redox conditions (which were subject to influence by the nutrient and dissolved oxygen status of any upwelling

deep water masses). The degree of restriction of the Late Pennsylvanian Midcontinent Sea is uncertain owing to potentially conflicting paleontologic and paleogeographic considerations. On the one hand, preserved invertebrate biotas suggest near-normal-marine salinity conditions (Bennington, 1996; Malinky and Heckel, 1998), yet on the other hand, the Late Pennsylvanian Midcontinent Sea was a nearly landlocked interior sea subject to considerable freshwater runoff from surrounding landmasses (as is the modern Baltic Sea, in which salinities are mostly <10‰; Glasby et al., 1997).

Connections of the Late Pennsylvanian Midcontinent Sea to the contemporaneous global ocean were limited to two straits, one of which (the Wyoming Straits) was exceedingly shallow and intermittently closed (Algeo et al., 2008a). The more important connection to the global ocean was through the ~30–40-km-wide Panhandle Strait, which was located in present-day northern Texas between the Bravo Dome and
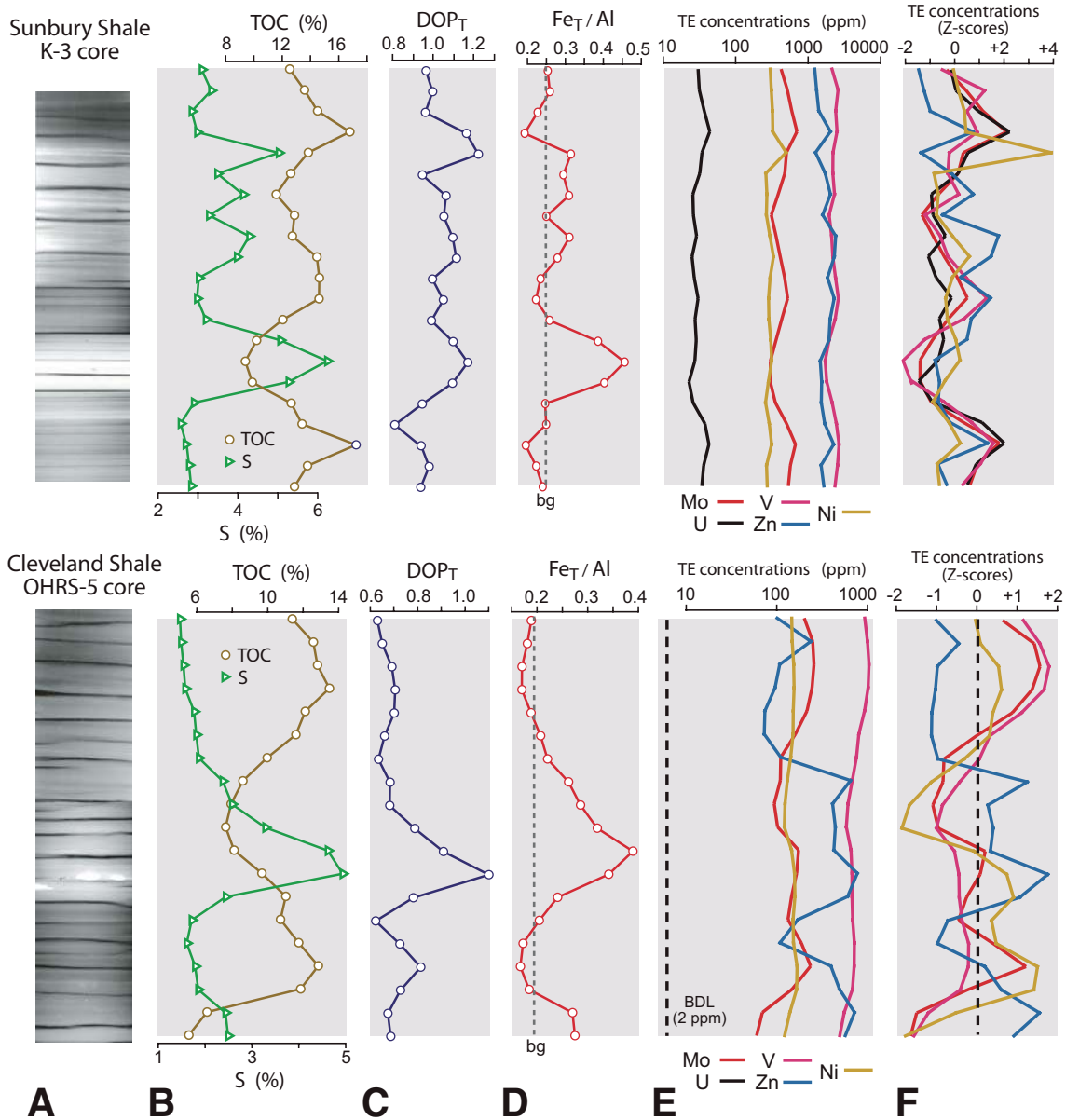
Figure 8. Detailed chemostratigraphic variation of the Cleveland and Sunbury shales in two 20-cm-thick drill core intervals. (A) X-ray radiograph. (B) Total organic carbon (TOC) and S. (C) Degree of pyritization (DOP$_T$). (D) Fe$_T$/Al. (E) Trace-metal concentrations (log scale). (F) Trace-metal concentrations (Z scores; see Methods discussion). In the X-ray radiograph image, lighter and darker hues represent more and less dense areas of the study core, respectively (opposite of Fig. 7); note the absence of fine stratigraphic lamination. BDL—below detection limit; bg—background; TE–trace element.

