An ancient estuarine-circulation nutrient trap: The Late Pennsylvanian Midcontinent Sea of North America

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ABSTRACT
The Late Pennsylvanian Midcontinent Sea (LPMS) of North America, which existed during glacioeustatic highstands of the Late Paleozoic ice age, was an immense (>1 × 10⁶ km²) cratonic interior sea exhibiting large-scale estuarine circulation, with a low-salinity surface plume overlaying a high-salinity, anoxic, deep water mass. As in river estuaries, these conditions resulted in trapping and recycling of nutrients and organic-reactive elements (e.g., trace metals such as Mo, U, and Zn) in the subpycnocinal water mass, leading to total organic carbon (TOC) to 40% and peak trace metal enrichment factors (EFs) of 540 (Mo), 73 (U), and 75 (Zn) in the black shale facies of the Hushpuckney Shale. Trace metal EFs increase gradually from distal (Oklahoma) to proximal (Iowa) areas of the Midcontinent Shelf before decreasing abruptly in the Illinois Basin, located to the east of the Mississippi River Arch (MRA). Owing to similar productivity (TOC) and redox (Fe-T/Al) proxy values on both sides of this arch, the large differences in trace metal EFs are interpreted to reflect divergent deep-water chemistries; specifically, much larger aqueous trace metal inventories on the Midcontinent Shelf than in the Illinois Basin. This condition implies that (1) deep waters of the Midcontinent Shelf and Illinois Basin were physically separated by the MRA, demonstrating its existence as a positive bathymetric feature during the Late Pennsylvanian, and (2) the saltwater wedge to the west of the MRA functioned as a nutrient trap in which organic-trace metal metals were strongly concentrated through water-column recycling.

INTRODUCTION
Estuaries commonly function as nutrient traps, in which nutrients (e.g., N and P) and organic-reactive elements (e.g., many trace metals) become concentrated through a combination of sinking organic matter (i.e., the biological pump) and proximally directed flow of the deep layer (Fig. 1A; Shiller, 1996). One contributing factor is strong vertical stratification, which develops due to a large density differential between the low-salinity surface plume and the underlying saltwater wedge. Another factor is elevated productivity levels, which are stimulated by recycling of nutrients (Fig. 1B; Edmond et al., 1981; Twomey and John, 2001) that can become concentrated through water-column recycling. Trace metal enrichment of estuarine sediments occurs through adsorption onto sinking organic particles or colloids, a process that is greatly accelerated if the deep layer is reducing (Dai et al., 1995). Trace metals commonly cycle between estuarine sediments and the water column as a function of redox transients (Audry et al., 2006), although factors such as salinity, pH, and particle loading can also be important (Hatje et al., 2003).

Large-scale estuarine circulation developed within the ~2000-km-wide, nearly land-locked Late Pennsylvanian Midcontinent Sea (LPMS) of North America as a result of a highly positive water balance and restricted outflow (Fig. 2A; Algeo and Heckel, 2008; Algeo et al., 2008). The deep-water layer of the LPMS was anoxic across a large area, a redox condition resulting from a combination of strong vertical stratification and lateral advection of oxygen-deficient thermocline waters from the eastern tropical Panthalassic Ocean (Fig. 2B). Apart from the deep Anadarko-Arkoma Basin on its southern margin, the LPMS was relatively shallow (<200 m) and exhibited limited bathymetric variation (Heckel, 1977; see Item DR1 (geological background) in the GSA Data Repository1 for further paleogeographic information).

Figure 1. A: Model of estuarine circulation with trapping and recycling of nutrients and organic-reactive elements (OM—organic matter). Landward flow of the deep-water layer leads to progressive concentration of these elements in the saltwater wedge, a signal that can be transferred to the sediment (arrow size reflects relative sedimentary trace metal enrichment). B, C: Example of nutrient trapping (aqueous phosphate and nitrate) in the lower Amazon River estuary, Brazil (adapted from Edmond et al., 1981).

