

Geochemical paleoredox indicators in Devonian–Mississippian black shales, Central Appalachian Basin (USA)

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Abstract

The degree of anoxia that existed during accumulation of Devonian–Mississippian black shales in central Kentucky has been debated widely. In this study, geochemical data were used to elucidate paleodepositional environments for these units. Using analyses from ten cores collected from the outcrop belt in central Kentucky, sulfur, carbon, and selected trace-element relationships were compared. The Sunbury Shale (Tournasian, Lower Mississippian) and the Cleveland and Huron members of the Ohio New Albany Shale (Fammenian, Upper Devonian) show different relationships between carbon, sulfur, and trace elements. C–S–Fe relationships for the Sunbury suggest anoxic, possibly even euxinic, conditions prevailed during sediment accumulation. Analysis of C–S–Fe data suggests that the Cleveland may have accumulated under anoxic conditions, with intermittent dysoxia, whereas the Huron Member may have accumulated under a relatively wide range of conditions, from anoxic, to dysoxic, to possibly oxic.

These three units exhibit different degrees of trace-element enrichment, with the approximate order of enrichment relative to an average shale being Mo>Pb>Zn>V>Ni>Cu>Cr>Co. The Sunbury shows the highest levels of enrichment, followed by the Cleveland, with the Huron showing only slight enrichment for most of these trace elements. Differing degrees of enrichment may reflect differences in depositional environment during accumulation. High Mo concentrations in the Sunbury (generally 200–550 ppm) may infer euxinic conditions prevailed during sediment accumulation. The Cleveland and the Huron both show considerably lower Mo contents (averaging around 100 ppm). Geochemical ratios, including Ni/Co, V/Cr, and V/(V + Ni), also indicate variable paleoredox conditions for these shales. Based on previously established thresholds, V/Cr and Ni/Co ratios infer at least anoxic conditions during accumulation of the Sunbury, anoxic to dysoxic conditions during Cleveland accumulation, and dysoxic to oxic conditions for the Huron. V/(V + Ni) ratios tend to indicate consistently lower oxygen regimes than do other paleoredox indicators, and this discrepancy is greatest for the Huron Member. It is suggested that thresholds established for paleoredox indicators in previous studies should not be applied strictly, but that *relative* differences in these indicators *collectively* can infer variations in the degree of anoxia. In addition, relationships between C_{org} and redox elements may help elucidate the role of anoxia in OM accumulation.

It may be concluded from this study that the Devonian–Mississippian black shales of central Kentucky accumulated under variable bottom-water conditions. At least anoxic conditions prevailed during accumulation of much of the Sunbury Shale and the upper part of the Cleveland Member, and possibly euxinic conditions for the Sunbury. Bottom-water conditions may have been intermittently anoxic and dysoxic during deposition of the lower Cleveland. During accumulation of the Huron Member, it

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is likely that conditions ranged from anoxic to dysoxic to marginally oxic, possibly being close to normal marine conditions at times during accumulation of the lowermost Huron sediments.

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1. Introduction

There has been much debate over the conditions required for accumulation of organic-rich sediments with models suggesting enhanced preservation of organic matter (OM) under reducing conditions (Demaison and Moore, 1980) or high primary productivity (Pedersen and Calvert, 1990; Caplan and Bustin, 1998) as the primary control, or combinations of these factors (Tyson and Pearson, 1991; Ingall et al., 1993; Arthur and Sageman, 1994; Ingall and Jahnke, 1994; Murphy et al., 2000b). Other factors thought to contribute to high OM content include sediment starvation (e.g., Ettensohn, 1998; Jaminski et al., 1998; Murphy et al., 2000b; Sageman et al., 2003), clay surface-area effects (e.g., Mayer, 1994; Kennedy et al., 2002; Macki and Bustin, 2002); and physical protection of OM by clays (Salmon et al., 2000).