the western end of the Wichita Uplift (Handford and Dutton, 1980) and formed the terminus of a serpentine, ~1000-km-long deep-water corridor that led from the eastern tropical Panthalassic Ocean through the Greater Permian Basin region and into the Anadarko Basin (the southern, deep-water end of the Late Pennsylvanian Midcontinent Sea; Fig. 4A) (Heckel, 1977; Hill, 1999; Algeo et al., 2008a). The deep-water flux through this strait was estimated to be ~0.09–

0.19×10^6 m³ s⁻¹, equivalent to a flow rate of 0.02–0.07 m s⁻¹ for an average water depth of 200 m at the strait's narrowest point (see Algeo et al., 2008a, for details of calculation). Although tentative, these estimates provide a basis for comparison with modern epicontinental seas such as the Baltic Sea and Hudson Bay.

Deep-water renewal in the Baltic Sea is related to recharge events that are episodic (every few years) and of short duration (1–10

days), yielding a time-averaged flux much lower than the instantaneous flux (~0.2×10^6 m³ s⁻¹; Lass and Matthäus, 1996). Nonetheless, aqueous trace-metal concentrations are close to those of normal modern seawater on a salinity-adjusted basis (Prange and Kremling, 1985), despite substantial trace-metal uptake by the sediment in anoxic deep-water areas (Sternbeck et al., 2000) that might be expected to draw down the trace-metal inventories of the overlying water mass

(Algeo and Lyons, 2006). This example serves to illustrate the point that significant water-mass restriction is necessary to alter aqueous trace-metal concentrations in epicontinental seas. The inference that the Late Pennsylvanian Midcontinent Sea water mass had nearly invariant aqueous trace-metal ratios is thus consistent with relatively unimpeded deep-water exchange with the global ocean, as restricted deep-water exchange typically causes water-mass chemistry to evolve away from that of contemporaneous global seawater (as in modern anoxic silled basins; Fig. 2), leaving a characteristic signature in the sediment (see discussion of Appalachian Devonian–Mississippian shales below).