The location of the LPMS in the humid tropics resulted in massive freshwater runoff into the sea, an effect accentuated by monsoonal circulation linked to the equator-straddling Alleghenian-Ouachita-Marathon orogens (Parrish, 1993; Tabor and Poulsen, 2008). Circulation within the LPMS was laterally confined with a connection to the global ocean through the narrow Panhandle Strait at its western end (Fig. 2A; Algeo and Heckel, 2008; Algeo et al., 2008). The deep-water layer of the LPMS was anoxic across a large area, a redox condition resulting from a combination of strong vertical stratification and lateral advection of oxygen-deficient thermocline waters from the eastern tropical Panthalassic Ocean (Fig. 2B). Apart from the deep Anadarko-Arkoma Basin on its southern margin, the LPMS was relatively shallow (<200 m) and exhibited limited bathymetric variation (Heckel, 1977; see Item DR1 (geological background) in the GSA Data Repository1 for further paleogeographic information).

Sedimentary trace metal enrichment factors have the potential to provide insights about aqueous chemical conditions, bio-cycling processes, and deep-water restriction. In this study we examined variation of trace metals and other geochemical proxies in the upper Pennsylvanian (Missourian) Hushpuckney Shale in 8 sections, 7 of which represent an ~580 km transect across the Midcontinent Shelf from Oklahoma to Iowa and 1 from the Illinois Basin to the east (Fig. DR1). Our analysis was limited to the black shale facies of the Hushpuckney (defined as total organic carbon (TOC) to 40%).

1GSA Data Repository item 2018033, geological background, drill core information, and geochemical datasets, is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.
organic carbon, TOC ≥ 5%), which ranges from 50 to 65 cm in thickness in all study units except for CTW (140 cm thick), contains as much as 40% TOC (mean ~15%), and exhibits substantial trace metal enrichment (Fig. 3). The main goals of this study were to evaluate lateral variation in trace metals and other geochemical proxies as possible evidence for (1) development of an estuarine nutrient trap within the LPMS, and (2) the degree of deep-water exchange or isolation between the Midcontinent Shelf and the Illinois Basin, and its implications for the bathymetric prominence of the Mississippi River Arch (MRA) during the Late Pennsylvanian.

METHODS

Major and trace element concentrations were measured using a wavelength-dispersive Rigaku 3040 X-ray fluorescence spectrometer with an analytical precision better than ±2% for major and ±5% for trace elements. Carbon and sulfur elemental concentrations were measured using an Eltra 2000 C-S analyzer with an analytical precision better than ±2.5% for carbon and ±5% for sulfur. All analyses were carried out at the University of Cincinnati (Ohio), and results were calibrated using U.S. Geological Survey and internal laboratory standards. Enrichment factors (EFs) were calculated as: $X_{EF} = \frac{(X/Al)_{sample}}{(X/Al)_{AUCC}}$, where X is the trace metal of interest and AUCC is average upper continental crust (from McLennan, 2001). To facilitate comparison of EFs between study units, we calculated the 16th, 50th, and 84th percentiles (i.e., median ±1σ) for each geochemical proxy (Fig. 3). See Item DR2 for detailed information about the study cores and full geochemical results.

RESULTS

All proxies exhibit systematic spatial variation across the LPMS from distal (oceanward) areas on the southwest to proximal (cratonward) areas on the northeast (Fig. 3). The vertical bars represent the 84th to 16th percentile range (the 50th to 16th percentile is colored) for each geochemical proxy at a given study locale (study locales are shown in Fig. 2; information given in Table DR1; see footnote 1). Note relative uniformity of TOC, TS, and FeT/Al versus changes in trace metal EFs across the Mississippi River Arch. Because the Hushpuckney black shale has a nearly uniform thickness across the study area (Algeo and Heckel, 2008), variations in elemental concentrations are not due to site-specific sedimentation rates (except for CTW, where dilution is linked to increased thickness).
on the northeast (Fig. 3). TOC exhibits relatively uniform values (median 15%–18%) except for CTW (11%), which is affected by siliciclastic dilution in the Anadarko Basin, and CC (22%), which is located in the Illinois Basin and shows divergent values for most proxies. Total sulfur (TS) shows similar values (~2.0%–2.4%) in all sections except for CTW (7.1%) and CL (3.5%), in which higher sulfur contents may have been due to more intense microbial sulfate reduction at deeper locales. The redox proxy Fe₄/Al exhibits nearly uniform values (0.55–0.58) in all sections except CTW (1.00) and CL (0.83), which are deeper, more reducing locales, and CC (0.44), a locale within the Illinois Basin that may have been somewhat less reducing. Trace metals exhibit increasing concentrations and EFs from distal to proximal regions of the Midcontinent Shelf, followed by large declines into the Illinois Basin (Fig. 3). Mo concentrations increase from 9 to 391 ppm (EF = 30–540), U concentrations increase from 7 to 60 ppm (EF = 7–73), and Zn concentrations increase from 124 to 2300 ppm (EF = 6–75) across the Midcontinent Shelf, before declining to 10, 18, and 62 ppm (EFs of 19, 18, and 7), respectively, in the Illinois Basin (Fig. 3; Tables DR1 and DR2).