The organic-rich black shales of the Appalachian Basin have been studied extensively in terms of depositional environments, stratigraphy, and tectonics, but with differing interpretations of the environmental conditions present at the time of sediment accumulation (e.g., Ettensohn et al., 1979; Ettensohn and Barron, 1981; Ettensohn, 1985a,b; Schieber, 1998; Murphy et al., 2000a,b,c; Werne et al., 2002; Sageman et al., 2003). In particular, the reasons for extensive OM accumulation and preservation in these sediments have been debated in the literature. Ettensohn (1998) proposed that extensive black-shale basins formed in response to foreland basin subsidence associated with the Acadian orogeny. He suggested that accumulation of high organic-carbon (>10%) black shales was associated with the deepening of the foreland basin. These he termed transgressive black shales, which include the Lower and Upper Huron, Cleveland, and Sunbury (e.g., see Fig. 10, Ettensohn, 1998), and proposed accumulation under conditions of sediment starvation and widespread water-column anoxia beneath a permanent pycnocline (Ettensohn, 1985b,

1998). Lower organic-carbon (<10%) shales, termed regressive black shales and including the Middle Huron, Three Lick, and Bedford (Fig. 10, Ettensohn, 1998), accumulated as subsidence moved cratonward and clastic influx increased. During deposition of regressive shales, organic richness was possibly driven by productivity, enhanced by the influx of terrestrially derived nutrients into restricted marine embayments, in the absence of widespread water-column anoxic conditions (Ettensohn, 1998). Higher sediment influx helped protect and preserve accumulating OM.

Other workers have proposed models that invoke only seasonal water-column stratification and emphasize the importance of nutrient cycling under variable bottom-water conditions that in turn enhances productivity in surface waters following periodic deep-water overturn (Murphy et al., 2000a,b,c; Werne et al., 2002; Sageman et al., 2003). For example, Werne et al. (2002) proposed eustatic global sea-level rise and sediment starvation as a factor in the initiation of black-shale deposition for the Oatka Creek Formation (Middle Devonian, Givetian) in the northern part of the Appalachian Basin (western New York). They propose that, subsequently, seasonal anoxia led to nutrient (P) regeneration that enhanced productivity and possibly resulted in euxinic conditions. Data from a study of the Genesee (Middle Devonian) from the same area supported only seasonal development of a stratified water column (Murphy et al., 2000a,b,c) and thus only periodic development of anoxia. In fact, an analysis of several black shale units from the same core in New York demonstrated that very few of the black shale units were deposited under persistently anoxic or euxinic conditions, and that most accumulated under seasonally stratified water columns (Sageman et al., 2003).

As the major area of debate has been the extent to which these black-shale basins were anoxic or euxinic, the purpose of this study was to evaluate geochemical differences between the Sunbury Shale

(Tournasian, Lower Mississippian), and the Cleveland and Huron members of the Ohio/New Albany Shale (Fammenian, Upper Devonian) specifically looking at parameters that have been used elsewhere as redox indicators (e.g., Berner and Raiswell, 1983; Dean and Arthur, 1989; Hatch and Leventhal, 1992; Arthur and Sageman, 1994; Jones and Manning, 1994) to possibly provide insight to the conditions that existing during OM accumulation. Extensive data sets that include carbon, sulfur, major and minor element and trace-element data, which were generated as part of an evaluation of oil-shale resources in Kentucky (Robl et al., 1983), were used as the basis for this study.

Previous studies of the Sunbury, Cleveland, and Huron Shales, organic-rich facies in east-central Kentucky have shown significant differences in C–S–Fe and trace-element relationships. For example, Robl and Barron (1987) showed different C–S relationships for the Huron and Cleveland: the Huron is higher in sulfur, has a lower C–S ratio, and significant correlations are seen for the Huron between C_{org} and S_T and C_{org} and DOP (degree of pyritization) whereas the Cleveland shows no such correlations. Other

