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Hydrographic conditions of the Devono–Carboniferous North American Seaway inferred from sedimentary Mo–TOC relationships

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Abstract

Deepwater anoxia developed widely within a series of silled intracratonic basins in North America during the Middle Devonian to Early Carboniferous, but the hydrographic factors contributing to this development are virtually unknown. The present study demonstrates that the degree of enrichment of strongly hydrogenous elements such as molybdenum (Mo) in the organic-rich shales that accumulated in these basins has the potential to provide information about paleohydrographic conditions. Most of the study units (49 of 55) exhibit significant positive covariation between elemental Mo and TOC concentrations, yet there is substantial variation in the statistical parameters that define these relationships. Specifically, the regression lines characterizing Mo–TOC covariation have slopes (m) ranging from ~2 to 65 ($\times 10^{-4}$), although a majority of the study units yield m values between 10 and 25 ($\times 10^{-4}$). The parameter m exhibits systematic stratigraphic variation within individual basins and geographic variation among basins, suggesting that Mo–TOC relationships were controlled by slowly evolving watermass characteristics of the Devono–Carboniferous North American Seaway. A recent study of modern anoxic silled basins [Algeo, T.J., Lyons, T.W., 2006. Mo-total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. Paleoceanography 21, PA1016. doi:10.1029/2004PA001112] demonstrated that m is closely linked to the degree of restriction of the subpycnoclinal watermass, as reflected in aqueous Mo concentrations ($[Mo]_{aq}$) and deepwater renewal times (τ_{dw}). These relationships reflect control of sedimentary Mo enrichment by both the amount of sedimentary organic matter (i.e., host-phase availability) and the concentration of aqueous Mo (i.e., source-ion availability). When applied to black shales of the Devono–Carboniferous North American Seaway, these relationships permit both qualitative and quantitative inferences regarding the degree of restriction of deepwaters in cratonic basins and the evolution of hydrographic conditions through time. Black shales associated with early stages of sea-level rise commonly exhibit low m values (<10) owing to limited transgression of basin-margin sills, implying $[Mo]_{aq}<20\%$ of the normal seawater concentration and $\tau_{dw}>1000$ yr. Higher sea-level stands resulted in more open-marine conditions and enhanced deepwater renewal, leading to deposition of black shales with m values up to ~65, equivalent to $[Mo]_{aq}>70\%$ of the normal seawater concentration and $\tau_{dw}<100$ yr. The regression lines characterizing Mo-TOC covariation also exhibit considerable variation in their X-intercepts (b_x). The source of this variation is less well understood but probably reflects facies-specific relationships between organic carbon sinking fluxes and benthic redox potential, which are influenced by sedimentation rates, organic matter lability, the oxygen status of renewing deepwaters, and other factors. This study

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demonstrates that sedimentary Mo–TOC data have considerable potential for analysis of paleohydrographic conditions in anoxic marine facies.

Keywords: Molybdenum; Organic carbon; Redox; Trace elements; Seawater chemistry; Residence time

1. Introduction

Sedimentary Mo concentrations are commonly employed as a paleoredox proxy, with higher values interpreted to reflect lower redox potentials (Jones and Manning, 1994; Piper, 1994; Dean et al., 1997, 1999; Werne et al., 2002; Sageman et al., 2003; Meyers et al., 2005). Anoxic facies are almost invariably enriched in Mo relative to oxic and suboxic facies, and the mechanism of this enrichment process has been elucidated by recent research. Mo uptake occurs primarily at or below the sediment-water interface via downward diffusion of MoO_4^{2-}, even in euxinic environments (Helz et al., 1996; Zheng et al., 2000; Algeo and Maynard, 2004). This process is catalyzed by a critical activity of hydrogen sulfide (in the range of 10^{-7} to 10^{-4}, depending on environmental conditions and the pathway of Mo uptake), which facilitates conversion of aqueous molybdate (MoO_4^{2-}) to thiomolybdates ($MoO_xS_{(4-x)}^{2-}$) that are subsequently scavenged by pyrite and/or humic materials (Emerson and Huested, 1991; Crusius et al., 1996; Helz et al., 1996; Zheng et al., 2000). Although other factors are thought to have an influence on the rate of Mo transfer to the sediment (Erickson and Helz, 2000; Vorlicek and Helz, 2002), this mechanism implies that a decrease in benthic redox potential within an anoxic marine environment generally should result in enhanced uptake of Mo by the sediment.

The relationship between benthic redox potential and sedimentary Mo concentrations is, in fact, not as simple as previously assumed owing to the influence of hydrographic factors on sedimentary Mo concentrations (Algeo and Lyons, 2006). Modern seawater contains ~105±5 nmol kg^{-1} (Wright and Colling, 1995), but anoxic silled basins generally exhibit lower concentrations as a consequence of rates of Mo uptake by the sediment exceeding rates of Mo resupply by deepwater renewal. As a fraction of the salinity-normalized seawater concentration, deepwater $[Mo]_{aq}$ is ~80–100% in Saanich Inlet, ~70–85% in the Cariaco Basin, ~20–30% in Framvaren Fjord, and ~3–5% in the Black Sea (Fig. 1; Emerson and Huested, 1991; Algeo and Lyons, 2006). Further, deepwater $[Mo]_{aq}$ exhibits a strong negative correlation to deepwater renewal time, which is ~1.5 yr in Saanich Inlet, ~50–100 yr in the Cariaco Basin, ~50–1600 yr in Framvaren Fjord, and ~500–4000 yr in the Black Sea. Deepwater Mo concentrations and renewal times both ultimately reflect the rate of deepwater exchange relative to basin volume, which is strongly influenced by basin and sill geometry. The subpycnoclinal watermass of large basins with shallow sills is less readily exchanged, resulting in shallower and more stable chemoclines (e.g., the Black Sea); the converse applies to small basins with deep sills (e.g., Saanich Inlet; Fig. 1).

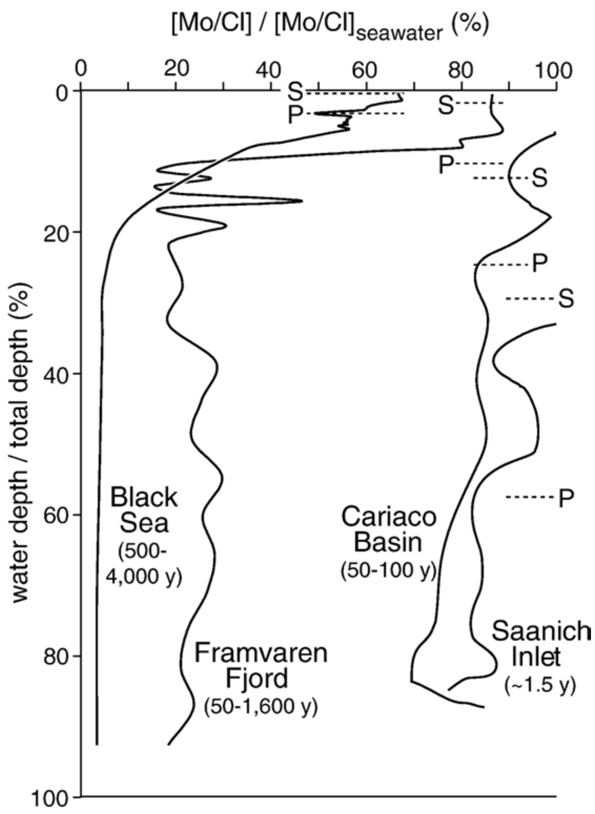

Fig. 1. Aqueous Mo concentration profiles for modern anoxic silled basins. $[Mo]_{aq}$ (abscissa) is given on a seawater-normalized basis to correct for salinity differences between environments; water depth (ordinate) is normalized to total basin depth to facilitate inter-basin comparisons. Basin sill (S) and pycnocline (P) depths and deepwater renewal times (in parentheses) are shown for each environment. Modified from Algeo and Lyons (2006).

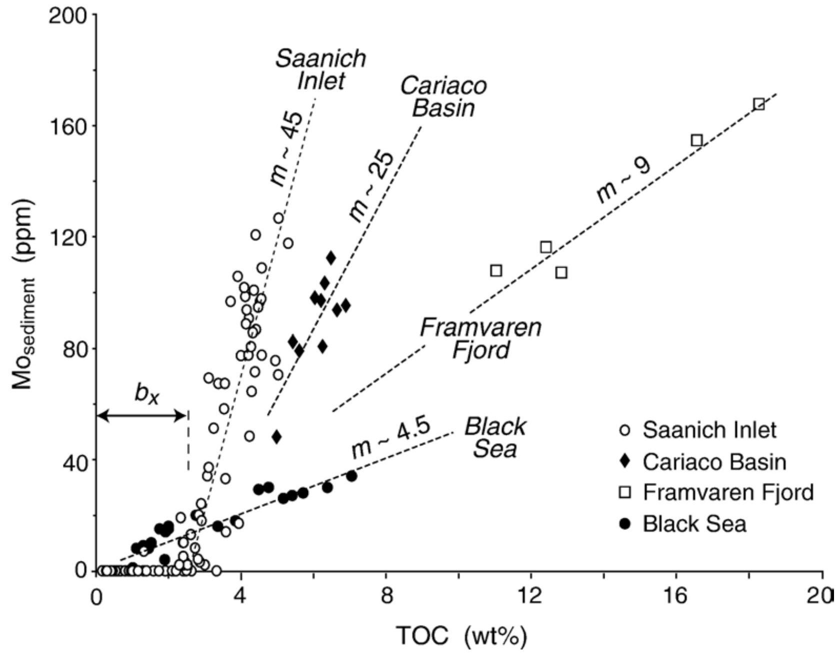

Fig. 2. Mo versus TOC for Recent sediments of modern anoxic silled basins. Regression-line slopes (m) shown for all environments, and example of X-intercept (b_x) shown for Saanich Inlet. Regression-line parameters (m in units of 10^{-4}, and b_x in units of % TOC): Saanich Inlet, $m \sim 45 \pm 5$, $b_x \sim 3.0$; Cariaco Basin: $m \sim 25 \pm 5$, $b_x \sim 2.5$; Framvaren Fjord: $m \sim 9 \pm 2$, $b_x \sim 0$; Black Sea: $m \sim 4.5 \pm 1$, $b_x \sim 0$. Modified from Algeo and Lyons (2006).

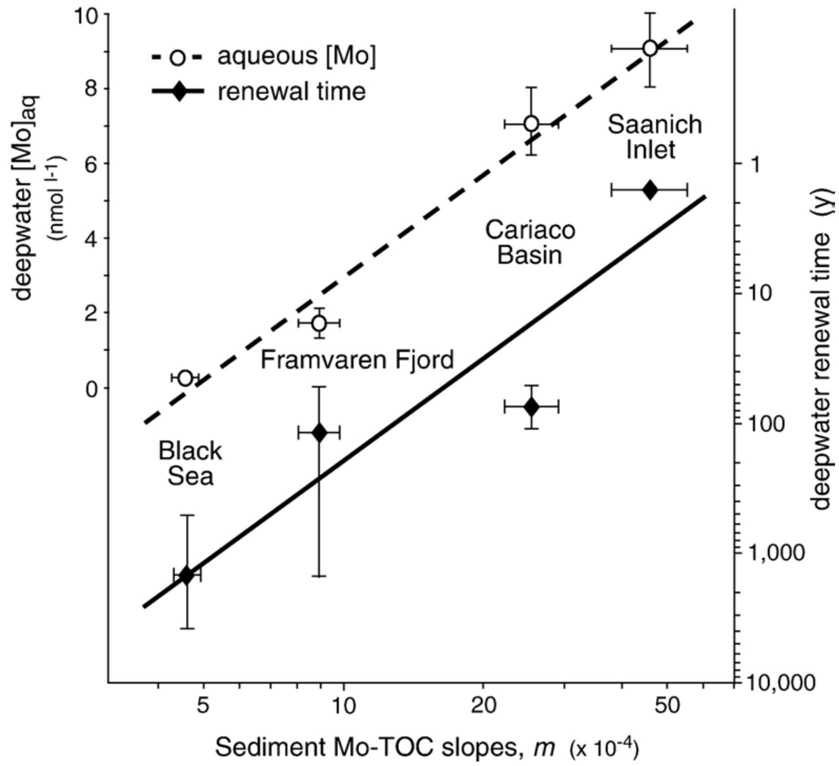

Fig. 3. Sediment Mo–TOC regression-line slopes (m) versus deepwater $[Mo]_{aq}$ (open circles) and renewal times (solid diamonds) for modern anoxic silled basins. Covariation of m with deepwater $[Mo]_{aq}$ and renewal time is statistically significant, yielding r^2 values of 0.99 ($p(\alpha) < 0.01$) and 0.87 ($p(\alpha) \sim 0.05$) for log–linear and log–log relationships, respectively. Modified from Algeo and Lyons (2006).

The amount of Mo taken up by sediments in modern anoxic marine environments is dependent on the concentrations of both sedimentary organic matter (i.e., host-phase availability) and aqueous Mo (i.e., source-ion availability):

$$[\mathrm{Mo}]_s \equiv [\mathrm{TOC}]_s \cdot [\mathrm{Mo}]_{aq}, \qquad (1)$$

or

$$[\mathrm{Mo}]_s / [\mathrm{TOC}]_s \equiv [\mathrm{Mo}]_{aq} \qquad (2)$$

where the subscripts s and aq denote sedimentary and aqueous, respectively (Algeo and Lyons, 2006). Sediments in modern anoxic silled basins exhibit characteristic $[\mathrm{Mo}]_s/[\mathrm{TOC}]_s$ regression-line slopes (m): $\sim 45\times10^{-4}$ for Saanich Inlet, $\sim 25\times10^{-4}$ for the Cariaco Basin, $\sim 9\times10^{-4}$ for Framvaren Fjord, and $\sim 4.5\times10^{-4}$ for the Black Sea (Fig. 2). Weakly restricted basins with strong deepwater renewal (e.g., Saanich Inlet) accumulate more Mo *per unit organic carbon*, reflected in higher m values, than strongly restricted basins subject to limited deepwater renewal (e.g., Black Sea). This is demonstrated by strong positive correlation of m with proxies for deepwater restriction, e.g., deepwater Mo availability and deepwater renewal times (Fig. 3; Algeo and Lyons, 2006). Sediment Mo concentrations are capable of recording benthic watermass characteristics because Mo scavenging by sediments occurs mainly at or just below the sediment-water interface (Emerson and Huested, 1991; Crusius et al., 1996; Zheng et al., 2000). Degree of hydrographic restriction may represent a fundamental control on aspects of sediment geochemistry, especially the concentrations of dominantly hydrogenous elements. Recognition of the importance of watermass restriction, and of the sedimentary chemical attributes that define it, significantly increases the utility of modern anoxic environments as analogs for anoxic paleoenvironments, even when the boundary conditions of the latter do not exactly match those of the former.

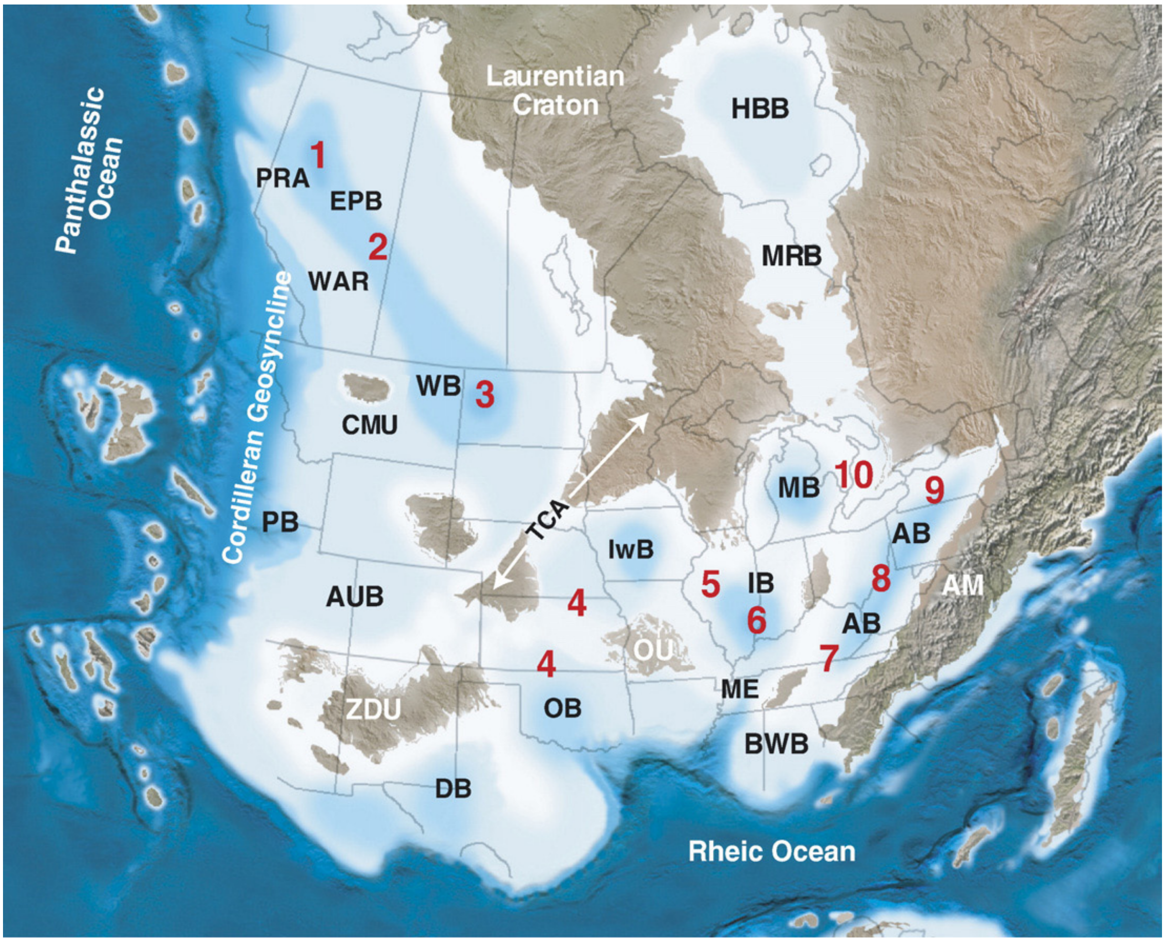

Fig. 4. Late Devonian paleogeography of North America. Geographic abbreviations: AB = Appalachian Basin, AM = Appalachian Mountains, AUB = Ancestral Uinta Basin, BWB = Black Warrior Basin, CMU = Central Montana Uplift, DB = Delaware Basin, EPB = Elk Point Basin, HBB = Hudson Bay Basin, IB = Illinois Basin, IwB = Iowa Basin, MB = Michigan Basin, ME = Mississippi Embayment, MRB = Moose River Basin, OB = Oklahoma Basin, OU = Ozark Uplift, PB = Pilot Basin, PRA = Peace River Arch, TCA = Trans-Continental Arch, WAR = West Alberta Ridge, WB = Williston Basin, ZDU = Zuni-Defiance Uplift. The numbers 1 to 10 are keyed to stratigraphic columns in Fig. 9.