MISSISSIPPI RIVER ARCH AS A BATHYMETRIC HIGH

The LPMS seafloor had limited bathymetric relief over wide areas, broken only by local structural highs such as the Nemaha uplift in Kansas and the Mississippi River and Cincinnati Arches that separated the Midcontinent Shelf, Illinois Basin, and Appalachian Basin (Fig. 2; Kolata and Nelson, 1990). These features were submergent during Late Pennsylvanian eustatic highstands and did not affect oceanward flow of the low-salinity surface plume of the LPMS (Heckel, 1977; Algeo et al., 2008). However, the extent of their influence on deep circulation within the LPMS remains uncertain. The LPMS is known to have exhibited marine influence (i.e., at least brackish conditions) into the Appalachian Basin, based on marine invertebrate fossils in the upper Pennsylvanian Conemaugh Group (e.g., Fahrer, 1996), yet the Hushpuckney black shale extends only as far east as the Illinois Basin (where it is known as the Macoupin shale). Its stratigraphic equivalent in the Appalachian Basin is the Brush Creek Limestone (Heckel, 2013), which was deposited on an oxygenated seafloor due to eastward shallowing or a bathymetric barrier (e.g., the Cincinnati Arch) to cratonward advection of anoxic deep waters.

The first issue we address is whether the Hushpuckney and Macoupin black shales represent a formerly continuous anoxic facies extending from the Midcontinent into the Illinois Basin that was later erosionally truncated through uplift of the MRA (Fig. 2). Our results indicate that the deep anoxic water mass of the Midcontinent Shelf exhibited slow, progressive changes in chemical composition over hundreds of kilometers, but that an abrupt change occurred across the MRA, implying that deep waters of the Illinois Basin were physically isolated from those of the Midcontinent Shelf. This inference is supported by gradually increasing concentrations and EFs of trace metals from distal to proximal regions of the Midcontinent Shelf, followed by large (5–25×), abrupt declines into the Illinois Basin (Fig. 3). In contrast, differences in productivity and redox proxies are small: TOC is only slightly higher in the Illinois Basin (22%) than on the Midcontinent Shelf (15%–18%) and Fe₄/Al values are only slightly lower (0.44 versus 0.55–0.58) (Fig. 3). Chemical differentiation of the deep-water masses required the existence of the MRA as a large bathymetric ridge during the Late Pennsylvanian. This inference is consistent with renewed uplift of the MRA during the Late Mississippian to early Permian in response to compressional forces of the Alleghenian orogeny (Kolata and Nelson, 1990).