Comparison with the modern Hudson Bay raises another issue: how was widespread benthic anoxia developed and maintained in the Late Pennsylvanian Midcontinent Sea despite largely uninhibited deep-water exchange? Hudson Bay, which is connected to the Labrador Sea through the ~600-km-long Hudson Strait, has a deep-water flux of ~0.07–0.27 × 10^6 m^3 s^{-1} (Drinkwater, 1986; Algeo et al., 2008a), comparable to estimates above for the Late Pennsylvanian Midcontinent Sea. This flux is sufficient to maintain oxic to weakly suboxic benthic redox conditions throughout Hudson Bay and to limit the accumulation of organic carbon and trace metals in the sediment (Pett and Roff, 1982; Pelletier, 1986; Biksham and d'Anglejan, 1989). Clearly, additional factors must have operated in the Late Pennsylvanian Midcontinent Sea in order for widespread sulfidic conditions to have developed, despite good communication with the global ocean. The key factor appears to have been the location of the entrance of the deep-water corridor leading to the Late Pennsylvanian Midcontinent Sea adjacent to an area of extreme shallowing of the OMZ in the eastern tropical Panthalassic Ocean, similar to shallowing of the OMZ (locally to <100 m) in the modern eastern tropical Pacific (Levitus, 1982; Algeo and Heckel, 2008; Algeo et al., 2008a, 2008b). Shallowing of the OMZ allowed lateral advection of oxygen-deficient intermediate waters through the Greater Permian Basin Sea and into the Late Pennsylvanian Midcontinent Sea. This process was most intense during deglacial stages of Late Pennsylvanian glacioeustatic cycles (corresponding to the lower black shale facies of core shales), as shown by N isotopic and other evidence (Algeo et al., 2008b). This model may resolve a major conundrum concerning the Late Pennsylvanian Midcontinent Sea, i.e., how strongly sulfidic conditions could have developed despite low primary productivity rates and a lack of deep-water restriction (Algeo and Heckel, 2008; Algeo et al., 2008a). Given the preconditioned oxygen-deficient character of laterally advected deep waters, only comparatively low levels of primary productivity were needed in order to completely consume dissolved oxygen below the Late Pennsylvanian Midcontinent Sea pycnocline. This model can also account for evidence of strong, high-frequency (~10^3 yr) environmental fluctuations in the Late Pennsylvanian Midcontinent Sea (Fig. 7), which were probably due to variations in upwelling intensity, freshwater runoff, and pycnocline strength (Algeo et al., 2004; Algeo and Heckel, 2008). The dynamic open-ended (i.e., laterally unconfined) character of the Late Pennsylvanian Midcontinent Sea pycnocline (Fig. 4A) would have made it particularly responsive to short-term climatic and oceanographic changes.

TRACE-METAL PATTERNS IN THE DEVONIAN–MISSISSIPPIAN APPALACHIAN SEA

Secular Trends

At a coarse (>10 m) stratigraphic scale, the Devonian–Mississippian black shale succession of the Central Appalachian Basin consists of intervals of internally uniform but alternately contrasting trace-metal character (Fig. 6D). Leaving aside the Givetian "Geneseo" Formation, which is separated from the overlying units by a highly condensed or missing Frasnian section, the succession begins with the Famennian Huron Member of the Ohio Shale. The lower Huron shale exhibits substantial trace-metal enrichment, particularly strong at its base and declining upsection. The reduced degree of trace-metal enrichment toward the top of the lower Huron shale is inconsistent with concurrent intensification of reducing conditions (Figs. 6B, 6C), suggesting that trace-metal enrichment at the base of the unit was due to stratigraphic condensation rather than to intensely reducing conditions. The overlying middle-upper Huron shale exhibits modest trace-metal enrichment, the degree of which is nearly uniform over a stratigraphic interval of ~30 m (Fig. 6D), in addition to only limited paleoredox variation (Figs. 6B, 6C). Both features are consistent with an inference of relatively static environmental and water-mass conditions during this depositional period. The Three Lick Bed, a series of alternating gray and black shales characterized by lower TOC values and variable trace-metal concentrations, marks the termination of relatively stable conditions in the Devonian–Mississippian Appalachian Sea and the beginning of a period of dynamic change that extended into the Early Mississippian. The overlying Cleveland Member of the Ohio Shale exhibits increasing TOC and divergent trace-metal patterns upsection (Fig. 6D). The degree of divergence among the trace metals becomes more pronounced toward the top of the unit, where Mo and U decrease and V and Zn increase (on both an absolute scale and relative to TOC; Ni also increases on an absolute scale but is constant relative to TOC). These changes coincide with a trend toward generally more reducing conditions (Figs. 6B, 6C). Following an interval of low TOC and trace-metal concentrations corresponding to shallow-marine facies of the Bedford-Berea interval, the overlying earliest Mississippian Sunbury Shale is characterized by strong upsection increases in TOC and trace-metal concentrations (Fig. 6D; note that the degree of enrichment of the trace metals exceeds that of TOC) that are concurrent with a strong intensification of benthic anoxia (Figs. 6B, 6C).