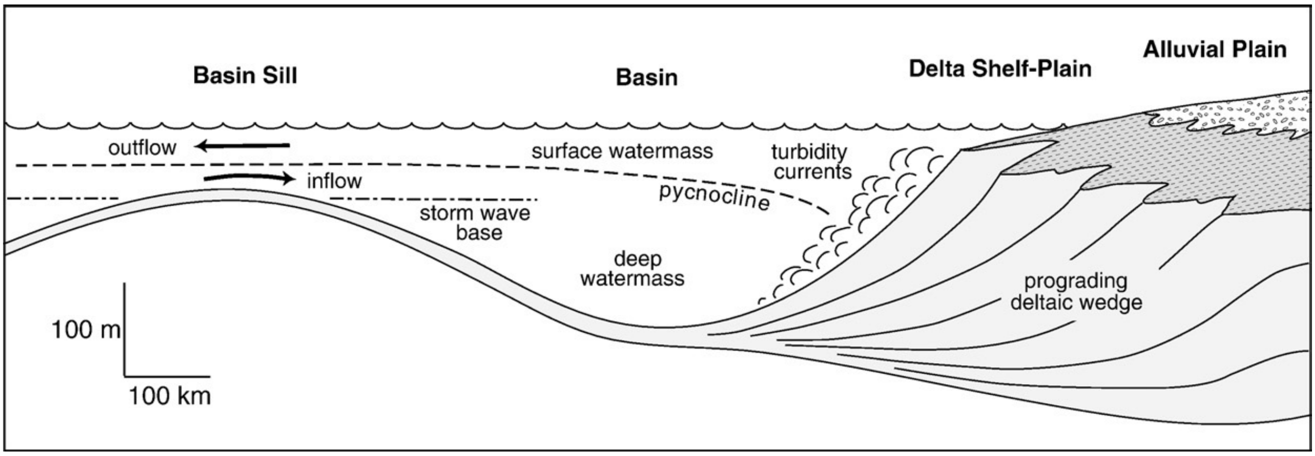

Fig. 5. Generalized depositional model for Devono-Carboniferous black shales of the Appalachian Basin. Scales are approximate. Modified from Potter et al. (1982) and Ettensohn and Elam (1985).

The relationships documented above provide a potential basis for assessing hydrographic conditions in ancient anoxic silled basins. Many organic-rich facies, both modern and ancient, exhibit significant positive covariation between Mo and TOC (e.g., Holland, 1984; Robl and Barron, 1988; Ripley et al., 1990), yet relatively few studies have examined the significance of such covariation (Algeo and Maynard, 2004; Wilde et al., 2004; Algeo and Lyons, 2006). In the present study, we examine Mo–TOC relationships among the many black shale formations of Middle Devonian to Early Carboniferous age that were deposited in anoxic silled basins across the North American craton. Most of these formations exhibit statistically significant linear covariation between Mo and TOC, with substantial variation in Mo/TOC ratios between and, in some cases, within individual formations. Our analysis suggests that patterns of Mo–TOC covariation in these shales may have been controlled largely by paleohydrographic factors, and that sedimentary Mo/TOC ratios may allow estimation of deepwater Mo concentrations and renewal times for the Devono–Carboniferous North American Seaway-parameters that heretofore have been difficult or impossible to reconstruct for paleoenvironments. In addition, we examine spatio-temporal trends in Mo–TOC relationships in these formations that might comment on larger eustatic and tectonic influences on penecontemporaneous sedimentation across the North American craton.

2. Devono–Carboniferous black shales of North America

2.1. Stratigraphic framework

Marine black shales of Middle Devonian to Early Carboniferous age were deposited widely across the North American craton (Fig. 4), and they have been correlated in detail on the basis of wireline logs and conodont biostratigraphy (Potter et al., 1982; Robl et al., 1983; de Witt and Roen, 1985; Robl and Barron, 1988; Woodrow et al., 1988; Landing and Brett, 1991; Roen and Kepferle, 1993; Over, 1997, 2002). In the northern Appalachian Basin (NAB), the marine black shale succession begins with the Esopus and Needmore shales of early Eifelian age. These are overlain by the Marcellus Group (the oldest unit examined in this study), the Hamilton Group, and the Geneseo through Dunkirk shales of late Eifelian to early Famennian age (Woodrow et al., 1988; Werne et al., 2002; Sageman et al., 2003; n.b., stratigraphic relationships are shown in Fig. 9 and are not duplicated here). Post-Dunkirk sediments in the NAB are dominantly terrigenous siliciclastics of the "Catskill facies." The marine black shale succession is younger in the central (CAB) and southern (SAB) Appalachian basins, ranging from mid-Frasnian to Early Tournaisian in age. The ~60-m-thick CAB succession includes the Upper Olentangy, Ohio, and Sunbury shales, whereas the correlative units of the SAB are thinner (1–10 m) and assigned to the Chattanooga Shale (Ettensohn et al., 1989; Ettensohn, 1992; Roen and Kepferle, 1993). Organic-rich sediments of pre-Late Devonian age are rare in the CAB and SAB. Givetian black shales are found in limited areas in northeastern Kentucky and have been designated the "Duffin facies" of the Portwood Member of the New Albany Shale by Ettensohn (1992). However, these units accumulated *east* of the Cincinnati Arch, in fault-bounded basins or incised valleys during initial transgressive onlap of the craton. They are approximately correlative with the Geneseo Formation of New York State and should be termed the "Geneseo Shale."

The Illinois Basin (IB) is divided by a structural ridge into southeastern and northwestern subbasins that have

Table 1
Mo–TOC data for Devonian–Mississippian black shales of cratonic North America

	(1) Formation/Member	(2) Location	(3) Age	(4) n	(5) TOC[a] (%)	(6) Mo[a] (ppm)	(7) Mo/TOC (ratio)[b] (10^{-4})	(8) Mo/TOC (m)[c] (10^{-4})	(9) TOC (b_x) (%)	(10) r[d]	(11) Source
1	Exshaw/Upper Black Shale	Peace River Embaym.	Tournaisian	9	3.0±0.5	39±8	12.9±0.4	9	0	0.64	Caplan (1997)
2	Exshaw/Lower Black Shale	Peace River Embaym.	Famennian	14	10.1±3.6	74±39	6.4±2.8	9	0	0.64	Caplan (1997)
3	Exshaw/Upper Black Shale	S. Alberta Shelf	Tournaisian	22	9.7±5.3	137±133	8.7±3.0	25	2.7	0.85	Caplan (1997)
4	Exshaw/Lower Black Shale	S. Alberta Shelf	Famennian	22	7.8±3.1	111±90	11.6±1.4	25	2.7	0.85	Caplan (1997)
5	Bakken/Upper Black Shale	Williston Basin (ND)	Tournaisian	42	11.1±1.6	163±102	13.2±1.5	–	–	(0.12)	Hartwell (1998)
6	Bakken/Lower Black Shale	Williston Basin (ND)	Famennian	35	13.0±3.8	293±134	23.2±1.1	35	4.4	0.97	Hartwell (1998)
7	Woodford Formation	Iowa–Oklahoma basins	Fras.–Fam.[e]	17	3.2±1.6	71±49	23.4±1.7	32	0.8	0.93	Lambert (1992)
8	New Alb./ Hannibal–Saverton	Illinois Basin (IL)	Famennian	23	3.4±1.5	29±23	8.4±1.6	11	0.3	0.89	Frost et al. (1985)
9	New Albany/ Grassy Creek	Illinois Basin (IL)	Famennian	170	6.5±1.9	73±34	11.4±0.3	15	1.0	0.69	Frost et al. (1985)
10	New Albany/ Sweetland Creek	Illinois Basin (IL)	Frasnian	59	5.0±1.9	43±35	9.4±0.7	20	1.7	0.63	Frost et al. (1985)
11	New Albany/up. Clegg Creek	Illinois Basin (IN)	Tournaisian	28	15.1±3.8	379±237	22.6±2.0	65	7.7	0.88	Shaffer et al. (1984)
12	New Albany/up. Clegg Creek	Illinois Basin (IN)	Tournaisian	12	19.5±4.0	455±363	18.3±3.9	55	7.7	0.90	Ripley et al. (1990)
13	New Albany/lwr. Clegg Creek	Illinois Basin (IN)	Famennian	9	9.4±3.0	111±46	11.2±0.5	15	2.0	0.96	Schieber and Lazar (2004 + unpubl.)
14	New Albany/ Morgan Trail–Camp Run–lwr. Clegg Creek	Illinois Basin (IL)	Famennian	8	8.3±4.2	78±59	9.8±1.6	12	0.5	0.81	Frost et al. (1985)
15	New Albany/ Camp Run	Illinois Basin (IN)	Famennian	14	5.0±2.4	26±15	4.5±0.5	6	0	0.85	Schieber and Lazar (2004 + unpubl.)
16	New Albany/ Morgan Trail	Illinois Basin (IN)	Famennian	5	8.0±1.2	70±13	8.7±0.3	11	1.3	0.93	Schieber and Lazar (2004 + unpubl.)
17	New Alb./Camp Run–Blocher	Illinois Basin (IN)	Famennian	86	7.8±2.9	90±55	11.5±2.0	10	0.5	0.87	Ripley et al. (1990)
18	New Albany/ Selmier	Illinois Basin (IN)	Frasnian	9	4.4±3.1	37±44	6.6±1.4	13	1.5	0.94	Schieber and Lazar, (2004 + unpubl.)
19	New Albany/ Selmier	Illinois Basin (IL)	Frasnian	28	4.0±1.8	53±48	9.4±2.1	20	0.9	0.72	Frost et al. (1985)
20	New Albany/ Blocher	Illinois Basin (IN)	Givet.–Fras.	4	6.7±3.3	34±27	4.5±1.3	8	2.2	0.96	Schieber and Lazar (2004 + unpubl.)
21	New Albany/ Blocher	Illinois Basin (IL)	Givet.–Fras.	24	5.3±1.5	41±16	7.9±0.6	7	0	0.61	Frost et al. (1985)
22	New Albany/ Portwood –Duffin ("Geneseo Shale")	Appal. Basin (KY)	Givet.–Fras.	14	9.0±5.1	31±17	2.8±0.9	2	0	0.66	Robl et al. (1983 + unpubl.)
23	Chattanooga/ Gassaway	Appal. Basin (WV)	Famennian	12	3.5±1.4	32±19	9.9±1.3	15	2.2	0.86	Leventhal and Hosterman (1982)
24	Chattanooga/ Gassaway	Appal. Basin (TN)	Famennian	14	9.1±2.8	98±58	10.6±1.2	15	2.2	0.78	Leventhal and Hosterman (1982)
25	Chattanooga/ Gassaway	Appal. Basin (AL)	Famennian	82	16.1±1.8	307±102	17.9±0.8	–	–	(0.01)	Rheams and Neathery (1988)

(continued on next page)

Table 1 (*continued*)

	(1) Formation/Member	(2) Location	(3) Age	(4) *n*	(5) TOC[a] (%)	(6) Mo[a] (ppm)	(7) Mo/TOC (ratio)[b] (10^{-4})	(8) Mo/TOC (m)[c] (10^{-4})	(9) TOC (b_x) (%)	(10) r[d]	(11) Source
26	Chattanooga/ Gassaway	Appal. Basin (TN)	Famennian	52	14.2±4.2	170±76	12.0±1.0	15	2.2	0.80	Mason (1989)
27	Chattanooga/ Gassaway	Appal. Basin (TN)	Famennian	18	11.8±4.4	113±54	10.0±0.9	15	2.2	0.81	Leventhal et al. (1983)
28	Chattanooga/ Dowelltown	Appal. Basin (TN)	Frasnian	32	8.6±5.3	56±50	6.1±0.9	13	4.2	0.85	Mason (1989)
29	Chattanooga/ Dowelltown	Appal. Basin (TN)	Frasnian	15	10.2±5.6	96±99	7.2±1.2	13	4.2	0.76	Leventhal et al. (1983)
30	Sunbury Shale	Appal. Basin (OH)	Tournaisian	33	6.1±1.7	198±47	32.3±0.6	16–28	0	0.87	Jaminski (1997)
31	Sunbury Shale	Appal. Basin (KY)	Tournaisian	47	11.9±1.9	346±140	28.2±1.1	27–50	2.5–4.0	0.89	Jaminski (1997)
32	Sunbury Shale	Appal. Basin (KY)	Tournaisian	44	12.7±2.2	297±124	22.3±1.3	50	6.0	0.60	Robl et al. (1983 + unpubl.)
33	Ohio Shale/up. Cleveland	Appal. Basin (OH)	Famennian	18	8.5±2.1	141±85	14.1±0.9	40	4.8	0.98	Jaminski (1997)
34	Ohio Shale/up. Cleveland	Appal. Basin (KY)	Famennian	20	12.4±3.3	128±67	9.2±1.1	9	0	0.72	Jaminski (1997)
35	Ohio Shale/lwr. Cleveland	Appal. Basin (OH)	Famennian	18	3.5±0.9	82±21	23.0±0.4	22	0	0.95	Jaminski (1997)
36	Ohio Shale/lwr. Cleveland	Appal. Basin (KY)	Famennian	9	4.8±1.7	102±27	20.9±0.9	20	0	0.96	Jaminski (1997)
37	Ohio Shale/up. Cleveland	Appal. Basin (KY)	Famennian	115	11.5±2.1	82±38	6.0±0.4	7	0	0.59	Robl et al. (1983 + unpubl.)
38	Ohio Shale/lwr. Cleveland	Appal. Basin (KY)	Famennian	88	7.2±1.3	132±26	19.3±0.4	18	0	0.46	Robl et al. (1983 + unpubl.)
39	Ohio Shale/Three Lick Bed	Appal. Basin (KY)	Famennian	23	6.1±1.0	111±18	17.3±0.8	17	0	0.82	Robl et al. (1983 + unpubl.)
40	Ohio Shale/up. Huron	Appal. Basin (KY)	Famennian	60	5.7±0.5	87±9	15.4±0.2	16	0	0.61	Robl et al. (1983 + unpubl.)
41	Ohio Shale/mid. Huron	Appal. Basin (KY)	Famennian	73	6.3±0.7	88±16	14.2±0.3	14	0	0.56	Robl et al. (1983 + unpubl.)
42	Ohio Shale/lwr. Huron	Appal. Basin (KY)	Famennian	79	7.3±2.8	106±40	14.6±0.4	12	0	0.86	Robl et al. (1983 + unpubl.)
43	Kettle Point Fm./ unit 6	Algonquin Arch (Ont.)	Famennian	7	11.4±1.9	177±78	13.3±1.9	12[f]	0[f]	0.79	Armstrong (1986)
44	Kettle Point Fm./ unit 5	Algonquin Arch (Ont.)	Famennian	7	7.6±1.1	110±10	14.8±0.5	12[f]	0[f]	0.79	Armstrong (1986)
45	Kettle Point Fm./ unit 4	Algonquin Arch (Ont.)	Famennian	5	3.3±2.7	42±37	12.3±1.4	12[f]	0[f]	0.79	Armstrong (1986)
46	Kettle Point Fm./ unit 3	Algonquin Arch (Ont.)	Famennian	6	5.5±1.2	50±6	10.3±0.9	12[f]	0[f]	0.79	Armstrong (1986)
47	Kettle Point Fm./ unit 2	Algonquin Arch (Ont.)	Famennian	6	6.0±0.9	80±21	13.6±1.2	12[f]	0[f]	0.79	Armstrong (1986)
48	Kettle Point Fm./ unit 1	Algonquin Arch (Ont.)	Famennian	14	6.9±3.4	57±29	7.7±0.9	12[f]	0[f]	0.79	Armstrong (1986)
49	Upper Olentangy	Appal. Basin (OH)	Frasnian	21	4.6±1.6	73±51	12.5±3.5	25	1.8	0.81	Leventhal et al. (1983)
50	West Falls–Canadaway/ Dunkirk & Hanover	Appal. Basin (NY)	Frasnian	20	2.8±0.4	18±13	5.5±1.6	–	–	(0.22)	Sageman et al. (2003)
51	West Falls/Pipe Creek	Appal. Basin (NY)	Frasnian	32	3.8±0.9	4±4	0.5±0.6	–	–	(0.00)	Sageman et al. (2003)
52	Sonyea/Middlesex	Appal. Basin (NY)	Frasnian	49	2.9±0.6	11±7	3.1±1.0	–	–	(0.14)	Sageman et al. (2003)

Table 1 (*continued*)

	(1) Formation/Member	(2) Location	(3) Age	(4) n	(5) TOC [a] (%)	(6) Mo [a] (ppm)	(7) Mo/TOC (ratio) [b] (10^{-4})	(8) Mo/TOC (m) [c] (10^{-4})	(9) TOC (b_x) (%)	(10) r [d]	(11) Source
53	Genesee/Geneseo	Appal. Basin (NY)	Frasnian	50	4.2±1.0	11±9	1.9±0.9	–	–	(0.27)	Sageman et al. (2003)
54	Marcellus/ Oatka Creek	Appal. Basin (NY)	Eifelian	88	7.0±3.3	103±105	12.3±1.5	24	1.8	0.90	Werne et al. (2002)
55	Marcellus/ Union Springs	Appal. Basin (NY)	Eifelian	77	5.9±2.0	108±60	19.2±1.8	30	2.0	0.75	DeSantis and Algeo, unpubl.