studies have examined C–S–Fe relationships for the New Albany in the Illinois Basin (Anderson et al., 1987; Beier and Hayes, 1989; Ripley et al., 1990). Carbon–sulfur–iron relationships and how they relate to depositional environments have been studied extensively for both modern and ancient sediments (e.g., Berner and Raiswell, 1983; Leventhal, 1983, 1987; Raiswell and Berner, 1986; Raiswell et al., 1988; Berner, 1989). Similarly, numerous studies have used trace-metal concentrations and ratios to differentiate between paleodepositional environments (e.g., Breit and Wanty, 1991; Hatch and Leventhal, 1992; Jones and Manning, 1994; Tribovillard et al., 1994), although, Calvert and Pedersen (1993) have added a note of caution because of the complexities of post-depositional processes. The black shales in this part of the Appalachian Basin are relatively immature ($R_o \sim 0.5\%$) (Rimmer et al., 1993; Curtis and Faure, 1997). There is little reason for concern about interpretation problems associated with the loss of carbon that accompanies thermal maturity (as discussed by Raiswell and Berner, 1987), thus S/C ratios may be used to evaluate original depositional environment.

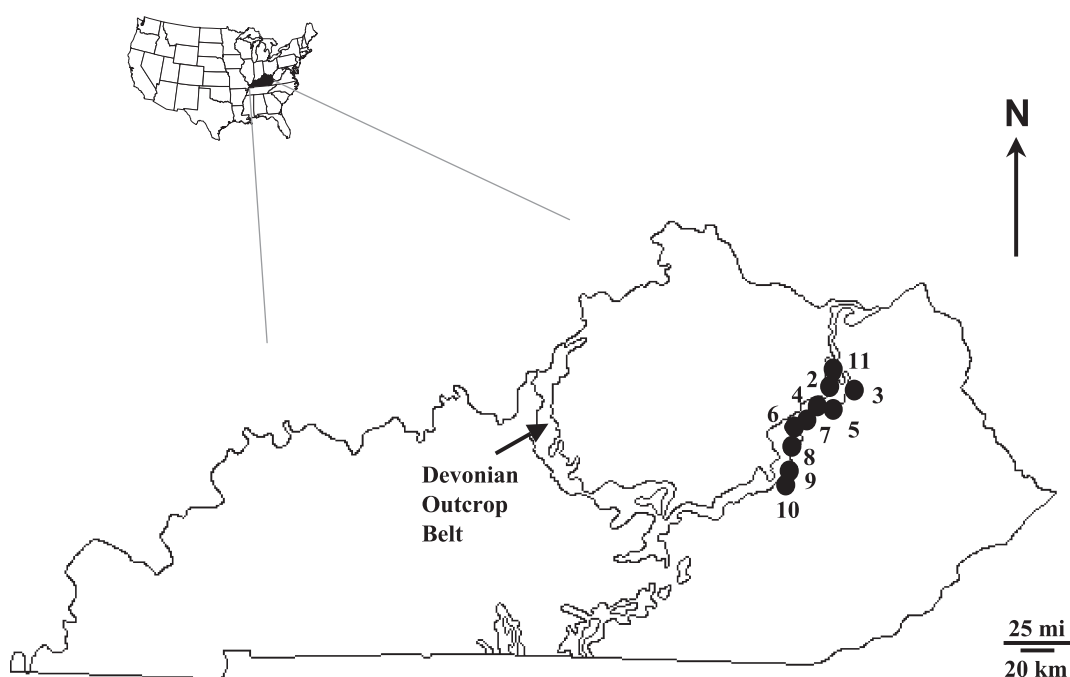


Fig. 1. Location of cores D2 through D11, east-central Kentucky.

2. Sampling and methods

Within the study area of the Devonian outcrop belt of east-central Kentucky, the New Albany/Ohio Shale thins onto the Cincinnati Arch to around 40–45 m (130–150 ft) thick. This study utilized data for the Sunbury–Huron interval for ten cores from Rowan, Bath, Montgomery, Powell, and Estill counties in east-central Kentucky (Fig. 1); in this area, USGS 7.5 min. geologic quadrangle maps use both New Albany Shale (cores D5 through D10) and Ohio Shale (cores D1 through D4) terminology. From the outcrop belt, the Devonian shales increase in thickness towards southeastern Kentucky (up to ~ 455 m, 1500 ft thick) as they dip down into the subsurface in the Appalachian Basin. Present-day burial depths for the shale increase towards the southeast, reaching ~ 730 m (2400 ft) in southeastern Kentucky. Even greater thicknesses and burial depths are seen in West Virginia (Provo, 1977).