High-Frequency Patterns

The greater thickness of the Devonian–Mississippian black shale succession necessarily results in a larger degree of time averaging of chemostratigraphic data in examining long-term secular trends (Fig. 6) relative to the midcontinent Pennsylvanian core shales (Fig. 5). However, a direct comparison of fine-scale chemostratigraphic patterns is possible owing to centimeter-scale analyses of the Cleveland and Sunbury shales (Jaminski, 1997; Jaminski et al., 1998; Kuhn, 1999). Outcrops of Devonian–Mississippian black shales of the Appalachian Basin exhibit a pervasive stratigraphic rhythmicity at length scales of 10–30 cm (decimeter-scale cyclicity) owing to differential weathering of organic-rich and organic-poor layers (Potter et al., 1982), a feature manifested in drill cores as alternating intervals of high and low TOC values (Fig. 8B; Jaminski et al., 1998). Other geochemical components tend to covary, either positively or negatively, with TOC, although not always in a consistent way within and between study units. The two 20-cm-thick intervals in Figure 8 show typical relationships: (1) total S, DOP$_T$, and Fe$_T$/Al tend to covary positively among themselves and inversely with TOC (Figs. 8B–8D), (2) Mo, V, and Ni tend to covary positively with TOC, as does U when present in measurable quantities (Fig. 8F), and (3) Zn varies unpredictably, sometimes in concert with TOC or total S (Fig. 8F). It should be noted, however, that the total range of concentration variation for trace metals is roughly a factor of two (Fig. 8E), considerably less than that shown by the midcontinent Pennsylvanian core shales above (Fig. 7E). Because TOC in the Devonian–Mississippian shales shows the same factor of two variation (Fig. 8B), there is little variation

in trace-metal concentrations within decimeter-scale cycles on a TOC-normalized basis.

Paleoceanographic Implications

Both the long-term and high-frequency patterns of trace-metal variation discussed above can be integrated into an emerging picture of the environmental and hydrographic conditions that existed in the Devonian–Mississippian Appalachian Sea. The basic control on the formation of decimeter-scale cycles in the Devonian–Mississippian black shale succession of the Central Appalachian Basin was clastic dilution (Jaminski, 1997; Jaminski et al., 1998; Murphy et al., 2000; Sageman et al., 2003). Secular variation in humidity and runoff in surrounding land areas, probably at Milankovitch orbital (20 k.y.?) time scales, resulted in a temporally variable flux of fine siliciclastic material to the Devonian–Mississippian Appalachian Sea (Jaminski et al., 1998). This material was delivered mainly via turbiditic interflows, resulting in a diffuse hemipelagic rainout that contributed to a general lack of discrete bedding features in the Devonian–Mississippian black shale succession (Fig. 8A; Potter et al., 1982; Jaminski et al., 1998; cf. highly laminar character of midcontinent Pennsylvanian core shales, Fig. 7A). The unusual inverse relationship between TOC and total S (which is ~90% pyrite S; Kuhn, 1999) was due to pyrite formation in an Fe-limited system: the TOC-rich layers were Fe poor, causing H_2S generated within them to migrate upward into the overlying more Fe-rich, organic-poor layers (Jaminski, 1997; Jaminski et al., 1998). For this reason, DOP_T and Fe_T/Al (Figs. 8C, 8D) cannot be regarded as faithful recorders of variation in benthic redox conditions at the time scales associated with decimeter-scale cycles. Rather, the limited variation in trace-metal concentrations (Fig. 8E; especially on a TOC-normalized basis) suggests that benthic redox conditions were relatively stable during formation of decimeter-scale cycles.