A contributing factor to differences in deep-water chemistry between the Midcontinent Shelf and Illinois Basin was reduced salinity in the latter. Deep waters of the LPMS were sourced from laterally advected, oxygen-deficient thermoclineal waters of the eastern tropical Panthalassic Ocean (Algeo et al., 2008), but lateral salinity gradients in the surface layers of the Midcontinent Shelf (Herrmann et al., 2015), Illinois Basin (Rosenau et al., 2014), and Appalachian Basin (Roark et al., 2017) have been inferred on the basis of conodont biofacies and oxygen isotopes. Illinois Basin waters are likely to have been brackish owing to strong freshwater runoff from uplands in eastern Laurentia (Archer and Greb, 1995). The degree of salinity reduction is not known, but the presence of marine fossils in the Appalachian Basin suggests salinities no lower than ~7–15 psu (practical salinity units); i.e., the threshold in modern estuarine systems at which dominantly marine faunas are replaced by hyposaline faunas (Pemberton and Wightman, 1992; Buatois and Mángano, 2011). This inference is supported by TOC-normalized trace metal data, which show that distal Midcontinent Shelf sections (which do not show the extreme enrichments of proximal sections) are nonetheless ~1.5–3× enriched in Mo, U, and Zn relative to the Illinois Basin (Fig. 3).

DEVELOPMENT OF A NUTRIENT TRAP ON THE MIDCONTINENT SHELF

The second issue we address is the effects of the MRA on deep-water circulation and chemistry of the Midcontinent Shelf. If the MRA was an effective bathymetric barrier during the Late Pennsylvanian (Fig. 2B), then the deep layer of the Midcontinent Shelf must have tapered northeastward, producing a saltwater wedge with distinct compositional characteristics, as in modern estuaries (Fig. 1A). The distinct chemistry of the saltwater wedge on the Midcontinent Shelf is shown by extraordinary trace metal enrichments from distal to proximal shelf regions; e.g., 28× for Mo (EF = 540/19), 4× for U (EF = 73/18), and 11× for Zn (EF = 757) (Fig. 3). These increases in the inner shelf region are not relative to low crustal background concentrations, but rather relative to average values for black shales on the outer to middle Midcontinent Shelf.

Lateral gradients in trace metal EFs might have been controlled by spatial variation in productivity or redox conditions, but TOC and Fe₄/Al values do not support such an interpretation because they are nearly uniform across the Midcontinent Shelf (15%–18% for TOC, and 0.55–0.58 for Fe₄/Al; Fig. 3). Given a lack of significant variation in the amount of organic matter available as a substrate for trace metal uptake, the most likely cause of sedimentary enrichments in a strongly reducing facies is elevated aqueous trace metal concentrations. The extreme trace metal enrichments observed in inner shelf regions of the Midcontinent Shelf are indicative of trapping and recycling of trace metals within an estuarine saltwater wedge (Fig. 1A; cf. Hatje et al., 2003; Audry et al., 2006). Such processes may have been particularly intense in the LPMS due to the size of the estuarine circulation cell that existed within this cratonic interior sea (Fig. 2) and the intensity of upwelling of nutrient-rich thermoclineal waters along its distal margin (Heckel, 1977; Algeo et al., 2008).

Patterns of relative enrichment among trace metals may provide information regarding trapping and recycling processes within the saltwater wedge. Modern estuarine systems invariably show spatial variations in EFs among different trace metals, although such patterns tend to be specific to individual estuaries and reflect a complex response to local variations in redox conditions and adsorption-desorption reactions involving various solid phases (e.g., organic matter, sulfides, Fe-oxides, and clay minerals; Dai et al., 1995; Hatje et al., 2003; Audry et al., 2006). In modern estuaries, recognition of enrichments related to recycling processes in the saltwater wedge is complicated by high anthropogenic trace metal loadings. In the LPMS, Mo shows by far the largest enrichments of proximal sections) are nonetheless ~1.5–3× enriched in Mo, U, and Zn relative to the Illinois Basin (Fig. 3).
CONCLUSIONS
Lateral variations in trace metal enrichment factors (EFs) can provide insights into cratonic sea circulation patterns, deep-water conditions, and mechanisms of trace metal enrichment. In the LPMS of North America, large increases in the EFs of Mo, U, and Zn from distal to proximal areas document the existence of a saltwater wedge within which intense trace metal trapping and recycling took place. Abrupt decline in trace metal EFs in the Illinois Basin indicates that the Mississippi River Arch was a positive bathymetric feature separating deep waters to its east and west during the Late Pennsylvanian, and that salinities were probably brackish in the Illinois Basin versus fully marine on the Midcontinent Shelf.

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