In the study area, the Ohio Shale/New Albany Shale consists of the Cleveland and the Huron members,

separated by the Three Lick Bed (a number of interbedded siltstones and shales) (Fig. 2). The uppermost black shale unit studied was the Sunbury Shale. Brown-black to green-black shales predominate throughout the Ohio/New Albany interval, interbedded with occasional thin beds of siltstone and silty shale. The Cleveland Member was subdivided into upper and lower segments for each core based on organic carbon content: the lower section consistently has a lower carbon content (less than 10%), whereas the upper subunit contains in excess of 10% and as much as 17%. The Huron was subdivided into 3 units, lower, middle, and upper. These units were established based on the position of the *Foerstia* zone and variations in carbon content and are not intended to correlate directly with Provo’s units (e.g., Provo, 1977). The *Foerstia* zone occurs in the lower part of the Huron Member and is utilized as a regional marker bed (e.g., Schopf and Schwietering, 1970). Throughout the study area, a zone of greenish gray silty shales and black shales occurs near the base of the Huron Member, and the lower most section of the Huron Member also may

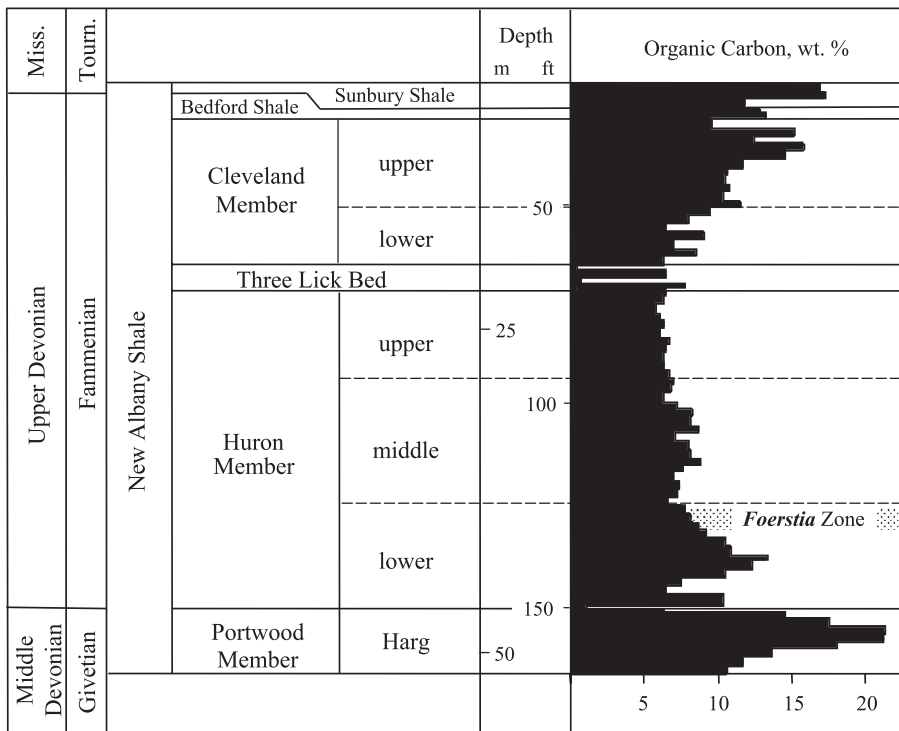


Fig. 2. Representative stratigraphic column (D6 core) showing organic carbon content (wt.%).