Environmental stability in the Devonian–Mississippian Appalachian Sea also existed over a much longer interval (i.e., several millions of years), as indicated by the limited amount of chemostratigraphic variation recorded by the middle-upper Huron shale (Fig. 6). This interval of stability was terminated toward the end of the Devonian by climatic cooling and ice sheet formation in the Southern Hemisphere (Streel et al., 2000; Cecil et al., 2004). Growth of continental ice mass caused eustatic elevations to drop in several pulses, probably first recorded by the Three Lick Bed and culminating in the lowstand deltaic siliciclastics of the Bedford-Berea interval (Fig. 6A; Pashin and Ettensohn,

1995). The Cleveland Member of the Ohio Shale, located stratigraphically between the Three Lick Bed and Bedford-Berea, provides a record of water-mass dynamics associated with this eustatic event. The lower Cleveland records a minor transgression following the regressive pulse of the Three Lick Bed. The upper Cleveland, which is the most strongly trace-metal-enriched interval of the Ohio Shale (Robl et al., 1984; Robl and Barron, 1988), has commonly been interpreted as a transgressive black shale (e.g., Johnson et al., 1985), but it is more likely a record of early phases of the eustatic regression that culminated in the Bedford-Berea lowstand (Algeo et al., 2007). This interpretation is supported by evidence of increasing water-mass restriction from both Mo/TOC ratios (Algeo et al., 2007) and divergent trace-metal concentration trends (this study, Fig. 6). The pattern of divergence of trace-metal concentrations in the upper Cleveland implies greater drawdown of the aqueous concentrations of Mo and U relative to Ni, V, and Zn (cf. Fig. 2). Increasing water-mass restriction was a likely consequence of eustatic regression, which resulted in shallowing of silled margins of the Devonian–Mississippian Appalachian Sea, thus limiting overspill of denser, deeper waters from surrounding water masses. A proper assessment of trace-metal concentration patterns is thus critical to interpretation of the sequence stratigraphy of the Devonian-Carboniferous boundary interval in the Appalachian Basin.

CONTRASTS BETWEEN THE LATE PENNSYLVANIAN MIDCONTINENT AND DEVONIAN–MISSISSIPPIAN APPALACHIAN SEAS

Although the two sets of organic-rich units examined in this study are both black shales, they exhibit striking differences in trace-metal patterns and other compositional features that reflect fundamentally different environmental conditions and water-mass dynamics between their respective depositional systems. Ultimately, these differences were a consequence of dissimilar boundary conditions. The Late Pennsylvanian Midcontinent Sea episodically inundated a low-relief cratonic interior as a consequence of large-scale glacioeustatic fluctuations (Heckel, 1986, 1991), resulting in development of widespread benthic anoxia for comparatively short intervals, probably <100 k.y. during each successive glacioeustatic highstand (Algeo et al., 2004). In contrast, the Devonian–Mississippian Appalachian Sea occupied a deep, sill-bounded foreland basin at a time of relative eustatic stability, resulting in the development of persistent anoxic conditions for ~15 m.y., during the Late

Devonian (Potter et al., 1982; Johnson et al., 1985; Ettensohn et al., 1988). The Late Pennsylvanian Midcontinent Sea was connected to the global ocean via a deep-water channel that allowed good water-mass exchange, limiting the potential for evolution of aqueous trace-metal concentrations in the Late Pennsylvanian Midcontinent Sea water mass as a consequence of enhanced removal to the sediment (Algeo and Heckel, 2008; Algeo et al., 2008a). In contrast, Devonian–Mississippian Appalachian Sea deep-waters were strongly restricted (with an estimated renewal time of ~100–500 yr; Algeo et al., 2007), creating the potential for evolution of water-mass chemistry as a function of removal of aqueous trace-metal species to the sediment without an adequate compensatory resupply. These differences influenced trace-metal patterns in the study units: near-constant concentrations (and interelemental ratios) of dissolved trace metals in the Late Pennsylvanian Midcontinent Sea contributed to strong covariation among trace metals in midcontinent Pennsylvanian core shales (Fig. 5), whereas varying concentrations (and ratios) of dissolved trace metals in the Devonian–Mississippian Appalachian Sea resulted in divergent trends in sedimentary trace-metal concentrations as water-mass chemistry evolved (Fig. 6).