[a] Mean+/−1 standard deviation.
[b] Median+/−1 standard error; approximately equal to column 6 divided by column 5.
[c] Slope of regression line (m) may differ from Mo/TOC ratio (col. 7) for reasons discussed in text.
[d] Correlation coefficient (r) for Mo–TOC relationships; all values are positive; insignificant values ($p(\alpha)>0.05$) are in parentheses.
[e] Samples are from the Middle Shale Member, probably of late Frasnian to middle Famennian age.
[f] Based on all data for Kettle Point Formation; insufficient data to calculate m and b_x values for individual units.

differing lithologic successions, even though Middle and Upper Devonian units in both areas are assigned to the New Albany Shale (or New Albany Group in Illinois) (Lineback, 1970; Frost et al., 1985; Hassenmueller, 1993). In the southeastern subbasin, which was deeper and contains a higher proportion of black shale, the New Albany Shale consists of the Portwood and lower Blocher members of Givetian age, separated by an early Frasnian unconformity from the overlying upper Blocher, Selmier, Morgan Trail, Camp Run, and Clegg Creek members of mid-Frasnian to Early Tournaisian age. In the northwestern subbasin, the Frasnian Sweetland Creek Shale is overlain by the Grassy Creek, Saverton, and Hannibal shales of Famennian age. The Sweetland Creek–Grassy Creek contact can be either conformable or unconformable, with the base of the Grassy Creek of latest Frasnian or early Famennian age, respectively. The Michigan Basin to the north contains the Frasnian–Famennian Antrim and Tournaisian Sunbury shales (Matthews, 1993), which shall not be considered in the present study owing to a lack of relevant geochemical data. The Algonquin Arch, which separates the Michigan Basin from the NAB/CAB, accumulated up to 70 m of Famennian black shales assigned to the Kettle Point Formation (Russell and Barker, 1984; Russell, 1993). Detailed correlation of wireline logs has demonstrated that this formation is correlative with the early to late Famennian Ohio Shale.

On the northwestern part of the North American craton, black shales were deposited widely but were confined stratigraphically to the uppermost Devonian and lowermost Carboniferous. The Bakken Shale was deposited in the Williston Basin of North Dakota, Montana, and southern Alberta, and its contiguous stratigraphic equivalent, the Exshaw Formation, was deposited within the Elk Point Basin extending from southern to northern Alberta (Fig. 4; Hartwell, 1998; Caplan and Bustin, 2001). Widespread black shales of Devono-Carboniferous age in the central and southern Midcontinent region are assigned to the Woodford Formation (Orth et al., 1988; Over, 1992, 2002). The Devonian–Carboniferous system boundary is typically within a meter or so of the top of the Woodford, which is up to 200 meters thick and mainly of Late(?) Devonian age. More areally limited occurrences of Devono-Carboniferous black shales are found in the far west and southwest, e.g., the Pilot Shale in the Pilot Basin of Nevada and Utah (Sandberg et al., 1988) and the Percha Shale of the Delaware Basin in New Mexico and Texas (Landis et al., 1992), but these will not be considered further in the present study owing to a lack of relevant geochemical data.

2.2. Sea-level patterns

Sea-level changes during the Middle and Late Devonian have been inferred from study of North American strata in several areas (Johnson et al., 1985; Savoy and Mountjoy, 1995; n.b., eustatic curves are shown in Fig. 9 and are not duplicated here). Both the Johnson et al. and the Savoy-Mountjoy curves show an overall transgression from the Eifelian through the late Frasnian, punctuated by a series of small-scale T–R cycles. In the Appalachian Basin, the transgressive phases of individual T–R cycles are generally associated with an expanded area of marine sedimentation and an increase in sediment organic carbon content, as with the Union Springs and Oatka Creek shales of the Marcellus Group (T–R cycles Id and Ie), the Skaneateles Formation of the Hamilton Group (T–R cycle If), and the Geneseo, Penn Yan, Middlesex–Rhinestreet, and Pipe Creek shales (T–R cycles IIa through IId). The

Frasnian–Famennian boundary is followed by an early Famennian transgression (T–R cycle IIe), recorded by the Dunkirk Shale in New York State and the Sassenach Formation in western Canada. Different sea-level trends are inferred for the middle to late Famennian. The Johnson et al. (1985) curve shows a slow regression punctuated by a late-Famennian transgressive event (T–R cycle IIf, equivalent to the Cleveland Member of the Ohio Shale and its stratigraphic equivalents) in the Appalachian Basin, whereas the Savoy and Mountjoy (1995) curve shows a slow transgression throughout the Famennian in western Canada. In both curves, the Devonian–Carboniferous boundary coincided with a major eustatic fall (see below).

The Frasnian–Famennian (F–F) stage boundary across North America is associated with a major eustatic event. It falls within the upper (highstand) part of the IId (2) T–R cycle in eastern and central North America, which terminates in the Lower *triangularis* Zone (Johnson et al., 1985; Brett et al., 1990; Schülke, 1998; Smith and Jacobi, 2001). The overlying Middle *triangularis* Zone is associated with a major transgression marking the base of a third-order sequence (IIe T–R cycle; Over, 2002). This horizon is characterized by increased concentrations of pyrite, phosphate nodules, and conodonts, and by a shift to deeper conodont biofacies (characterized by *Palmatolepis*), suggesting a sea-level rise and consequent reduction of terrigenous sediment influx. Subaqueous erosion is indicated by basal pyritic lag beds in the NAB (Baird and Brett, 1986) and elsewhere, but conodont zonation provides little evidence of a major hiatus in sedimentation (Over, 2002). The transgressive horizon is widely associated with a transition from green–gray to black mudstones, e.g., Hanover to Dunkirk shales in the NAB, Upper Olentangy to Ohio shales in the CAB, Dowelltown to Gassaway Member of the Chattanooga Shale in the SAB, Selmier to Morgan Trail members of the New Albany Shale in the southeastern IB, and Sweetland Creek to Grassy Creek shales in the northwestern IB (Over, 2002). Because it can be correlated intercontinentally, the IIe transgressive event is likely to be eustatic in origin.

The Devonian–Carboniferous (D–C) boundary is also associated with a major eustatic event. In the Appalachian Basin, this is recorded in prograding lowstand deltaic facies of the Bedford–Berea succession and, in more proximal facies to the east, by the nonmarine middle member of the Rockwell Formation in Maryland and West Virginia, the Cussewago Sandstone in New York, and the Murrysville Sandstone in Pennsylvania (Kammer and Bjerstedt, 1986; Bjerstedt and Kammer, 1988; Cecil et al., 2004). The underlying Oswayo and overlying Riddlesburg members of the Rockwell Formation are marine units equivalent to the Cleveland Member of the Ohio Shale and the Sunbury Shale, respectively (Cecil et al., 2004). In the Illinois Basin, the D–C boundary is located in the upper Clegg Creek Member of the New Albany Shale, probably within the gray–green shale interval known as the Ellsworth "member," which has been correlated with the Bedford Shale of Kentucky and Ohio (Lineback, 1968, 1970; Hassenmueller, 1993). In the Iowa and Oklahoma basins, the D–C boundary is variably located within the upper Woodford Formation or at its erosional contact with overlying units (Over, 1992). In the Williston and Elk Point basins of western North America, the D–C boundary is located within the middle siltstone (or sandstone) members of the Bakken and Exshaw formations, respectively, which are underlain and overlain by deeper-water black shales (Playford and McGregor, 1993; Hartwell, 1998; Caplan and Bustin, 2001). The D–C boundary T–R event also has global expression. In Germany, the Hangenberg black shales just below the boundary are interpreted as transgressive deposits, whereas the Hangenberg Sandstone, which contains the D–C boundary, is considered to be a lowstand deposit (Streel, 1986; Bender et al., 1988; Streel et al., 2000). The eustatic fall at the D–C boundary has been attributed to a brief but intense episode of continental glaciation (Streel et al., 2000). The ensuing earliest Carboniferous transgression resulted in deposition of the most geographically extensive blanket of black shale across the North American craton, comprising the Sunbury Shale and upper Gassaway Member of the Chattanooga Shale in the SAB, the upper Clegg Creek Member of the New Albany Shale in the IB, the Upper Black Shale members of the Bakken and Exshaw formations in the Williston and Elk Point basins, and stratigraphic equivalents elsewhere.

2.3. Paleogeography and depositional models

During the Late Devonian and Early Carboniferous, the North American craton south and west of the Canadian Shield was largely flooded, with small emergent areas associated with the Transcontinental Arch, the Ozark Uplift, and other structural highs (Fig. 4). The Devono–Carboniferous North American Seaway was subdivided into a series of deeper basins (e.g., the Appalachian, Illinois, Michigan, Iowa, and Williston–Elk Point basins) separated by shallower sills, resulting in conditions favoring development of benthic anoxia within the deeper waters of the basin centers. A well-studied example of one of these silled basins is the

Appalachian Basin, in which sedimentologic features provide evidence of varying water depths. Frasnian–Famennian strata from New York southward to central Kentucky are mostly laminated black shales with few bedforms or other features indicative of current transport or disturbance, which is consistent with deepwater deposition (n.b., all references to "deep water" in North American cratonic basins signify water depths of no more than a few hundred meters; Potter et al., 1982; Algeo and Maynard, 1997; Jaminski et al., 1998). However, correlative portions of the Chattanooga Shale contain a variety of sedimentary features indicative of shallow water depths (perhaps a few tens of meters), including hummocky cross stratification, mud tempestites, lag deposits, and erosion surfaces (Schieber, 1994a,b, 1998). Because such features are widely present in southern Kentucky and Tennessee, they suggest that the Appalachian Basin shallowed considerably to the southwest and that a silled margin existed in this area. Sediment dispersal patterns (Potter et al., 1982) indicate that the western margin of the Appalachian Basin, which was coextant with the Cincinnati Arch, also was shallowly submergent at this time. These observations imply that the southwestern and western margins of the Appalachian Basin were sills that limited deepwater exchange (Fig. 5).

The depositional systems represented by North American Devono–Carboniferous black shales have been the subject of many studies (Ettensohn and Barron, 1981; Potter et al., 1982; Ettensohn, 1985a,b; Ettensohn and Elam, 1985; Ettensohn, 1992; Algeo and Maynard, 1997; Jaminski, 1997; Jaminski et al., 1998; Hartwell, 1998; Schieber, 1998; Murphy et al., 2000a,b; Caplan and Bustin, 2001; Smith and Jacobi, 2001; Werne et al., 2002; Sageman et al., 2003; Rimmer, 2004; Rimmer et al., 2004). The Appalachian Basin black shale succession represents the distal, deepwater facies of the Catskill Delta system, which prograded into an epicratonic foreland basin (Fig. 5). Turbiditic sedimentation from shallow-water areas to the northeast and east resulted in episodic oxygenation of portions of the deep-basin seafloor (Potter et al., 1982; Baird and Brett, 1986). Most studies have inferred stable vertical stratification of the water column, although a recent hypothesis invokes seasonal mixing in order to drive a productivity-anoxia feedback mechanism associated with elevated levels of primary productivity (Murphy et al., 2000a,b; Sageman et al., 2003). The more organic-rich intervals within the black shale succession generally have been attributed to eustatic transgression and consequent sediment starvation (Ettensohn, 1985b; Johnson et al., 1985; Woodrow, 1985; Ettensohn, 1992; Sageman et al., 2003).

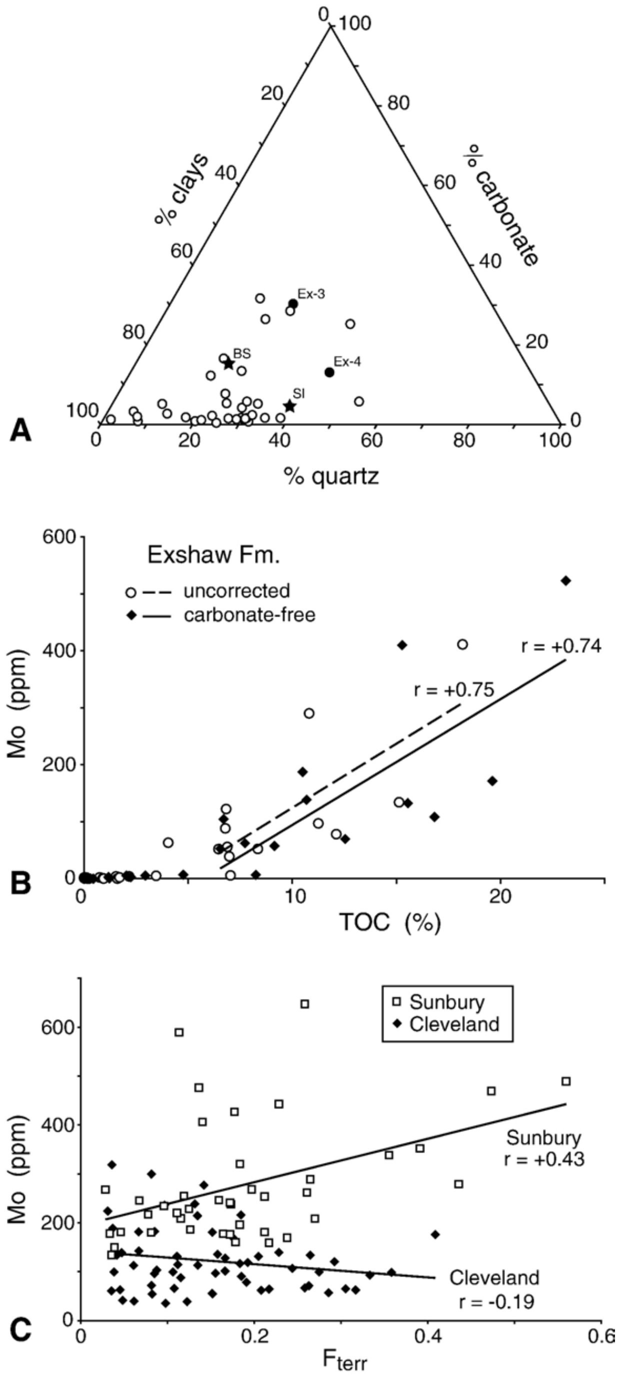

Fig. 6. (A) Ternary diagram of major non-organic phases in North American Devono-Carboniferous black shales. The modern Black Sea (BS) and Saanich Inlet (SI) are shown for comparison; Ex-3 and Ex-4 are the study formations in panel B. (B) Sediment Mo versus TOC for the Exshaw Formation of the southern Elk Point Basin (Table 1, records 3 and 4) on an uncorrected and a carbonate-free basis. Note the similarity of the correlation lines and correlation coefficients; correcting for carbonate content has little effect on Mo–TOC relationships. (C) Sediment Mo versus the terrigenous fraction of OM (F_{terr}) for the Famennian Cleveland Member of the Ohio Shale and the Tournaisian Sunbury Shale (Ohio–Kentucky). F_{terr} is calculated as the volume ratio of vitrinite plus inertinite to total organic macerals; raw data from Jaminski (1997). The Cleveland and Sunbury samples yield correlation coefficients (r) of +0.43 (n=41; $p(\alpha)\sim 0.01$) and −0.19 (n=60; $p(\alpha)$ non-significant), respectively.

3. Sedimentary Mo–TOC data

3.1. Data compilation and reporting conventions

We have compiled elemental Mo–TOC data for 55 formation-studies of black shales of Middle Devonian through Early Carboniferous age from North America (Table 1). All of the formations chosen represent laminated, organic-rich units (>2 wt.% TOC) lacking (or showing minimal evidence of) bioturbation and, hence, are inferred to have been deposited under (largely) anoxic conditions. For each study formation, Mo and TOC concentrations are reported as the mean value plus or minus one standard deviation (Table 1, cols. 5 and 6). The amount of Mo per unit TOC, i.e., the ratio of Mo to TOC, is given as the median plus-or-minus one standard error (Table 1, col. 7); for ratios, the median is preferable to the mean as the latter statistic has the potential to be skewed by one or a few extreme values resulting from samples with very small denominators. For each formation, we also crossplotted Mo versus TOC and determined the slope (m) and X-intercept (b_x) of the Mo–TOC regression line (Table 1, cols. 8 and 9). Although m has the same units (i.e., 10^{-4}) as the Mo/TOC ratio (Table 1, col. 7), these variables are equal only if the regression line has a b_x value of zero. If this is not the case (as for most of the study formations), then these variables are unequal. For most of the formations studied, the Mo–TOC regression line has a positive b_x (we report X-intercepts rather than Y-intercepts, as in customary in algebra, because the former may have significance for mechanisms of Mo–TOC accumulation; see Section 6). A regression line with a positive b_x value results in a value of m (Table 1, col. 8) that exceeds Mo/TOC (Table 1, col. 7). For simplicity, the units of these two variables (i.e., 10^{-4}, or ppm/wt.%) are omitted in subsequent discussion but should be assumed to be present. The data given in Table 1 provide the basis for much of the subsequent analysis of spatial and temporal variation in Mo–TOC relationships.

Mo concentrations are given as raw values rather than on an Al-normalized basis, as is common in many studies. Normalization of trace-element concentrations to Al yields an "enrichment factor" representing a multiple of the background concentration associated with the siliciclastic matrix of a sample. Enrichment factors can be useful in facilitating comparisons between facies, particularly when dilution by biogenic components is severe (e.g., Piper, 1994; Dean et al., 1997, 1999). However, normalization to Al serves no purpose when examining intraformational variation of a trace element relative to TOC. Use of Al-normalized concentrations for trace elements and raw concentrations for TOC can lead to introduction of unwanted variance in trace element-TOC relationships (Van der Weijden, 2002; Tribovillard et al., 2006). Because Mo is hosted mainly by organic matter (see Section 3.2), Mo and TOC are subject to roughly equal degrees of dilution by mineral phases such as clays, quartz, and carbonates, and, hence, any normalization procedure to correct for sample dilution must be applied to both components. Most of the study formations are close to being simple mixtures of OM and detrital siliciclastics and contain little if any carbonate (Fig. 6A). However, to check for the possible influence of non-detrital diluents, we compared Mo–TOC relationships on an uncorrected and a carbonate-free basis for carbonate-rich units; corrections for carbonate content had no apparent influence on Mo–TOC relationships (Fig. 6B). Algeo and Lyons (2006) reached a similar conclusion regarding corrections for carbonate content in sediments of the Black Sea and other modern anoxic environments.

3.2. Influences on Mo–TOC relationships

Organic matter (OM) is the primary host phase for Mo in the study formations. This inference is supported by strong covariation between Mo and TOC concentrations in most of the study units. For example, the eight formations shown in Figs. 7 and 8 yield Mo–TOC correlation coefficients (r) greater than +0.70 (and mostly > +0.80) with significance levels $p(\alpha) < 0.001$. Such strong and nearly ubiquitous covariation would not exist unless Mo was hosted mainly by OM (cf. Algeo and Maynard, 2004). The amount of Mo resident in the detrital phases of average shales is ~3 ppm (Taylor and McLennan, 1985; McLennan, 2001), which is typically only a small fraction of the Mo in the organic-rich black shale formations examined in this study and, hence, negligible in terms of total Mo budgets. Also, strong Mo enrichment of authigenic Fe-sulfide phases is uncommon (e.g., Morse and Luther, 1999).