Table 1

Summary data for geochemical analyses of cores DN-2 through DN-11, east-central Kentucky (CT, C_{org}, and S_T, raw sample basis; oxides, percent 500 °C ash; trace elements, ppm 550 °C ash)

Variable	Sunbury (n=44)			Upper Cleveland (n=115)			Lower Cleveland (n=88)			Upper Huron (n=60)			Middle Huron (n=73)			Lower Huron (n=91)		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
C _T	9.31	18.60	12.95	7.96	17.11	11.61	4.82	9.94	7.30	4.45	6.52	5.79	4.77	8.36	6.50	0.83	12.34	6.70
C _{org} ^a	9.46	18.47	13.50	7.89	16.89	11.68	5.29	9.73	7.26	5.23	6.41	5.88	5.36	8.29	6.58	0.94	11.99	6.88
S _T	1.98	7.06	3.70	1.71	7.62	2.98	1.82	6.80	2.65	2.29	4.03	3.04	2.28	5.03	3.46	1.99	7.78	4.46
SiO ₂	57.30	72.50	64.98	49.43	71.07	66.05	60.65	69.48	65.89	60.50	67.92	63.02	61.01	69.92	65.57	56.86	64.78	60.94
Al ₂ O ₃	13.14	18.08	15.59	12.16	18.35	15.15	13.26	18.20	16.00	15.27	19.33	17.86	13.02	17.72	15.22	14.07	19.81	16.64
TiO ₂	0.61	1.06	0.75	0.66	0.93	0.82	0.76	0.97	0.90	0.82	0.98	0.91	0.72	0.91	0.81	0.78	1.06	0.89
Fe ₂ O ₃	4.87	13.89	8.10	4.85	14.64	6.92	4.92	12.34	6.41	6.24	8.58	7.37	5.72	10.29	7.64	6.54	15.35	9.98
K ₂ O	3.45	4.66	4.08	3.36	4.75	4.11	3.65	4.68	4.22	4.14	4.81	4.60	3.43	4.75	4.11	3.55	5.11	4.27
MgO	1.15	1.79	1.44	1.14	1.68	1.37	1.14	1.56	1.36	1.31	1.58	1.47	1.06	1.70	1.36	1.07	2.76	1.66
CaO	0.19	4.26	0.66	0.33	9.57	0.82	0.30	2.85	0.82	0.27	1.49	0.66	0.29	1.89	0.81	0.19	2.80	0.86
Na ₂ O	0.18	0.57	0.36	0.20	0.71	0.46	0.30	0.75	0.53	0.41	0.73	0.58	0.37	0.71	0.53	0.19	0.78	0.51
P ₂ O ₅	0.09	1.21	0.23	0.10	4.59	0.32	0.08	0.80	0.11	0.06	0.12	0.09	0.07	0.11	0.09	0.08	0.22	0.13
Co	17	32	24	15	26	19	16	24	20	22	27	25	20	32	25	21	41	30
Cr	121	322	178	138	269	198	92	155	113	82	119	99	69	103	84	75	121	90
Cu	74	195	132	72	222	121	43	146	68	44	77	59	44	93	64	36	127	75
Mo	103	559	297	36	207	82	69	185	132	72	113	87	48	118	88	14	180	95
Ni	128	503	282	110	208	144	80	165	113	95	120	105	47	113	83	46	165	90
Pb	72	812	234	50	163	89	60	104	73	67	93	81	53	113	82	46	277	114
V	532	3098	1166	370	1714	843	251	966	463	220	375	265	140	274	202	139	275	193
Zn	171	3208	1154	91	1313	539	79	929	261	91	299	157	46	337	161	54	1972	240
V/(V+Ni)	0.69	0.90	0.79	0.67	0.90	0.84	0.73	0.87	0.79	0.68	0.77	0.71	0.64	0.76	0.71	0.59	0.78	0.69
Ni/Co	6.62	18.29	11.79	5.18	10.83	7.62	4.18	8.31	5.66	3.77	5.04	4.23	2.13	4.71	3.33	1.92	4.85	2.93
V/Cr	3.72	9.62	6.29	1.82	6.98	4.26	2.41	6.74	4.00	2.00	3.51	2.67	1.57	3.31	2.40	1.58	2.77	2.13