Differences in boundary conditions are also reflected in differences in the degree of high-frequency environmental variability exhibited by the two depositional systems. The Late Pennsylvanian Midcontinent Sea had an open-ended (laterally unconfined) pycnocline that could expand and contract spatially in response to short-term climatic and oceanographic changes related to upwelling intensity and freshwater runoff. This situation created a potential for environmental dynamism that is recorded in midcontinent Pennsylvanian core shales as high-frequency ($<10^3$ yr) benthic redox variation over a redox range that probably spanned suboxic to strongly sulfidic conditions (Fig. 7). In contrast, the silled Central Appalachian Basin was a relatively static depositional system for long intervals. The frequency of turbidite interflows within the basin varied in response to changes in humidity and freshwater runoff within the basin watershed at intermediate (~20 k.y.) time scales (Fig. 8; Jaminski, 1997; Jaminski et al., 1998), but the basin maintained a pycnocline that varied only marginally in strength during much of the Late Devonian (Fig. 6). Trace-metal patterns provide one other piece of information about conditions in the Devonian–Mississippian Appalachian Sea, i.e., that benthic redox variation must have been frequent at time scales too short for stratigraphic resolution. This inference is based upon the contrasting behaviors of Mo

and U in the Devonian–Mississippian black shale succession (Figs. 6 and 8). Mo is markedly enriched (to several hundred ppm) over background detrital levels (~3 ppm), providing evidence that sulfidic conditions must have been common (Helz et al., 1996; Vorlicek and Helz, 2002). In contrast, U concentrations are generally low (few ppm to tens of ppm) and prone to change abruptly, frequently declining to <2 ppm in association with pyrite-rich layers (Fig. 8). Because U is the most easily remobilized redox-sensitive trace metal when benthic redox conditions switch from reducing to oxidizing (Thomson et al., 1995, 1998), this pattern suggests that sediments on the Devonian–Mississippian Appalachian Sea seafloor must have been frequently exposed to dissolved oxygen (e.g., via turbiditic interflows; Jaminski, 1997; Jaminski et al., 1998), and that the frequency of oxygenation events increased in association with the organic-poor clay-rich layers (which reflect an increased flux of fine siliciclastics, thus diluting the organic carbon content of the sediment; Fig. 8; Jaminski et al., 1998; Murphy et al., 2000; Sageman et al., 2003). Trace-metal patterns thus have the potential to provide insights regarding paleoenvironmental dynamics over a wide range of temporal scales.

CONCLUSIONS

Strong positive covariation among trace metals in the Hushpuckney Shale, a cyclothemic core shale deposited in the Late Pennsylvanian Midcontinent Sea, provides evidence of derivation from a water mass of temporally invariant trace-metal composition, i.e., contemporaneous "normal" seawater. Stratigraphic variation in trace-metal concentrations was controlled primarily by benthic redox fluctuations at short time scales (~10^3 yr), reflecting dynamic exchange of Late Pennsylvanian Midcontinent Sea deep waters with the global ocean via a deep-water corridor through the Greater Permian Basin Sea. In contrast, the Upper Devonian Ohio Shale exhibits divergent trace-metal concentration trends, with increases in V and Zn and concurrent decreases in Mo and U upsection. By analogy with modern anoxic silled basins having restricted deep waters prone to secular changes in trace-metal concentrations, this pattern suggests that deep waters of the Devonian–Mississippian Appalachian Sea evolved chemically through time as a result of differential rates of removal of trace metals to the sediment. Thus, patterns of chemostratigraphic covariation among trace metals have the potential to reveal aspects of the evolution of water-mass chemistry and basin hydrography in anoxic marine paleoenvironments.

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