The Devonian Period was a time of rapid evolution of land plants and, hence, potentially large changes in the source fluxes of OM to marine sediments (Algeo et al., 1995, 2001). As land plants spread, larger quantities of refractory OM of terrigenous origin are likely to have been deposited in epicontinental seas. Some studies have argued that terrigenous and marine OM exhibit differences in their tendency to take up dissolved trace metals (e.g., Coveney et al., 1991). We examined this possibility using the organic petrographic and whole-rock geochemical datasets of Jaminski (1997) for the Late Devonian Cleveland and Early Carboniferous Sunbury

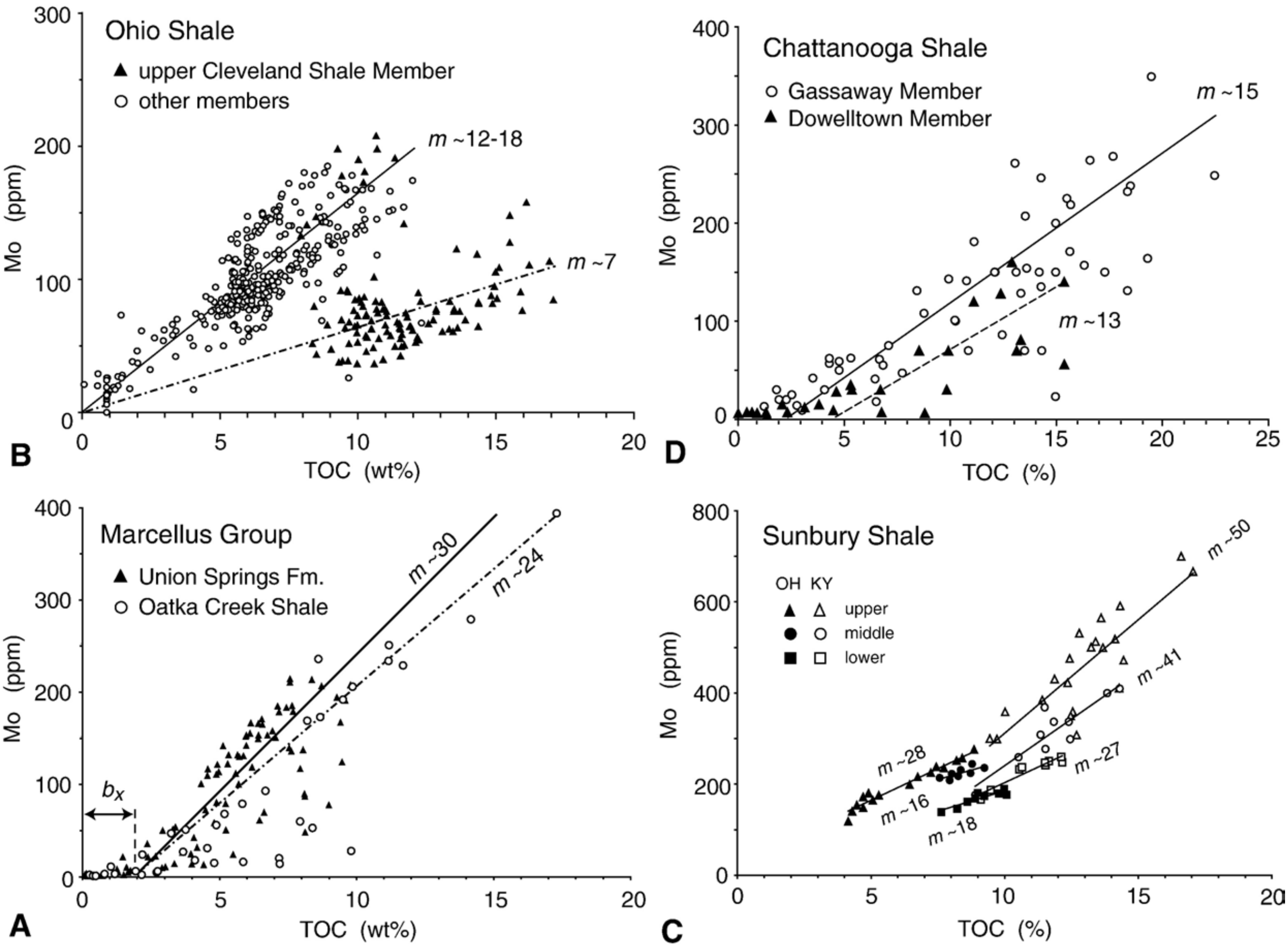

Fig. 7. Sediment Mo versus TOC for Devono-Carboniferous black shales of eastern North America. (A) Marcellus Group (Eifelian, New York); (B) Ohio Shale (Famennian, Kentucky); (C) Sunbury Shale (Tournaisian, Kentucky and Ohio); and (D) Chattanooga Shale (Frasnian–Tournaisian, Tennessee and Alabama). Regression-line slopes (m) shown in all panels, and example of X-intercept (b_x) shown in A; note variations in m and b_x between study formations. Data sources: (A) Werne et al. (2002), and DeSantis and Algeo (unpubl.); (B) Robl et al. (1983), Robl and Barron (1988), and Robl (unpubl.); (C) Jaminski (1997); and (D) Leventhal and Hosterman (1982), Leventhal et al. (1983), and Mason (1989).

shales. Crossplots of Mo concentrations versus F_{terr} (defined as the volume ratio of vitrinite plus inertinite to total organic macerals, as determined by 300 point counts per sample) showed no significant relationship for the Cleveland Shale and only a moderately significant relationship ($r=+0.43$; $p(\alpha)\sim 0.01$) for the Sunbury Shale (Fig. 6C). The significance of the latter relationship must be questioned because (1) removal of just the two Sunbury samples having F_{terr} values >0.45 would result in a non-significant relationship, and (2) the highest Mo concentrations are exhibited by Sunbury samples of intermediate (rather than high) F_{terr} values. Even if OM type exerts a limited influence on sediment Mo concentrations, it is too weak a relationship to account for the strong Mo–TOC covariation observed in the study formations (e.g., Figs. 7, 8, $r>+0.70$). With regard to stratigraphic trends, there does appear to be a small secular increase in F_{terr} from the Middle Devonian (<0.05) to the Early Carboniferous (0.05–0.40; Table 2); nonetheless, the bulk of OM in all black shales examined here is of marine provenance.

One additional issue of importance for ancient black shales is the potential loss of organic carbon through catagenesis, i.e., thermal maturation of the sediment and generation and export of hydrocarbons (Raiswell and Berner, 1986). This process might affect sedimentary Mo–TOC relationships in source rocks if Mo is retained when liquid hydrocarbons are expelled. Few if any published studies have examined this specific issue, but tentative inferences are possible on the basis of geochemical studies of crude oils. The trace-metal inventory of crude oils is thought to derive primarily from the source rock rather than from rock–fluid interaction during hydrocarbon migration (Hitchon et al., 1975; Filby and Van Berkel,

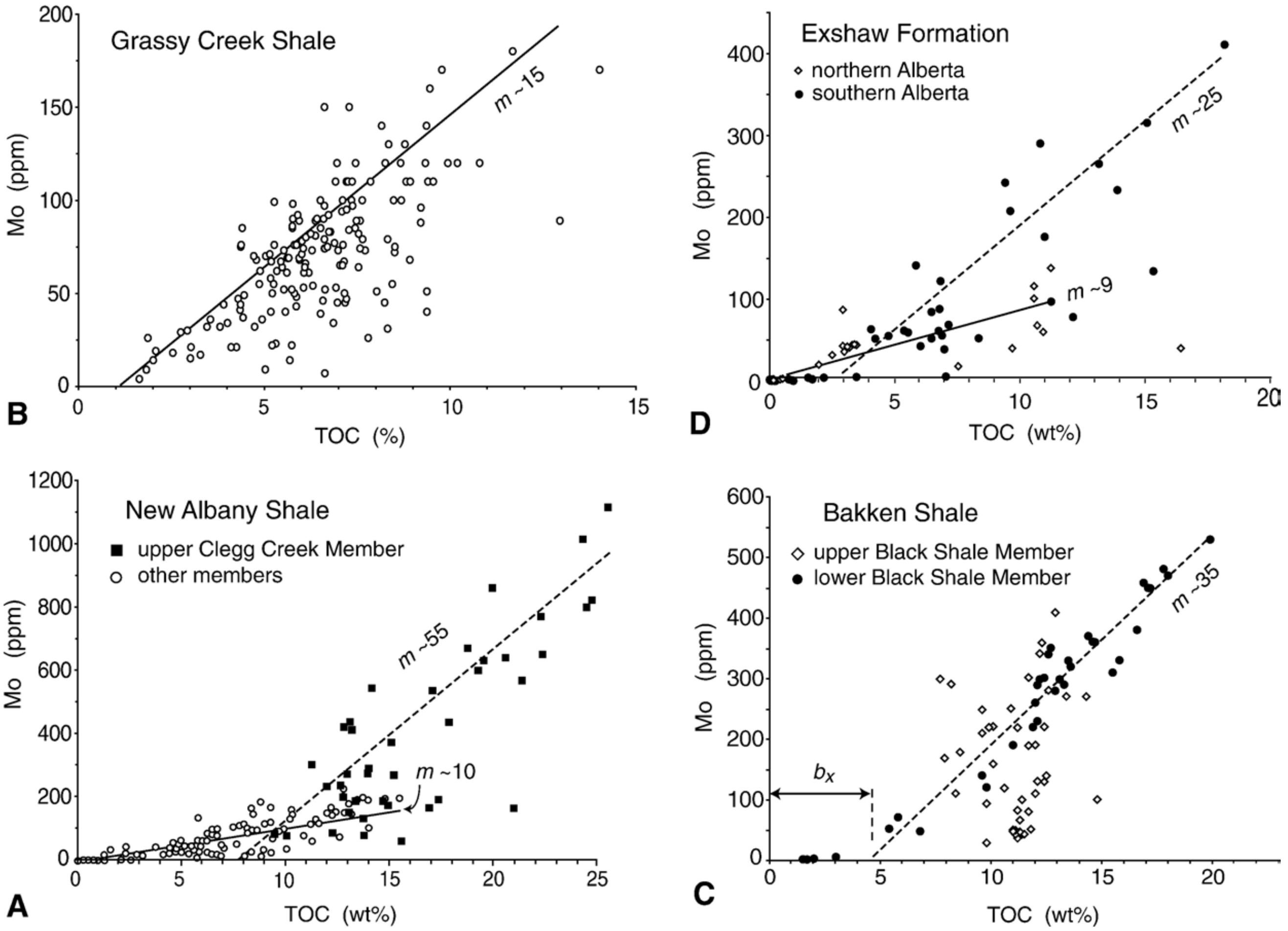

Fig. 8. Sediment Mo versus TOC for Devono-Carboniferous black shales of central and western North America. (A) New Albany Shale (Givetian–Tournaisian, Indiana); (B) Grassy Creek Shale (Famennian, Illinois); (C) Bakken Shale (Famennian–Tournaisian, North Dakota); and (D) Exshaw Formation (Famennian–Tournaisian, Alberta). Regression-line slopes (m) shown in all panels, and example of X-intercept (b_x) shown in C; note variations in m and b_x between study formations. Data sources: (A) Shaffer et al. (1984) and Ripley et al. (1990); (B) Frost et al. (1985); (C) Hartwell (1998); and (D) Caplan (1997).

1987; Hunt, 1996). Crude oils are commonly enriched in V and Ni (to > 100 ppm) owing to the affinity of these metals for porphyrins (Lewan, 1984; Filby and Van Berkel, 1987; Quirke, 1987; Barwise, 1990). Other trace metals are generally enriched to a lesser degree, although exceptionally high concentrations are found in some crude oils (Hitchon et al., 1975; Hirner, 1987). Trace-metal concentrations generally exhibit a strong relationship to API gravity: heavier (i.e., low-gravity) crudes tend to be more enriched in trace metals, including Mo (Gleim et al., 1975; Yen, 1975; Hirner, 1987; Hunt, 1996). These observations suggest that catagenesis of source rocks is likely to result in preferential loss of organic carbon relative to trace metals. However, it is unclear that this process is sufficiently extensive to measurably influence observed Mo–TOC relationships in the study formations, and more research into trace-metal mobility during burial diagenesis will be needed to adequately address this issue.

3.3. Results

For 49 of the 55 North American Devono-Carboniferous black shales examined in this study statistically significant positive covariation between Mo and TOC exists (e.g., Figs. 7, 8). This is true for formations ranging in age from the Middle Devonian to the Early Carboniferous and distributed geographically across the North American craton, from the Marcellus Group of the Northern Appalachian Basin (Fig. 7A) to the Exshaw Shale of the Western Canadian Basin (Fig. 8D). Apart from the unifying characteristic of positive Mo–TOC covariation, the study formations display substantial variation in their Mo–TOC relationships, as reflected in differences in the slopes and X-intercepts of their Mo–TOC regression lines (Table 1, cols. 8–9). Regression-line slopes (m) vary from a low of ~2 ("Geneseo Shale"; Table 1, line 22) to a high of ~55–65 (Clegg Creek

Table 2
OM source data for selected North American Devono-Carboniferous black shales

Unit	Age	Location [a]	F_{terr} (%) [b]	OM type [c]	Sources
Marcellus Group	Middle Devonian (Givetian)	NAB	<5	II	(Goodarzi et al., 1990; Van Tyne, 1993; Murphy et al., 2000a,b)
Genesee–Sonyea–West Falls–Canadaway	Upper Devonian (Frasnian)	NAB	<5	II	(Breger et al., 1983; Goodarzi et al., 1990; Van Tyne, 1993; Murphy et al., 2000a,b)
Chattanooga Shale	Upper Devonian (Frasn.–Famen.)	SAB	<10	II	(Lewan, 1987; Rheams and Neathery, 1988; Adams, 1992)
Woodford Shale	Upper Devonian (Frasn.–Famen.)	Ouachita–Anadarko	<10 (30–100) [d]	II–(III) [d]	(Lewan, 1987; Kirkland et al., 1992; Lambert, 1992; Landis et al., 1992; Landais et al., 1994; Leo and Cardott, 1994; Wang and Philp, 1997)
New Albany Shale	Upper Devonian (Frasn.–Famen.)	Illinois Basin	0–15	II	(Barrows et al., 1979; Barrows and Cluff, 1984; Ripley et al., 1990; Robl and Taulbee, 1995)
Ohio–Sunbury shales	Upper Devonian–Lower Mississippian (Famen.–Tournais.)	CAB	5–40	II	(Breger et al., 1983; Rimmer and Cantrell, 1989; Robl et al., 1991; Thompson et al., 1992; Robl and Taulbee, 1995; Jaminski, 1997)
Exshaw Fm.	Upper Devonian–Lower Mississippian (Famen.–Tournais.)	Alberta	5–20 (70–90) [d]	II–(III) [d]	(Radke et al., 1986; Robison, 1994; Caplan, 1997)

[a] NAB = Northern Appalachian Basin; CAB = Central Appalachian Basin; SAB = Southern Appalachian Basin.
[b] F_{terr} is the terrigenous fraction of organic matter, calculated as the volume ratio of vitrinite and inertinite to total organic macerals.
[c] As determined by van Krevelen or HI/OI (modified van Krevelen) crossplots.
[d] Units contain both high–TOC shales with a preponderance of OM of marine origin and moderate–TOC shales with a preponderance of OM of terrigenous origin (values for the latter are given in parentheses).

Member, New Albany Shale; Table 1, lines 11–12), although most of the study formations exhibit slopes in the range of 10 to 25. Regression-line X-intercepts (b_x) range from a low of ~0% TOC (several formations) to a high of 7.7% TOC (Clegg Creek Member, New Albany Shale; Table 1, lines 11–12). Although it is impractical to illustrate Mo–TOC relationships for all of the study formations individually, a representative subset of Mo–TOC crossplots is shown in Figs. 7 and 8, and spatio-temporal patterns of variation in m are shown in Fig. 9.

In the NAB, the Union Springs and Oatka Creek shales yield m ~24–30 (Fig. 7A; Table 1, lines 54–55; Werne et al., 2002; DeSantis and Algeo, unpubl. data). Other black shales in the Givetian–Famennian succession of western New York State are relatively organic-poor (mostly <4%; Sageman et al., 2003) and do not exhibit significant Mo–TOC covariation (Table 1, lines 50–53). On the Algonquin Arch in Ontario, the Kettle Point Formation yields m ~12 (Table 1, lines 43–48; Armstrong, 1986). In the CAB, the correlative Ohio Shale yields similar values, i.e., m ~12–18 for the Huron and lower Cleveland members and m ~7–9 for the upper Cleveland Member (Fig. 7B; Table 1, lines 33–42; Robl et al., 1983; Robl and Barron, 1988; Jaminski, 1997; Algeo, 2004). The overlying Sunbury Shale yields higher values (m ~32–50; Fig. 7C; Table 1, lines, 30–32). When examined stratigraphically, systematic variation in m is observed within the Ohio Shale–Sunbury Shale succession (Fig. 10; see Section 5.3). In the SAB, the Dowelltown and Gassaway members of the Chattanooga Shale yield m ~13–15 (Fig. 7D; Table 1, lines 23–29; Leventhal and Hosterman, 1982; Leventhal et al., 1983; Rheams and Neathery, 1988; Mason, 1989).

In the southeastern subbasin of the IB, the various members of the New Albany Shale yield m ~6–20 (Fig. 8A; Table 1, lines 11–21; Shaffer et al., 1984; Ripley et al., 1990). The single exception is the upper Clegg Creek Member which has m ~55–65, similar to the correlative Sunbury Shale of the CAB. In the northwestern subbasin of the IB, the various members of the New Albany Shale such as the Grassy Creek Shale yield m ~10–20 (Fig. 8B; Table 1, lines 8–10; Frost et al., 1985). The stratigraphic equivalent of the highly organic-rich upper Clegg Creek Member is the more organic-poor Hannibal Shale in the northwestern subbasin, which lacks strong Mo enrichment and high m values (Frost et al., 1985). In the Midcontinent area, the Woodford Formation yields m ~32 (Table 1, line 7; Lambert, 1992). Similar values are observed in the Williston Basin where the Lower Black Shale Member of the Bakken Shale yields m ~35 (Fig. 8C; Table 1, line 6; Hartwell, 1998) and in the southern Elk Point Basin where the Exshaw Formation yields m ~25 (Fig. 8D; Table 1, lines 3–4; Caplan, 1997). However, the Exshaw Formation of the northern Elk Point Basin yields lower values (m ~9; Fig. 8D; Table 1, lines 1–2).

The geochemical datasets compiled for this study vary in the number and stratigraphic distribution of

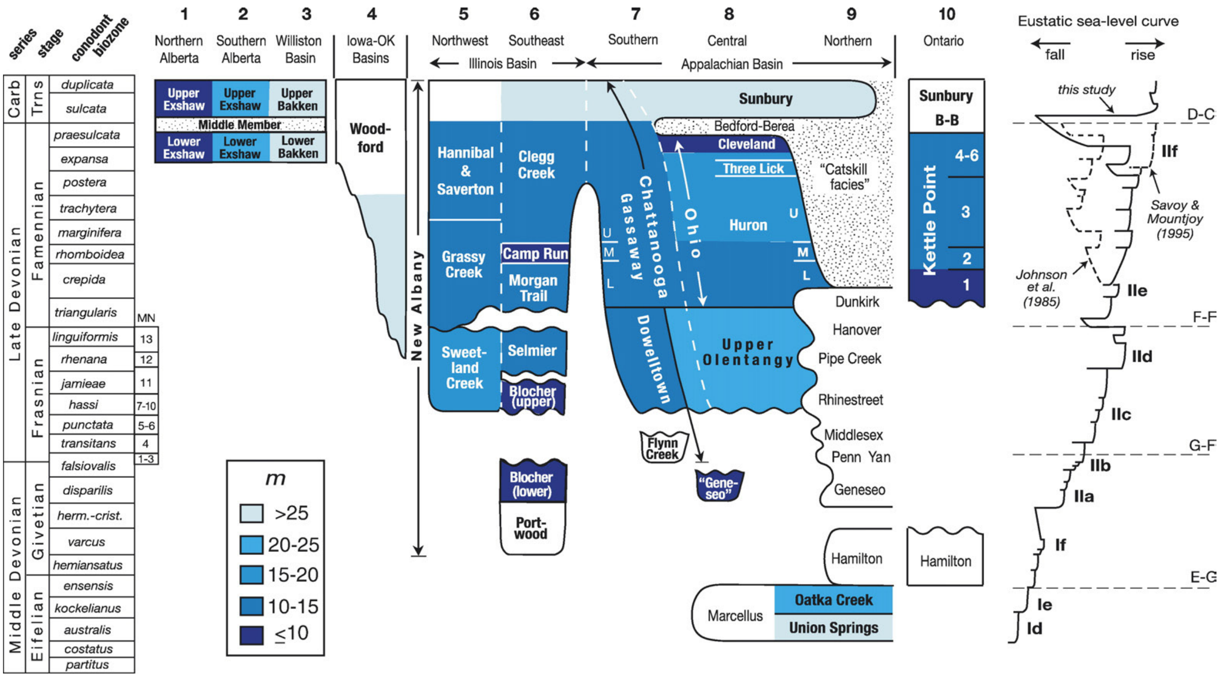

Fig. 9. Time–space diagram for Devono-Carboniferous black shales of North America showing variation in Mo–TOC regression-line slopes (m; Table 1) on a semiquantitative scale (colored fields). Values of m were determined for organic-rich shale facies only; formations consisting of other lithologies are mostly omitted. Biostratigraphic data are from Over (1992, 1997, 2002, and unpubl.); MN indicates Frasnian biozones from Montagne Noire, France. Conodont biozones average ca. 2 to 3 Myr during the Middle Devonian and ca. 1 to 2 Myr during the Late Devonian (Gradstein et al., 2004). See Fig. 4 for location of numbered stratigraphic columns. The Johnson et al. (1985) and Savoy and Mountjoy (1995) eustatic curves are shown at right (labels identify T–R cycles); note our proposed modification of late Famennian–Early Tournaisian sea-level trends. Abbreviations: B–B = Bedford–Berea, E–G = Eifelian–Givetian, G–F = Givetian–Frasnian, F–F = Frasnian–Famennian, D–C = Devonian–Carboniferous, L = lower, M = middle, and U = upper.

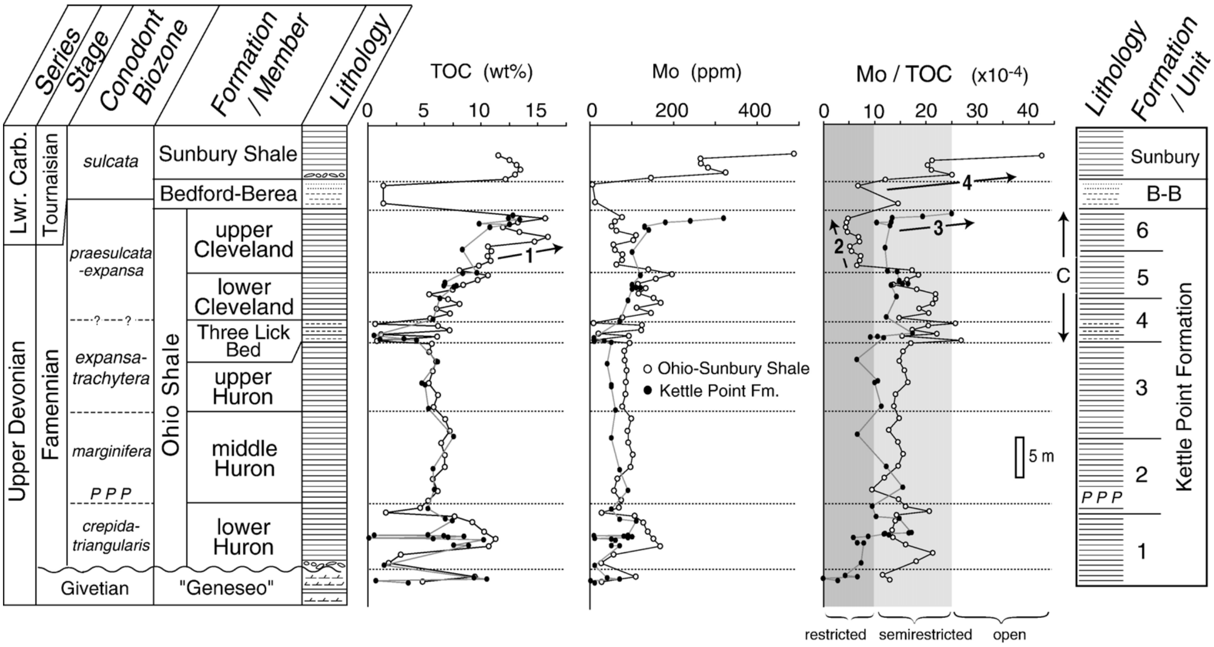

Fig. 10. High-resolution Mo–TOC chemostratigraphy of the Ohio–Sunbury shales (Central Appalachian Basin) and the Kettle Point Formation (Algonquin Arch, Ontario). These study formations are found in columns 8 and 10, respectively, of Fig. 9. Stratigraphic data for the CAB and the Algonquin Arch area are shown on the left and right of the figure, respectively. Ohio–Sunbury chemostratigraphic data are from Robl et al. (1983), Robl and Barron (1988), and Robl (unpublished); Kettle Point chemostratigraphic data are from Armstrong (1986). Stratigraphic alignment of the Ohio–Sunbury and Kettle Point datasets was achieved through wireline correlations and a biostratigraphic tie-point (PPP = *Protosalvinia*, an index fossil within the Appalachian Basin and adjacent areas; Russell and Barker, 1984). Numbered arrows indicate trends in TOC and Mo/TOC (see text for discussion). The bar scale applies to both chemostratigraphic records except for the interval of the Kettle Point Formation marked "C," where the vertical scale has been reduced to 75% of that of the bar scale.

samples as well as the area encompassed by the dataset-factors that may influence Mo–TOC relationships. Such variation in source data is inevitable for studies based on literature surveys; "normalization" of the datasets is generally not possible. One pattern evident among the datasets of the present study is that the more geographically and stratigraphically limited the range of sample collection, the more strongly correlated the Mo–TOC data. Thus, the Grassy Creek Shale dataset, which includes samples from many drillcores across Illinois, exhibits only a moderate correlation (r=+0.70; Fig. 8B), whereas the Sunbury Shale datasets, comprised of samples collected from short (~20 cm) stratigraphic intervals in individual drillcores, exhibit strong correlations (r=+0.84 to +0.98; Fig. 7C). In the case of the Sunbury Shale, it is notable that Mo–TOC relationships can vary over relatively small distances (i.e., central Ohio vs. northeastern Kentucky; Fig. 7C). This underscores the fact that spatial and temporal variation in Mo–TOC relationships may be possible at a fine scale, and that such variation may go largely unrecognized owing to the coarse geographic and stratigraphic scales of sampling and reporting employed in most geochemical studies. Higher-resolution geochemical studies such as those of Jaminski (1997) and Hartwell (1998) will be needed to assess fine-scale variation in Mo–TOC relationships.

A few study formations do not yield significant Mo–TOC covariation patterns. The reasons for this are probably diverse, including (1) an insufficient range of TOC variation, as possibly for the Upper Black Shale Member of the Bakken Shale (Fig. 8C; Table 1, line 5; Hartwell, 1998), (2) uniformly low TOC values (possibly reflecting suboxic or fluctuating anoxic rather than permanently anoxic depositional conditions), as for the New York Frasnian black shale succession (Table 1, lines 50–53; Sageman et al., 2003); (3) an overly broad geographic or stratigraphic range of sample collection, as for the Chattanooga Shale (Table 1, line 25; Rheams and Neathery, 1988); and (4) differential loss of TOC and Mo during burial diagenesis, e.g., through generation and migration of hydrocarbons. Note that, despite the absence of significant Mo–TOC covariation in the Upper Black Shale Member of the Bakken Shale, the average Mo and TOC values of this unit and, hence, its Mo/TOC ratio are nearly identical to those of the Lower Black Shale Member of the same formation (Fig. 8C).

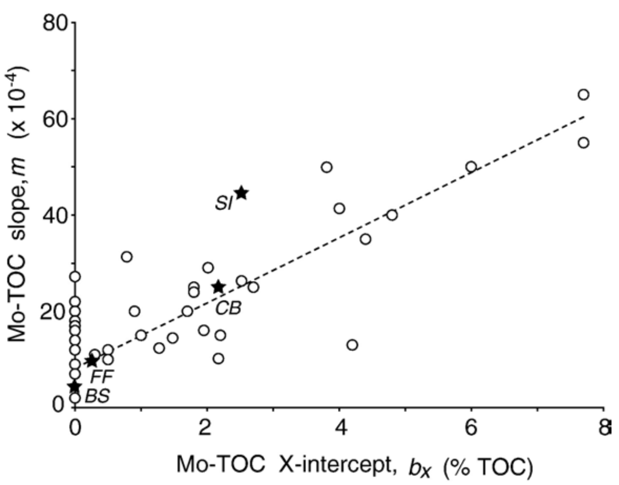

Fig. 11. Mo–TOC regression-line slope (m) versus X-intercept (b_x) for North American Devono-Carboniferous black shales (open circles; Table 1). Shown for comparison are values for organic-rich sediments from modern anoxic marine environments (solid stars): BS = Black Sea, CB = Cariaco Basin, FF = Framvaren Fjord, SI = Saanich Inlet (cf. Fig. 2). Note trend toward larger b_x with increasing m (dashed line).

Although the focus of the preceding discussion has been on the regression-line slopes (m) of Mo–TOC datasets (e.g., Figs. 7, 8), the regression-line X-intercepts (b_x) may be of interest also. In particular, there is a strong positive correlation between m and b_x for the study formations as a group (Fig. 11). Formations with $m<20$ generally have $b_x<2$, whereas those with $m>20$ generally have $b_x>2$. The largest m values (>50) are associated with the largest b_x values (>6), e.g., the upper Clegg Creek Member of the New Albany Shale (Table 1, lines 11–12). Given the large number of study formations with well-defined Mo–TOC regression lines (n ~49), this relationship is unlikely to be due to random factors. Further, variation in Mo–TOC relationships is scale-dependent: m and b_x tend to exhibit more limited variation within smaller areas compared with larger areas (e.g., Sunbury Shale, Fig. 7C). The significance of b_x and its relationship to m will be considered in Section 6.

4. Discussion

4.1. General considerations

Important insights can be gained regarding controls on Mo–TOC covariation from study of modern anoxic marine environments for which ambient aqueous chemical and physical environmental data are available (Figs. 1–3; see Introduction). A key point is that Mo–TOC regression-line slopes (m) are strongly influenced by the degree of hydrographic restriction of anoxic silled basins, even for basins exhibiting only a weak degree of deepwater restriction, as for modern Saanich Inlet (Algeo and Lyons, 2006). Most or all of the Devono-Carboniferous black shales considered in the present study were deposited in silled basins on the North American craton that were subject to at least minimal and, in some cases, a strong degree of restriction of deepwater exchange (Figs. 4 and 5). Thus, these formations collectively are good candidates to investigate whether Mo–TOC relationships in ancient black shales can be interpreted in terms of hydrographic controls. It may be significant that the range of *m* values observed in North American Devono-Carboniferous black shales (~2 to 65; $n=49$; Table 1) is similar to that encountered in modern anoxic marine environments (~4.5–45; $n=4$; Fig. 2); the slightly larger range of the former may simply reflect the larger size of the sample population. The similar ranges of *m* values suggest that (1) the degrees of hydrographic restriction recorded by anoxic silled-basin facies of Devono-Carboniferous and Recent age are similar, and that (2) aqueous Mo concentrations in open-ocean (i.e., undepleted) seawater may have been similar for the Devono-Carboniferous and the Recent.

4.2. Broad spatio-temporal variation in m

General patterns of stratigraphic and geographic variation in Mo–TOC relationships for the study formations can be evaluated by plotting values of *m* on a space–time diagram (Fig. 9). This approach reveals a broad pattern of systematic stratigraphic variation in *m* in the basins for which data is available from multiple stratigraphic units, i.e., the Central Appalachian and Illinois basins. The basal units in both basins, i.e., the late Givetian "Geneseo Shale" (or Duffin facies of Portwood Member of New Albany Shale; Ettensohn, 1992) in the CAB and the Givetian–Frasnian Blocher Member of the New Albany Shale in the Illinois Basin, yield low *m* values (<10). The bulk of the black shale succession in both basins, which is of middle Frasnian to late Famennian age, yields *m* of ~10 to 25, a relatively narrow range of intermediate values. The youngest black shales in both basins, the Early Carboniferous Sunbury Shale and its lateral equivalents, yield relatively high *m* values (mostly >25). Thus, there appears to be a general increase in *m* values from the Givetian through the Early Carboniferous in both the CAB and IB.

Systematic geographic variation in *m* may exist as well, although the limited number of sampled sites for most time slices makes identification of such patterns tentative. The time slice for which the largest amount of data is available, the Early Tournaisian, appears to be characterized by systematic geographic variation in *m* values (Fig. 9). The highest values (~55–65) are associated with the upper Clegg Creek Member of the New Albany Shale in the southeastern Illinois Basin (Fig. 8A; Table 1, lines 11–12). The lateral equivalents of this unit exhibit progressively lower *m* values with increasing distance from the IB. Eastward, the Sunbury Shale yields *m* ~27–50 in Kentucky and ~16–28 in Ohio (Fig. 7C; Table 1, lines 30–32). Westward, the Upper Black Shale Member of the Bakken Shale in North Dakota exhibits a Mo/TOC ratio of ~35 (n.b., no Mo–TOC covariance exists, so no *m* value can be determined), and the Upper Black Shale Member of the Exshaw Formation yields *m* values of ~25 in southern Alberta and ~9 in northern Alberta (Fig. 8C–D; Table 1, lines 1, 3, 5). Thus, during the Early Carboniferous *m* values appear to have been greatest in the Illinois Basin and to have declined progressively with distance from that basin.

Stratigraphic variation in *m* within a single basin can be interpreted in terms of changes in degree of deepwater restriction as a consequence of eustatic or tectonic factors. For example, an increase in *m* in stratigraphically younger units is likely to reflect decreasing deepwater restriction and increasing aqueous Mo resupply. Such changes can be initiated by a eustatic rise or by tectonic subsidence of the basin-margin sill, in either case raising the pycnocline relative to sill depth (Fig. 12A; cf. Middelburg et al., 1991). Conversely, a decrease in *m* in stratigraphically younger units may result from increasing deepwater restriction and decreasing aqueous Mo resupply. Changes of this type can be initiated by a eustatic fall or by tectonic elevation of the basin-margin sill, in either case lowering the pycnocline relative to sill depth (Fig. 12B). Geographic variation in *m* is likely to reflect (1) varying "connectedness" to the global ocean, which is the ultimate source of undepleted seawater for resupply of Mo to cratonic-interior basins, and (2) varying degrees of watermass brackishness associated with freshwater discharge into semi-restricted cratonic basins. Sites located closer to the open ocean and further from cratonic runoff can be expected to yield higher *m* values than those located in cratonic-interior basins subject to strong freshwater discharge (cf. modern Baltic Sea; Algeo et al., in press).

In modern anoxic silled basins, $m<10$ is characteristic of strong hydrographic restriction, $10<m<25$ of moderate restriction, and $m>25$ of weak restriction (Figs. 2, 3; Algeo and Lyons, 2006). Based on these relationships, we infer that the low values of *m* in basal black shales of the CAB and IB reflect strong restriction of deepwaters during the initial stages of the Givetian-Frasnian transgression, and that subsequent increases in *m* indicate generally less restricted conditions during the mid-Frasnian to Tournaisian (Figs. 9, 12). These inferences are consistent with the depositional history of these basins. The basal black shales in the CAB and IB (the "Geneseo Shale" and lower Blocher Member of the

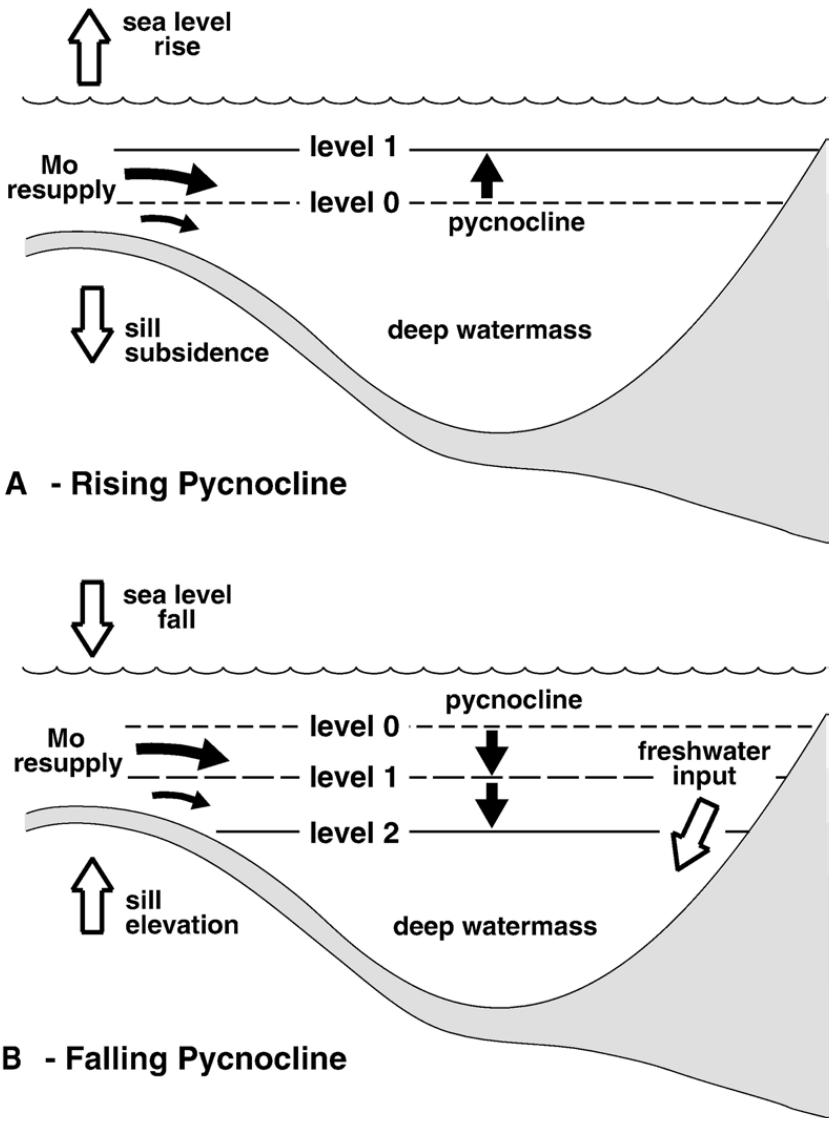

Fig. 12. Model of influence of relative sea-level changes on silled-basin hydrography. (A) A rising pycnocline (e.g., owing to sea-level rise or sill subsidence) creates more open-marine conditions that enhance deepwater renewal (curved arrows), resulting in higher $[Mo]_{aq}$ and shorter renewal times. (B) Conversely, a falling pycnocline (e.g., owing to sea-level fall or sill elevation) creates more restricted conditions that limit deepwater renewal (curved arrows), resulting in lower $[Mo]_{aq}$ and longer renewal times (cf. Figs. 2, 3). A moderate pycnocline fall (e.g., from level 0 to level 1) may maintain deepwaters of near-normal-marine salinity, whereas a large pycnocline fall (e.g., to level 2) may result in brackish deepwater conditions owing to freshwater input greatly in excess of deepwater renewal.

New Albany Shale, respectively) accumulated in geographically restricted areas, possibly representing small fault-bounded basins or incised valleys that were subjected to early flooding during the Givetian–Frasnian transgression of the craton (Fig. 9; Ettensohn, 1992). In contrast, the Sunbury Shale and its stratigraphic equivalents were deposited over a wide area during a major eustatic highstand in the Early Carboniferous. High sea-level elevations resulted in more open watermass conditions across the North American Seaway, facilitating renewal of deepwaters in all cratonic-interior basins. Even with generally improved watermass circulation, however, lateral variations in m (Fig. 9) suggest that geographic gradients in watermass conditions existed. Specifically, the high values of m exhibited by the upper Clegg Creek Member of the New Albany Shale imply that the Illinois Basin was well connected to the global ocean, possibly with exchange of deepwaters through the Mississippi Embayment area (Fig. 4). The progressively lower values of m encountered to the east in the CAB and NAB and to the west in the Williston and Elk Point basins suggest that these basins were further removed from open-ocean exchange, more strongly influenced by freshwater discharge, or both. These inferences are consistent with the Devono-Mississippian paleogeography of North America (Fig. 4).

4.3. High-resolution stratigraphic variation in Mo/TOC ratios

High-resolution chemostratigraphic datasets are available for the Famennian to Early Tournaisian Ohio-Sunbury shale succession of the Central Appalachian Basin and for the largely correlative Famennian Kettle Point Formation of Ontario (Fig. 10; Robl et al., 1983; Robl and Barron, 1988; Robl, unpubl. data; Armstrong, 1986). Although biostratigraphic studies of the Kettle Point Formation are lacking, wireline logs and other data have established its correlation to the Upper Devonian black shale succession of the CAB (Russell and Barker, 1984). Key tie-points are (1) the bases of the two units, which are correlative; (2) the *Protosalvinia* zone (an enigmatic index fossil), which appears at the base of the Middle Huron Member of the Ohio Shale and the base of Unit 2 of the Kettle Point Formation; (3) the silty Three Lick Bed of the CAB and its equivalent in Ontario; and (4) the Bedford–Berea gray shale–sandstone unit, which conformably separates the Famennian black shales from the overlying Sunbury Shale in both areas. Similarities in geochemical trends support the wireline-log correlations: the TOC records for the Ohio Shale and Kettle Point Formation are nearly identical, even showing similar features at a meter scale (Fig. 10; n.b., no geochemical data available for the Sunbury Shale in Ontario).

On the other hand, the Mo and Mo/TOC records of the two successions show some potentially significant differences. First, for all but the uppermost Famennian, Mo and Mo/TOC values are higher by nearly a factor of two in the Ohio Shale relative to the Kettle Point Formation (Fig. 10). Higher Mo/TOC values imply less restriction of the deep watermass, which is consistent with paleogeographic considerations: the CAB was closer to the open ocean than the Algonquin Arch area of Ontario, facilitating deepwater renewal, and it may have been less affected by salinity reduction associated with cratonic runoff. Second, the two successions exhibit sharply divergent trends in Mo and Mo/TOC values for the uppermost Famennian interval, despite similar trends in TOC (arrow 1, Fig. 10). In the Ohio Shale, Mo/TOC values decline from ~15–20 to ~5–8 in going from the lower to the upper Cleveland Member (arrow 2), whereas in the Kettle Point Formation, Mo/TOC values rise from ~10–15 to ~25 near the top of Unit 6 (arrow 3). The interpretation of this pattern is that the eustatic fall that led to deposition of the lowstand Bedford–Berea succession at the Devonian–Carboniferous boundary was initiated during latest Famennian time, and that the initial drop in sea-level elevation triggered differing responses in the CAB and on the Algonquin Arch owing to differences in bathymetry or watermass circulation. One possibility is that sea-level fall lowered the pycnocline in the CAB relative to the basin-margin sill, reducing deepwater renewal and aqueous Mo resupply (e.g., Fig. 12B), while concurrent climatic drying reduced freshwater discharge into the Algonquin Arch area, causing aqueous Mo concentrations to rise as a function of higher watermass salinity.

High-resolution chemostratigraphic records allow tests of the hypothesis of hydrographic control of Mo accumulation in anoxic marine environments. One test is whether Mo/TOC records exhibit short-term stability and gradual changes, as might be expected to result from a basinal watermass with slowly evolving physical and chemical properties. The Ohio-Sunbury and Kettle Point black shale successions exhibit relatively stable Mo/TOC ratios through most of the Famennian, although it is evident that rapid shifts can occur in conjunction with abrupt changes in environmental conditions, which are often associated with major changes in lithology (Fig. 10). A second test is whether different depositional basins show independent stratigraphic trends in Mo/TOC. If all basins of the Devono-Carboniferous North American Seaway yielded identical trends, this would provide evidence of a global-scale process such as changes to the trace-element inventory of global seawater, as proposed by Algeo (2004). On the other hand, if each basin exhibits a unique pattern of stratigraphic variation, then the dominant controls on Mo/TOC ratios are likely to be local, e.g., associated with variable degrees of deepwater restriction and watermass brackishness among basins (Algeo and Lyons, 2006). In this regard, the divergent Mo/TOC trends observed for late Famennian black shales of the CAB and Algonquin Arch (Fig. 10; see above) favor local hydrographic controls.

Although local hydrographic controls are clearly important, secular changes in the global trace-metal inventory of seawater (Algeo, 2004) nonetheless may have occurred during the Devono-Carboniferous. One instance may have been recorded by the Early Tournaisian Sunbury Shale and its stratigraphic equivalents, which were deposited in response to a major eustatic rise following the Devono-Carboniferous boundary lowstand (Fig. 9). The Sunbury exhibits a large increase in m relative to underlying Famennian black shales throughout the North American Seaway, most of which have $m<20$ (Fig. 10, arrow 4; Table 1). The highest m values in the Sunbury (~55–65) exceed those of even the least restricted of modern anoxic silled-basin environments, Saanich Inlet (Algeo and Lyons, 2006). Because Saanich Inlet has a short renewal time (<2 yr) and a high aqueous Mo concentration (~90% of that of fully marine seawater), it is difficult or impossible to account for m values higher than that of Saanich Inlet (~45) as a function of improved watermass exchange. An alternative explanation is that paleo-seawater Mo concentrations were higher than at present. With regard to the Sunbury Shale, the major eustatic lowstand at the Devonian–Carboniferous boundary may have resulted in widespread erosion of earlier-deposited black shales and transfer of large quantities of Mo from the sedimentary to the seawater reservoir. The increase in seawater Mo concentrations was not manifested by boundary lowstand sediments, which were deposited in oxic settings, but widespread development of anoxic facies during the subsequent Early Tournaisian transgression provided a sink for elevated quantities of seawater Mo. This hypothesis remains tentative at present, but it might be testable using an independent proxy for global anoxia such as Mo isotopes (Anbar, 2004; Arnold et al., 2004).

4.4. Significance of X-intercepts and m–b_x covariation

Although not widely recognized to date, many modern and ancient anoxic facies exhibit a non-zero TOC "threshold" for enrichment of trace metals (including Mo). Below the threshold, Mo concentrations typically are close to "background" detrital values of ~3 ppm (Taylor and McLennan, 1985; McLennan, 2001), whereas above this threshold Mo values can range as high as several hundred parts per million. The TOC threshold for Mo enrichment varies considerably among organic-rich facies. In modern anoxic silled basins, the threshold is ~0.5–2.0% for Black Sea sediments and ~2.5–3.5% for Saanich Inlet sediments (Fig. 2; Algeo and Lyons, 2006). In some ancient black shales the threshold is even higher, e.g., ~7% for the Upper Jurassic Kimmeridge Formation (Tribovillard et al., 1994, 2005) and ~10% for Upper Carboniferous cyclothemic core shales of the North American Midcontinent region (Algeo and Maynard, 2004). Many of the North American Devono–Carboniferous black shales considered in the present study also exhibit a non-zero TOC threshold for Mo enrichment. The threshold, which is equal to the X-intercepts (b_x) of Mo–TOC regression lines (Table 1, col. 9), ranges as high as ~6.8% TOC, although a majority of the study formations exhibit values of <2.5% TOC. A potentially important observation is that the slopes (m) and X-intercepts (b_x) of the Mo–TOC regression relationships for the study formations (e.g., Figs. 7, 8) exhibit significant positive covariation (Fig. 11).

Because the existence of TOC thresholds for trace-metal enrichment in anoxic facies has largely gone unnoticed, their significance has received little consideration. Algeo and Maynard (2004) proposed that the threshold is equivalent to the minimum sinking flux of organic matter needed to sustain a benthic redox potential low enough to catalyze trace-metal uptake (e.g., $[HS^-]_{aq}$ of >~0.1 μM is required to catalyze Mo uptake; Helz et al., 1996; Zheng et al., 2000). Organic matter sinking fluxes insufficient to sustain the critical redox potential will result in little increase in trace-metal concentrations above detrital background levels. In suboxic but nonsulfidic benthic settings trace-metal enrichment is limited or absent, but organic matter may nonetheless accumulate in quantity if preservation is facilitated by rapid burial or the refractory character of the organic material (Canfield, 1994; Zheng et al., 2000; Algeo and Lyons, 2006). Differences in TOC thresholds between anoxic facies (e.g., Figs. 7, 8; Table 1, col. 9) are likely due to facies-specific relationships between organic matter sinking fluxes and benthic redox potential, which can be influenced by sedimentation rates, organic matter lability, oxygen deficiency of renewing deepwaters, and other factors. Higher TOC thresholds are associated with higher sedimentation rates in modern anoxic silled basins (Algeo and Lyons, 2006), probably because higher organic carbon burial fluxes are required to sustain a critical benthic redox potential in less-restricted environments. However, this factor seems unlikely to account for the exceptionally large thresholds (~10% TOC) observed in Upper Carboniferous cyclothemic black shales of the North American Midcontinent region, which accumulated very slowly (Algeo and Maynard, 2004; Algeo et al., 2004). In the latter case, the key factors may be a high proportion of refractory terrestrial organic matter (~70% on average; Algeo, unpubl. data) and the strongly oxygen-deficient character of waters upwelling onto the Midcontinent Shelf (Algeo et al., in press). The relationships governing TOC thresholds for trace-metal enrichment in anoxic facies are likely to be complex and will require further research.

4.5. Estimation of paleohydrographic variables

Few sedimentary proxies are available for characterization of the physical hydrographic and aqueous chemical characteristics of marine paleoenvironments. For this reason, the relationships between sediment Mo/TOC and deepwater $[Mo]_{aq}$ and renewal time recognized among modern anoxic silled basins (Fig. 3; Algeo and Lyons,

2006) provide a potentially important tool for reconstructing aspects of the watermass characteristics of ancient anoxic silled basins. That modern anoxic silled basins may be good hydrographic analogs for similar Devono-Carboniferous marine environments is suggested by (1) similar ranges of *m* values (Fig. 2, Table 1), and (2) similar relationships between *m* and b_x (Fig. 11). Presumably, modern and Devono-Carboniferous anoxic silled-basin facies exhibit similar Mo–TOC relationships owing to similar environmental conditions and influences.

Based on modern relationships (Fig. 3), the $[Mo]_{aq}$ and renewal time of deepwaters in ancient anoxic silled basins may be estimated from sediment Mo–TOC regression-line slopes (*m*). The majority of North American Devono-Carboniferous black shales exhibit *m* between 10 and 25 (“intermediate-*m* black shales”; Fig. 13). These values are indicative of deepwater $[Mo]_{aq}$ equal to ~40–65% of the modern seawater concentration and to deepwater renewal times of ~100–500 yr. These conditions are intermediate between those found in modern Framvaren Fjord (*m* ~9) and Cariaco Basin (*m* ~25) and suggest a moderate degree of deepwater restriction. A few Devono-Carboniferous black shales yield $m<10$, e.g., the Blocher Member of the New Albany Shale and upper Cleveland Member of the Ohio Shale (“low-*m* black shales”; Fig. 13). These values imply deepwater $[Mo]_{aq}<20\%$ of the modern seawater concentration and deepwater renewal times >1000 yr, i.e., a degree of restriction similar to that of the modern Black Sea. However, it is possible that some of these units were deposited under brackish rather than fully marine conditions; this is suspected in particular for the “Geneseo Shale” of Kentucky, which exhibits *m* ~2 (Table 1, line 22). Conversely, a few Devono-Carboniferous black shales yield $m>25$, e.g., the Sunbury Shale, upper Clegg Creek Member of the New Albany Shale, and Bakken and Exshaw formations (“high-*m* black shales”; Fig. 13). These values imply deepwater $[Mo]_{aq}>70\%$ of the modern seawater concentration and deepwater renewal times <100 yr, i.e., a degree of restriction less than that of the modern Cariaco Basin and possibly similar to that of Saanich Inlet. Although such estimates are clearly tentative, they are in good accord with the known paleogeography of the Devono-Carboniferous North American Seaway. Given the paucity of sedimentary geochemical proxies that can provide quantitative estimates for hydrographic and aqueous chemical properties of marine paleoenvironments, the utility of sedimentary Mo–TOC relationships for this purpose warrants further study.

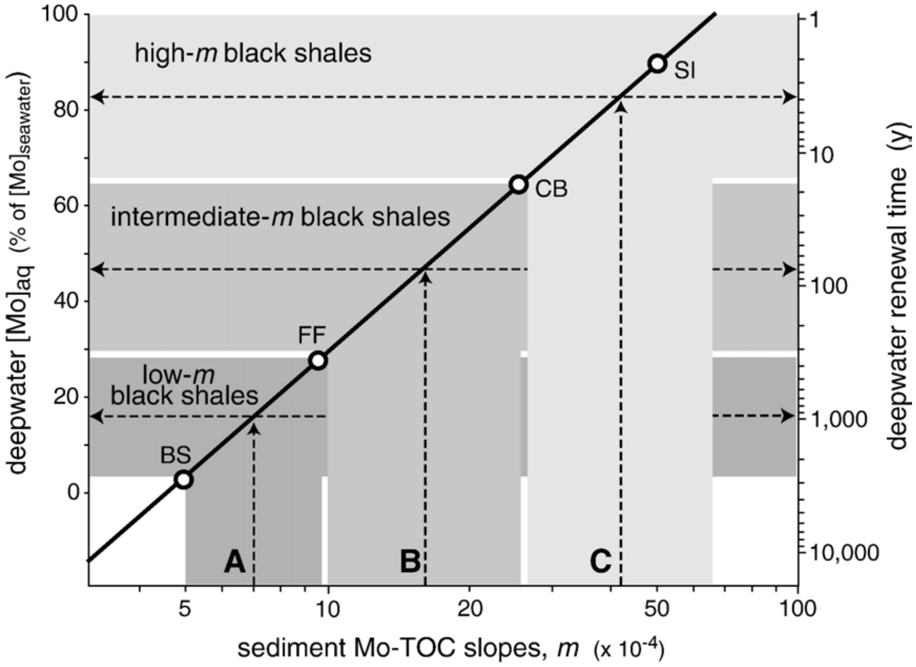

Fig. 13. Estimation of paleohydrographic parameters for deep watermasses of Devono-Carboniferous anoxic silled basins of the North American craton: (A) “low-*m* black shales” ($m<10$); (B) “intermediate-*m* black shales” ($10<m<25$); (C) “high-*m* black shales” ($m>25$). Most study formations fall in category B. Deepwater $[Mo]_{aq}$ and renewal time for paleoenvironments are estimated by plotting sediment Mo–TOC slopes (*m*) on the abscissa and tracking along the dashed lines to the left and right ordinate scales of each graph. The hydrographic relationships shown are based on modern anoxic silled basins (Fig. 3); abbreviations: BS = Black Sea, CB = Cariaco Basin, FF = Framvaren Fjord, and SI = Saanich Inlet.

4.6. Use of sedimentary Mo as a paleohydrographic or paleoredox proxy

A cautionary note needs to be sounded concerning the use of sedimentary Mo as a paleohydrographic proxy in the manner undertaken in the present study. Aqueous Mo depletion and its signal in the sedimentary record, i.e., lower Mo–TOC regression-line slopes (m), are likely to develop only in anoxic marine systems with at least a limited degree of deepwater restriction. This is likely to have been the case for the depositional environments of most of the North American Devono-Carboniferous black shales of the present study, but there are other types of anoxic facies, e.g., continent-margin upwelling systems, that may be unsuitable for the type of analysis undertaken here (see Algeo and Lyons, 2006). Thus, it is essential that researchers can show or reasonably infer deepwater restriction in a paleoenvironment before attempting to apply sedimentary Mo as a paleohydrographic proxy. Even in systems with restricted deepwater renewal, other factors can potentially influence sedimentary Mo concentrations, including benthic redox potential, sedimentation rates, the type and degree of sulfurization of sedimentary organic matter (e.g., Helz et al., 1996; Lyons et al., 2003; Tribovillard et al., 2004; Meyers et al., 2005).

A second caveat is that sedimentary Mo concentrations and Mo/Al ratios must be used cautiously to assess paleoredox variation. Because sedimentary Mo concentrations are generally enriched in anoxic facies relative to oxic and suboxic facies, broad distinctions of this type are certainly possible. However, within modern anoxic marine facies, little consistent covariation is observed between redox conditions and sedimentary Mo concentrations owing to the strong influence of hydrographic restriction on the latter (Algeo and Lyons, 2006). Indeed, in some anoxic environments sedimentary Mo tends to covary positively with benthic redox potential, i.e., lower Mo concentrations are associated with higher aqueous sulfide concentrations. This does not represent direct control of sedimentary Mo accumulation by $[H_2S]_{aq}$ but, rather, a common response to variations in the degree of hydrographic restriction and rate of deepwater renewal in silled anoxic basins. Thus, the prevailing "paradigm" of lower redox potentials resulting in higher sedimentary Mo concentrations does not apply in environments characterized by more-or-less continuously anoxic conditions. This conclusion appears to be valid regardless of whether the dominant mechanism of Mo transfer to the sediment is scavenging by organic matter, authigenic sulfides, or Fe–Mn oxyhydroxides in the water column, or diffusion of Mo across the sediment-water interface (Lyons et al., 2003).

5. Conclusions

Sedimentary Mo–TOC relationships have considerable potential as a paleohydrographic proxy in anoxic silled-basin environments owing to dependence of Mo uptake on concentrations of both sedimentary organic matter (i.e., host-phase availability) and aqueous Mo (i.e., source-ion availability). Such environments were common in North American intracratonic basins during the Middle Devonian to Early Carboniferous interval. A large majority of the anoxic facies deposited in these basins exhibits significant positive covariation between Mo and TOC concentrations, but with substantial variation in the slopes (m) and X-intercepts (b_x) of the regression lines defining these relationships. Systematic patterns of spatio-temporal variation in m, which ranges from ~ 2 to 65 ($\times 10^{-4}$), suggest that Mo uptake was controlled by broad and slowly evolving hydrographic characteristics of the Devono-Carboniferous North American Seaway. Based on comparisons with modern anoxic marine environments, variation in m can be used to assess certain hydrographic and aqueous chemical variables related to watermass restriction, i.e., deepwater $[Mo]_{aq}$ and renewal time (τ_{dw}). Low m values (<10) are associated with early stages of eustatic transgression and imply $[Mo]_{aq} < 20\%$ of the normal seawater concentration and $\tau_{dw} > 1000$ yr, whereas high m values (>25) are associated with maximum eustatic highstands and imply $[Mo]_{aq} > 70\%$ of the normal seawater concentration and $\tau_{dw} < 100$ yr. The significance of variation in b_x is less well understood but probably reflects facies-specific relationships between organic matter sinking fluxes and benthic redox potential, which are influenced by sedimentation rates, organic matter lability, oxygen deficiency of renewing deepwaters, and other factors. Because sedimentary Mo concentrations do not exhibit a simple relationship to benthic redox potential in anoxic silled-basin environments, a broader implication of this study is that sedimentary Mo data must be used cautiously as a paleoredox proxy.

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References

Adams, J., 1992. Organic geochemistry of the Chattanooga Shale in Tennessee. M.S. thesis, Southern Illinois University, Carbondale, Illinois, 22 pp.

Algeo, T.J., 2004. Can marine anoxic events draw down the trace-element inventory of seawater? Geology 32, 1057–1060.

Algeo, T.J., Maynard, J.B. (Eds.), 1997. Cyclic Sedimentation of Appalachian Devonian and Midcontinent Pennsylvanian Black Shales: Analysis of Ancient Anoxic Marine Systems—A Combined Core and Field Workshop: Joint Meeting of Eastern Section AAPG and The Society for Organic Petrography (TSOP), Lexington, Kentucky. Univ. of Cincinnati, Dept. of Geology, Cincinnati, Ohio. Sept. 27–28, 147 pp.

Algeo, T.J., Maynard, J.B., 2004. Trace element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. Chem. Geol. 206, 289–318.

Algeo, T.J., Lyons, T.W., 2006. Mo-total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. Paleoceanography 21, PA1016. doi:10.1029/2004PA001112.

Algeo, T.J., Berner, R.A., Maynard, J.B., Scheckler, S.E., 1995. Late Devonian oceanic anoxic events and biotic crises: "Rooted" in the evolution of vascular land plants? GSA Today 5 (45), 64–66.

Algeo, T.J., Heckel, P.H., Maynard, J.B., Blakey, R., Rowe, H., in press. Modern and ancient epicratonic seas and the superestuarine circulation model of marine anoxia. In: Holmden, C., Pratt, B.R. (Eds.), Dynamics of Epeiric Seas: Sedimentological, Paleontological and Geochemical Perspectives. Geological Association of Canada Special Publication.

Algeo, T.J., Scheckler, S.E., Maynard, J.B., 2001. Effects of early vascular land plants on weathering processes and global chemical fluxes during the Middle and Late Devonian. In: Gensel, P., Edwards, D. (Eds.), Plants Invade the Land: Evolutionary and Environmental Perspectives. Columbia Univ. Press, pp. 213–236.

Algeo, T.J., Schwark, L., Hower, J.C., 2004. High-resolution geochemistry and sequence stratigraphy of the Hushpuckney Shale (Swope Formation, eastern Kansas): Implications for climato-environmental dynamics of the Late Pennsylvanian Midcontinent Seaway. Chem. Geol. 206, 259–288.

Anbar, A.D., 2004. Molybdenum stable isotopes: observations, interpretations and directions. In: Johnson, C.M., Beard, B.L., Albarede, F. (Eds.), Geochemistry of Non-traditional Stable Isotopes. Rev. Mineral. Geochem., vol. 55, pp. 429–454.

Armstrong, D.K., 1986. Trace element geochemistry and petrology of the Kettle Point Formation (Upper Devonian), a black shale unit of southwestern Ontario. M.S. thesis, Univ. of Waterloo, Waterloo, Ontario, Canada, 234 pp.

Arnold, G.L., Anbar, A.D., Barling, J., Lyons, T.W., 2004. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. Science 304, 87–90.

Baird, G.C., Brett, C.E., 1986. Erosion of an aerobic seafloor: significance of reworked pyrite deposits from the Devonian of New York State. Palaeogeogr. Palaeoclimatol. Palaeoecol. 57, 157–193.

Barrows, M.H., Cluff, R.M., 1984. New Albany Shale Group (Devonian–Mississippian) source rocks and hydrocarbon generation in the Illinois basin. In: Demaison, G.J., Muris, R.J. (Eds.), Petroleum Geochemistry and Basin Evaluation. Am. Assoc. Petrol. Geol. Mem., vol. 35, pp. 111–138.

Barrows, M.H., Cluff, R.M., Harvey, R.D., 1979. Petrology and maturation of dispersed organic matter in the New Albany Shale Group of the Illinois Basin. Proc. 3rd Eastern Gas Shales Symp., Morgantown, West Virginia. Report, vol. METC/SP-79/6. U.S. Dept. of Energy, Morgantown Energy Technology Center, pp. 85–114.

Barwise, A.J.G., 1990. Role of nickel and vanadium in petroleum classification. Energy Fuels 4, 647–652.

Bender, P., Hörmann, S., Lottmann, J., Sandberg, C.A., Schindler, E., Walliser, O.H., Ziegler, W., 1988. Field Trip B: Rhenish and Harz Mountains. In: Ziegler, W. (Ed.), 1st International Senckenberg Conference and 5th European Conodont Symposium (ECOS V). Part 1: Guide to Field Trips: Cour. Forsch.-Inst. Senckenberg, vol. 102, pp. 157–224.

Bjerstedt, T.W., Kammer, T.W., 1988. Genetic stratigraphy and depositional systems of the Upper Devonian–Lower Mississippian Price–Rockwell deltaic complex in the central Appalachians. U.S.A. Sediment. Geol. 54, 265–301.

Breger, I.A., Hatcher, P.G., Romankiw, L.A., Miknis, F.P., Maciel, G.E., 1983. Upper Devonian black shales of the eastern United States: organic geochemical studies — past and present. In: Miknis, F.P., McKay, J.F. (Eds.), Geochemistry and Chemistry of Oil Shales. Am. Chem. Soc. Symp. Ser., vol. 230, pp. 181–198. Washington, D.C.

Brett, C.E., Goodman, W.M., LoDuca, S.T., 1990. Sequences, cycles, and basin dynamics in the Silurian of the Appalachian Basin. Sediment. Geol. 69, 191–244.

Canfield, D.E., 1994. Factors influencing organic carbon preservation in marine sediments. Chem. Geol. 114, 315–329.

Caplan, M.L., 1997. Factors Influencing the Formation of Organic-Rich Sedimentary Facies: Example from the Devonian–Carboniferous Exshaw Formation, Alberta, Canada. Ph.D. Dissertation, Univ. of British Columbia, Vancouver, 688 pp.

Caplan, M.L., Bustin, R.M., 2001. Palaeoenvironmental and palaeoceanographic controls on black, laminated mudrock deposition: example from Devonian–Carboniferous strata, Alberta, Canada. Sediment. Geol. 145, 45–72.

Cecil, C.B., Brezinski, D.K., DuLong, F., 2004. The Paleozoic record of changes in global climate and sea level: Central Appalachian Basin. In: Southworth, S., Burton, W. (Eds.), Geology of the National Capital Region-Field Trip Guidebook. U.S. Geol. Surv. Circ., vol. 1264, pp. 77–133.

Coveney Jr., R.M., Watney, W.L., Maples, C.G., 1991. Contrasting depositional models for Pennsylvanian black shale discerned from molybdenum abundances. Geology 19, 147–150.

Crusius, J., Calvert, S., Pedersen, T., Sage, D., 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. Earth Planet. Sci. Lett. 145, 65–78.

Dean, W.E., Gardner, J.V., Piper, D.Z., 1997. Inorganic geochemical indicators of glacial–interglacial changes in productivity and anoxia of the California continental margin. Geochim. Cosmochim. Acta 61, 4507–4518.

Dean, W.E., Piper, D.Z., Peterson, L.C., 1999. Molybdenum accumulation in Cariaco basin sediment over the past 24 k.y.: A record of water-column anoxia and climate. Geology 27, 507–510.

de Witt Jr., W., Roen, J.B., 1985. Correlation and geographic extent of some Middle and Upper Devonian and Lower Mississippian black shales in the Appalachian Basin. U.S. Geol. Surv. Bull. 1605-A, 45–57.

Emerson, S.R., Huested, S.S., 1991. Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. Mar. Chem. 34, 177–196.

Erickson, B.E., Helz, G.R., 2000. Molybdenum(VI) speciation in sulfidic waters: stability and lability of thiomolybdates. Geochim. Cosmochim. Acta 64, 1149–1158.

Ettensohn, F.R., 1985a. The Catskill delta complex and the Acadian orogeny: a model. In: Woodrow, D.L., Sevon, W.D. (Eds.), The Catskill Delta. Geol. Soc. Am. Spec. Paper, vol. 201, pp. 39–49.

Ettensohn, F.R., 1985b. Controls on development of Catskill delta complex basin facies. In: Woodrow, D.L., Sevon, W.D. (Eds.), The Catskill Delta. Geol. Soc. Am. Spec. Paper, vol. 201, pp. 65–77.

Ettensohn, F.R., 1992. Changing Interpretations of Kentucky Geology-Layer-Cake, Facies, Flexure, and Eustacy. Kentucky Geol. Surv. Misc. Rept., vol. 5. Lexington, Kentucky, 184 pp.

Ettensohn, F.R., Barron, L.S., 1981. Depositional model for the Devonian–Mississippian black shales of North America: a paleoclimatic–paleogeographic approach. In: Roberts, T.C. (Ed.), Geol. Soc. Am. Cincinnati '81 Field Trip Guidebooks. Economic Geology, Structure, Stratigraphy, vol. II, pp. 344–361.

Ettensohn, F.R., Elam, T.D., 1985. Defining the nature and location of a Late Devonian–Early Mississippian pycnocline in eastern Kentucky. Geol. Soc. Amer. Bull. 96, 1313–1321.

Ettensohn, F.R., Goodman, P.T., Norby, R., Shaw, T.H., 1989. Stratigraphy and biostratigraphy of the Devonian–Mississippian black shales in west-central Kentucky and adjacent parts of Indiana and Tennessee. Proc. 1988 Eastern Oil Shale Symp. Univ. of Kentucky, Inst. Mining Minerals Res., Lexington, Kentucky, pp. 237–245.

Filby, R.H., Van Berkel, G.J., 1987. Geochemistry of metal complexes in petroleum, source rocks, and coals: An overview. In: Filby, R.H., Branthaver, J.F. (Eds.), Metal Complexes in Fossil Fuels. Am. Chem. Soc. Symp. Ser., vol. 344, pp. 2–39. Washington, D.C.

Frost, J.K., Zierath, D.L., Shimp, N.F., 1985. Chemical Composition and Geochemistry of the New Albany Shale Group (Devonian–Mississippian) in Illinois. Illinois State Geol. Surv. Contract Report, vol. 1985-4. U.S. Dept of Energy contract DE-AC21-76ET12142, 134 pp.

Gleim, W.K.T., Gatsis, J.G., Perry, C.J., 1975. The occurrence of molybdenum in petroleum. In: Yen, T.F. (Ed.), The Role of Trace Metals in Petroleum. Ann Arbor Science Publishers, Ann Arbor, Michigan, pp. 161–166.

Goodarzi, F., Fowler, M.G., Nassichuk, W.W., 1990. Organic geochemistry and organic petrology of Paleozoic oil shales in Canada. Proc. 1989 Eastern Oil Shale Symp. Univ. of Kentucky, Inst. Mining Minerals Res., Lexington, Kentucky, pp. 233–238.

Gradstein, F., Ogg, J., Smith, A., 2004. A Geologic Time Scale. Cambridge Univ. Press, Cambridge. 589 pp.

Hartwell, W.J., 1998. Geochemical and petrographic analysis of the Upper Devonian–Lower Mississippian Bakken black shales from the Williston Basin, North Dakota. M.S. Thesis, Univ. of Cincinnati, Cincinnati, Ohio, 256 pp.

Hassenmueller, N.R., 1993. New Albany Shale (Devonian and Mississippian) of the Illinois Basin. In: Roen, J.B., Kepferle, R.C. (Eds.), Petroleum Geology of the Devonian and Mississippian Black Shale of Eastern North America. U.S. Geol. Surv. Bull., vol. 1909, pp. C1–C19.

Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Pattrick, R.A.D., Garner, C.D., Vaughan, D.J., 1996. Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. Geochim. Cosmochim. Acta 60, 3631–3642.

Hirner, A.V., 1987. Metals in crude oils, asphaltenes, bitumen, and kerogen in Molasse Basin, southern Germany. In: Filby, R.H., Branthaver, J.F. (Eds.), Metal Complexes in Fossil Fuels. Am. Chem. Soc. Symp. Ser., 344, pp. 146–153. Washington, D.C.

Hitchon, B., Filby, R.H., Shah, K.R., 1975. Geochemistry of trace elements in crude oils, Alberta, Canada. In: Yen, T.F. (Ed.), The Role of Trace Metals in Petroleum. Ann Arbor Science Publishers, Ann Arbor, Michigan, pp. 111–121.

Holland, H.D., 1984. The Chemical Evolution of the Atmosphere and Oceans. Princeton Univ. Press, Princeton, New Jersey. 582 pp.

Hunt, J.M., 1996. Petroleum Geochemistry and Geology, 2nd ed. W.H Freeman and Company, New York. 743 pp.

Jaminski, J., 1997. Geochemical and petrographic patterns of cyclicity in the Devonian–Mississippian black shales of the Central Appalachian Basin. Ph.D. dissertation, Univ. of Cincinnati, Cincinnati, Ohio, 333 pp.

Jaminski, J., Algeo, T.J., Maynard, J.B., Hower, J.C., 1998. Climatic origin of dm-scale compositional cyclicity in the Cleveland Member of the Ohio Shale (Upper Devonian), Central Appalachian Basin, USA. In: Schieber, J., Zimmerle, W., Sethi, P.S. (Eds.), Shales and Mudstones, vol. 1. Schweizerbart'sche, Stuttgart, pp. 217–242.

Johnson, J.G., Klapper, G., Sandberg, C.A., 1985. Devonian eustatic fluctuations in Euramerica. Geol. Soc. Amer. Bull. 96, 567–587.

Jones, B., Manning, D.A.C., 1994. Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. Chem. Geol. 111, 111–129.

Kammer, T.W., Bjerstedt, T.W., 1986. Stratigraphic framework of the Price Formation (Upper Devonian–Lower Mississippian) in West Virginia. Southeast. Geol. 27, 13–32.

Kirkland, D.W., Denison, R.E., Summers, D.M., Gormly, J.R., 1992. Geology and organic geochemistry of the Woodford Shale in the Criner Hills and western Arbuckle Mountains, Oklahoma. In: Johnson, K.S., Cardott, B.J. (Eds.), Source Rocks in the Southern Midcontinent, 1990 Symposium. Oklahoma Geol. Surv. Circ., vol. 93, pp. 38–69.

Lambert, M.W., 1992. Lithology and geochemistry of shale members within the Devonian–Mississippian Chattanooga (Woodford) Shale, Midcontinent, USA. Ph.D. dissertation, Univ. of Kansas, Lawrence, Kansas, 163 pp.

Landais, P., Elie, M., Michels, R., 1994. Are time and temperature the only constraints to the simulation of organic matter maturation? Org. Geochem. 22, 617–630.

Landing, E., Brett, C.E. (Eds.), 1991. Dynamic stratigraphy and depositional environments of the Hamilton Group (Middle Devonian) in New York State. Part II: New York State Geol. Surv. Bull., vol. 469.

Landis, C.R., Trabelsi, A., Strathearn, G., 1992. Hydrocarbon potential of selected Permian Basin shales as classified within the organic facies concept. In: Johnson, K.S., Cardott, B.J. (Eds.), Source Rocks in the Southern Midcontinent, 1990 Symposium. Oklahoma Geol. Surv. Circ., vol. 93, pp. 229–247.

Leo, H.B., Cardott, B.J., 1994. Detection of natural weathering of upper McAlester Coal and Woodford Shale, Oklahoma, U.S.A. Org. Geochem. 22, 73–83.

Leventhal, J.S., Hosterman, J.W., 1982. Chemical and mineralogical analysis of Devonian black-shale samples from Martin County, Kentucky; Carroll and Washington counties, Ohio, Wise County, Virginia; and Overton County, Tennessee, U.S.A. Chem. Geol. 37, 239–264.

Leventhal, J.S., Briggs, P.H., Baker, J.W., 1983. Geochemistry of the Chattanooga Shale, Dekalb County, central Tennessee. Southeast. Geol. 24, 101–116.

Lewan, M.D., 1984. Factors controlling the proportionality of vanadium to nickel in crude oils. Geochim. Cosmochim. Acta 48, 2231–2238.

Lewan, M.D., 1987. Petrographic study of primary petroleum migration in the Woodford Shale and related rock units. In: Doligez, B. (Ed.), Migration of Hydrocarbons in Sedimentary Basins. Ēditions Technip, Paris, pp. 113–130.

Lineback, J.A., 1968. Subdivisions and depositional environments of New Albany Shale (Devonian–Mississippian) in Indiana. Am. Assoc. Pet. Geol. Bull. 52, 1291–1303.

Lineback, J.A., 1970. Stratigraphy of the New Albany Shale in Indiana. Indiana Geol. Surv. Bull. 44 (73 pp.).

Lyons, T.W., Werne, J.P., Hollander, D.J., Murray, R.W., 2003. Contrasting sulfur geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in the Cariaco Basin, Venezuela. Chem. Geol. 195, 131–157.

Mason, G.M., 1989. The association of trace elements with sulfide minerals in Chattanooga Shale. Proc. 1988 Eastern Oil Shale Symp. Univ. of Kentucky, Inst. Mining Minerals Res., Lexington, Kentucky, pp. 197–211.

Matthews, R.D., 1993. Review and revision of the Devonian–Mississippian stratigraphy in the Michigan Basin. In: Roen, J.B., Kepferle, R.C. (Eds.), Petroleum Geology of the Devonian and Mississippian Black Shale of Eastern North America. U.S. Geol. Surv. Bull., vol. 1909, pp. D1–D37.

McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochem. Geophys. Geosyst. 2 (G3) (paper # 2000GC000109).

Meyers, S.R., Sageman, B.B., Lyons, T.W., 2005. Organic carbon burial rate and the molybdenum proxy: theoretical framework and application to Cenomanian–Turonian oceanic anoxic event 2. Paleoceanography 20, A2002 (19 pp.).

Middelburg, J.J., Calvert, S.E., Karlin, R., 1991. Organic-rich transitional facies in silled basins: response to sea-level change. Geology 19, 679–682.

Morse, J.W., Luther III, G.W., 1999. Chemical influences on trace metal-sulfide interactions in anoxic sediments. Geochim. Cosmochim. Acta 63, 3373–3378.

Murphy, A.E., Sageman, B.B., Hollander, D.J., 2000a. Eutrophication by decoupling of the marine biogeochemical cycles of C, N, and P: a mechanism for the Late Devonian mass extinction. Geology 28, 427–430.

Murphy, A.E., Sageman, B.B., Hollander, D.J., Lyons, T.W., Brett, C.E., 2000b. Black shale deposition and faunal overturn in the Devonian Appalachian Basin; clastic starvation, seasonal water-column mixing, and efficient biolimiting nutrient recycling. Paleoceanography 15, 280–291.

Orth, C.J., Quintana, L.R., Gilmore, J.S., Barrick, J.E., Haywa, J.N., Spesshart, S.A., 1988. Pt-group metal anomalies in the Lower Mississippian of southern Oklahoma. Geology 16, 627–630.

Over, D.J., 1992. Conodonts and the Devonian–Carboniferous boundary in the Upper Woodford Shale, Arbuckle Mountains, south-central Oklahoma. J. Paleontol. 66, 293–311.

Over, D.J., 1997. Conodont biostratigraphy of the Java Formation (Upper Devonian) and the Frasnian–Famennian boundary in western New York State. In: Klapper, G., Murphy, M.A., Talent, J.A. (Eds.), Paleozoic Sequence Stratigraphy, Biostratigraphy and Biogeography: Studies in Honor of J. Granville ("Jess") Johnson. Geol. Soc. Am. Spec. Paper, vol. 321, pp. 161–177.

Over, D.J., 2002. The Frasnian/Famennian boundary in central and eastern United States. Palaeogeogr. Palaeoclimatol. Palaeoecol. 181, 153–169.

Piper, D.Z., 1994. Seawater as the source of minor elements in black shales, phosphorites and other sedimentary rocks. Chem. Geol. 114, 95–114.

Playford, G., McGregor, D.C., 1993. Miospores and organic-walled microphytoplankton of Devonian–Carboniferous boundary beds (Bakken Formation), southern Saskatchewan; a systematic and stratigraphic appraisal. Geol. Surv. Can. Bull. 445 (112 pp.).

Potter, P.E., Maynard, J.B., Pryor, W.A., 1982. Appalachian gas-bearing Devonian shales: Statements and discussion. Oil Gas J. 80, 290–318.

Quirke, J.M.E., 1987. Rationalization for the predominance of nickel and vanadium porphyrins in the geosphere. In: Filby, R.H., Branthaver, J.F. (Eds.), Metal Complexes in Fossil Fuels. Am. Chem. Soc. Symp. Ser., vol. 344, pp. 74–83. Washington, D.C.

Radke, M., Welte, D.H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: Influence of organic matter type. Org. Geochem. 10, 51–63.

Raiswell, R., Berner, R.A., 1986. Pyrite and organic matter in Phanerozoic normal marine shales. Geochim. Cosmochim. Acta 50, 1967–1976.

Rheams, K.F., Neathery, T.L., 1988. Characterization and Geochemistry of Devonian Oil Shale, North Alabama, Northwest Georgia, and South-Central Tennessee (A Resource Evaluation). Alabama Geol. Surv. Bull. 128 (214 pp.).

Rimmer, S.M., 2004. Geochemical paleoredox indicators in Devonian–Mississippian black shales, central Appalachian Basin (U.S.A.). Chem. Geol. 206, 373–391.

Rimmer, S.M., Cantrell, D.J., 1989. Organic maturation of the Cleveland Member of the Ohio Shale (eastern Kentucky). Proc. 1988 Eastern Oil Shale Symp. Univ. of Kentucky, Inst. Mining Minerals Res., Lexington, Kentucky, pp. 401–410.

Rimmer, S.M., Thompson, J.A., Goodnight, S.A., Robl, T.L., 2004. Multiple controls on the preservation of organic matter in Devonian–Mississippian marine black shales: Geochemical and petrographic evidence. Palaeogeogr. Palaeoclimatol. Palaeoecol. 215, 125–154.

Ripley, E.M., Shaffer, N.R., Gilstrap, M.S., 1990. Distribution and geochemical characteristics of metal enrichment in the New Albany Shale (Devonian–Mississippian). Indiana Econ. Geol. 85, 1790–1807.

Robison, V.D., 1994. The Exshaw Formation: a Devonian/Mississippian hydrocarbon source in the Western Canada Basin. In: Katz, B.J. (Ed.), Petroleum Source Rocks. Springer, New York, pp. 9–24.

Robl, T.L., Barron, L.S., 1988. The geochemistry of Devonian black shales in central Kentucky and its relationship to interbasinal correlation and depositional environment. In: McMillan, N.J., Embry, A.F., Glass, D.J. (Eds.), Devonian of the World, v. 2: Sedimentation. Canad. Soc. Petrol. Geol. Mem., vol. 14, pp. 377–392.

Robl, T.L., Taulbee, D.N., 1995. Demineralization and kerogen maceral separation and chemistry. In: Snape, C. (Ed.), Composition, Geochemistry and Conversion of Oil Shales. Kluwer, Dordrecht, pp. 35–50.

Robl, T.L., Bland, A.E., Koppenaal, D.W., Barron, L.S., 1983. Geochemistry of oil shales in eastern Kentucky. In: Miknis, F.P., McKay, J.F. (Eds.), Geochemistry and Chemistry of Oil Shales. Am. Chem. Soc. Symp. Ser., vol. 230, pp. 159–180. Washington, D.C.

Robl, T.L., Rimmer, S.M., Barron, L.S., 1991. Organic petrography of Mississippian and Devonian shales in east-central Kentucky. Proc.

1990 Eastern Oil Shale Symp. Univ. of Kentucky, Inst. Mining Minerals Res., Lexington, Kentucky, pp. 173–178.

Roen, J.B., Kepferle, R.C. (Eds.), 1993. Petroleum Geology of the Devonian and Mississippian Black Shale of Eastern North America. U.S. Geol. Surv. Bull., vol. 1909.

Russell, D.J., 1993. Stratigraphy of the Kettle Point Formation (Upper Devonian of southwestern Ontario, Canada)—Implications for depositional setting and resource potential. In: Roen, J.B., Kepferle, R.C. (Eds.), Petroleum Geology of the Devonian and Mississippian Black Shale of Eastern North America. U.S. Geol. Surv. Bull., vol. 1909, pp. E1–E11.

Russell, D.J., Barker, J.F., 1984. Stratigraphy and geochemistry of the Kettle Point Formation, Ontario. Proc. 1983 Eastern Oil Shale Symp. Univ. of Kentucky, Inst. Mining Minerals Res., Lexington, Kentucky, pp. 169–179.

Sageman, B.B., Hollander, D.J., Lyons, T.W., Murphy, A.E., Ver Straeten, C.A., Werne, J.P., 2003. A tale of shales; the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle–Upper Devonian, Appalachian Basin. Chem. Geol. 195, 229–273.

Sandberg, C.A., Poole, F.G., Johnson, J.G., 1988. Upper Devonian of western United States. In: McMillan, N.J., Embry, A.F., Glass, D.J. (Eds.), Devonian of the World, v. 1: Regional Syntheses. Canad. Soc. Petrol. Geol. Mem., vol. 14, pp. 183–220.

Savoy, L.E., Mountjoy, E.W., 1995. Cratonic-margin and Antler-age foreland basin strata (Middle Devonian to Lower Carboniferous) of the southern Canadian Rocky Mountains and adjacent plains. In: Dorobek, S.L., Ross, G.M. (Eds.), Stratigraphic Evolution of Foreland Basins. Soc. Sediment. Geol. Spec. Publ., vol. 52, pp. 213–231.

Schieber, J., 1994a. Evidence for high-energy events and shallow-water deposition in the Chattanooga Shale, Devonian, central Tennessee, USA. Sediment. Geol. 93, 193–208.

Schieber, J., 1994b. Reflection of deep vs. shallow water deposition by small-scale sedimentary features and microfabrics of the Chattanooga Shale in Tennessee. In: Embry, A.F., Beauchamp, B., Glass, D.J. (Eds.), Pangea: Global Environments and Resources. Canad. Soc. Petrol. Geol. Mem., vol. 17, pp. 773–784.

Schieber, J., 1998. Sedimentary features indicative of erosion, condensation, and hiatuses in the Chattanooga Shale of central Tennessee: Relevance for sedimentary and stratigraphic evolution. In: Schieber, J., Zimmerle, W., Sethi, P.S. (Eds.), Shales and Mudstones, v. 1. Schweizerbart'sche, Stuttgart, pp. 187–215.

Schieber, J., Lazar, R.O. (Eds.), 2004. Devonian Black Shales of the Eastern U.S.: New Insights into Sedimentology and Stratigraphy from the Subsurface and Outcrops in the Illinois and Appalachian Basins. Field Guide 2004 Great Lakes Section SEPM Annual Field Conference. Indiana Geol. Surv. Open-File Study, vol. 04–05. 90 pp.

Schülke, I., 1998. Conodont community structure around the 'Kellwasser mass extinction event' (Frasnian/Famennian boundary interval). Senckenb. Lethaea 77, 87–99.

Shaffer, N.R., Leininger, R.K., Gilstrap, M.S., 1984. Composition of the uppermost beds of the New Albany Shale in southeastern Indiana. Proc. 1983 Eastern Oil Shale Symp. Univ. of Kentucky, Inst. Mining Minerals Res., Lexington, Kentucky, pp. 195–205.

Smith, G.J., Jacobi, R.D., 2001. Tectonic and eustatic signals in the sequence stratigraphy of the Upper Devonian Canadaway Group, New York State. Am. Assoc. Pet. Geol. Bull. 85, 325–357.

Streel, M., 1986. Miospore contribution to the upper Famennian–Strunian event stratigraphy. Ann. Soc. Geol. Belg. 109, 75–92.

Streel, M., Caputo, M.V., Loboziak, S., Melo, J.H.G., 2000. Late Frasnian–Famennian climates based on palynomorph analyses and the question of the Late Devonian glaciations. Earth Sci. Rev. 52, 121–173.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell, Oxford. 312 pp.

Thompson, J.A., Rimmer, S.M., Robl, T.L., 1992. Organic facies in Devonian shales of east-central Kentucky: Preliminary results. Proc. 1991 Eastern Oil Shale Symp. Univ. of Kentucky, Inst. Mining Minerals Res., Lexington, Kentucky, pp. 405–414.

Tribovillard, N., Desprairies, A., Lallier-Vergès, E., Moureau, N., Ramdani, A., Ramanampisoa, L., 1994. Geochemical study of organic-rich cycles from the Kimmeridge Clay Formation of Yorkshire (G.B.): productivity vs. anoxia. Palaeogeogr. Palaeoclimatol. Palaeoecol. 108, 165–181.

Tribovillard, N., Riboulleau, A., Lyons, T., Baudin, F., 2004. Enhanced trapping of molybdenum by sulfurized marine organic matter of marine origin in Mesozoic limestones and shales. Chem. Geol. 213, 385–401.

Tribovillard, N., Ramdani, A., Trentesaux, A., 2005. Controls on organic accumulation in Late Jurassic shales of Northwestern europe as inferred from trace-metal geochemistry. In: Harris, N. (Ed.), The Deposition of Organic–Carbon-Rich Sediments: Models, Mechanisms, and Consequences. Soc. Sediment. Geol. Spec. Publ., vol. 82, pp. 145–164.

Tribovillard, N., Algeo, T.J., Lyons, T.W., Riboulleau, A., 2006. Application of trace metals as paleoredox and paleoproductivity proxies. Chem. Geol. 232, 12–32.

Van der Weijden, C.H., 2002. Pitfalls of normalization of marine geochemical data using a common divisor. Mar. Geol. 184, 167–187.

Van Tyne, A.M., 1993. Detailed study of Devonian black shales encountered in nine wells in western New York State. In: Roen, J.B., Kepferle, R.C. (Eds.), Petroleum Geology of the Devonian and Mississippian black shale of eastern North America. U.S. Geol. Surv. Bull., vol. 1909, pp. M1–M16.

Vorlicek, T.P., Helz, G.R., 2002. Catalysis by mineral surfaces: implications for Mo geochemistry in anoxic environments. Geochim. Cosmochim. Acta 66, 3679–3692.

Wang, H.D., Philp, R.P., 1997. Geochemical study of potential source rocks and crude oils in the Anadarko Basin, Oklahoma. Am. Assoc. Pet. Geol. Bull. 81, 249–275.

Werne, J.P., Hollander, D.J., Lyons, T.W., Sageman, B.B., 2002. An integrated assessment of a "type euxinic" deposit; evidence for multiple controls on black shale deposition in the Middle Devonian Oatka Creek Formation. Am. J. Sci. 302, 110–143.

Wilde, P., Lyons, T.W., Quinby-Hunt, M.S., 2004. Organic carbon proxies in black shales: molybdenum. Chem. Geol. 206, 167–176.

Woodrow, D.L., 1985. Paleogeography, paleoclimate and sedimentary processes of the Late Devonian Catskill Delta. In: Woodrow, D.L., Sevon, W.D. (Eds.), The Catskill Delta. Geol. Soc. Am. Spec. Paper, vol. 201, pp. 51–64.

Woodrow, D.L., Dennison, J.M., Ettensohn, F.R., Sevon, W.T., Kirchgasser, W.T., 1988. Middle and Upper Devonian stratigraphy and paleogeography of the central and southern Appalachians and eastern Midcontinent, U.S.A. In: McMillan, N.J., Embry, A.J., Glass, D.J. (Eds.), Devonian of the World, v. 1: Regional Syntheses. Canad. Soc. Petrol. Geol. Mem., vol. 14, pp. 277–301.

Wright, J., Colling, A., 1995. Seawater: Its Composition, Properties and Behaviour, 2nd ed. Pergamon, Oxford. 168 pp.

Yen, T.F., 1975. Chemical aspects of metals in native petroleum. In: Yen, T.F. (Ed.), The Role of Trace Metals in Petroleum. Ann Arbor Science Publishers, Ann Arbor, Michigan, pp. 1–30.

Zheng, Y., Anderson, R.F., van Geen, A., Kuwabara, J.S., 2000. Authigenic molybdenum formation in marine sediments: A linkage to pore water sulfide in the Santa Barbara Basin. Geochim. Cosmochim. Acta 64, 4165–4178.