^a C_{org} available on a subset of samples: Sunbury n=8; Upper Cleveland n=58; Lower Cleveland n=43; Upper Huron n=23; Middle Huron n=38; Lower Huron n=42.

contain burrowed shales (Robl et al., 1983). The *Foerstia* zone was taken as the boundary between the middle and lower subunits; the boundary between the middle and upper subunits was based on carbon profiles, the upper part having a somewhat consistent and lower carbon content (generally less than 5–6%), the middle unit exhibiting a pulse of carbon (usually about 7%) towards its center. In addition, several cores contain a carbon-rich, dolomitic shale topped by a bone bed towards the base of the core. This unit, the Harg facies of the Portwood Member of the New Albany Shale (Campbell, 1964) or the “Duffin lithology” of Robl and Barron (1987), is older (Middle Devonian) than the remainder of the New Albany and deposition of this unit was followed by a hiatus of non-deposition and erosion. Because of its discontinuous distribution (and hence lack of sufficient samples) this unit was not included in this study.

Data used in this study were collected on core composites representing ~ 0.6 m (2 ft) intervals for organic rich zones (Sunbury and Cleveland) and ~ 1.5 m (5 ft) intervals for those zones that contain less organic carbon (Huron). The data set includes 44 Sunbury, 115 upper Cleveland, 88 lower Cleveland, 60 upper Huron, 73 middle Huron, and 91 lower Huron samples. Lithologic descriptions, scintillometer measurements, sampling, and chemical analysis were performed by the Center for Applied Energy Research (CAER) at the University of Kentucky (formerly, the Kentucky Center for Energy Research Laboratory, or KCERL) as part of a Kentucky oil-shale resource assessment project.

Carbon and sulfur analyses were performed using standard methods (Robl et al., 1983); carbon was determined in duplicate using a Carlo-Erba Model 1106 elemental analyzer, and sulfur was determined using a Fisher Model 470 sulfur analyzer. Organic carbon was determined by difference between total carbon and mineral carbon. Major element oxides and trace elements were determined by X-ray fluorescence, using a Philips AXS automated spectrometer. Total carbon (C_T), organic carbon (C_{org}), and total sulfur (S_T), are reported on a raw sample basis; major oxide and trace element data are reported as percent of and ppm in the 500 °C ash, respectively. Complete data for all ten cores are presented in Robl et al. (1983), as are details of analytical techniques and data reproducibility; summary data are presented in Table 1.

These samples are low in carbonate content, and for some comparisons (e.g., for Sunbury samples) C_T was used rather than C_{org} because relatively few C_{org} values were available (the correlation coefficient between C_{org} and C_T for these data is 0.999, $n=212$). In addition, S_T was assumed to approximate pyritic sulfur (S_{pyr}) as little organic sulfur is present. Geochemical analyses of relatively pure kerogen concentrates show that S_{org} constitutes less than 2% of the organic matter (Taulbee et al., 1990). The degree of pyritization, or DOP, is defined as pyritic iron/(pyritic iron plus HCl-soluble iron) (Berner, 1970). In this study, DOP_T was determined from pyritic iron/total iron (Raiswell and Berner, 1986). Pyritic iron was calculated from total sulfur, assuming all of the sulfur was in the form of pyrite, using the stoichiometry of FeS_2 .

Redox terms used here—oxic, dysoxic, and anoxic—comply with those of Tyson and Pearson (1991) and refer to bottom-water oxygen levels (8.0–2.0, 2.0–0.2, and 0.0 mLO_2/l , respectively) associated with the accumulation of aerobic, dysaerobic, and anaerobic facies, respectively. Euxinic environments are those in which free H_2S is present in the water column (Raiswell and Berner, 1985).

3. Results

3.1. Carbon–sulfur–iron relationships

Redox conditions at the time of sediment accumulation may result in different carbon–sulfur relationships. For example, sediments that show no correlation between S_{pyr} and C_{org} and for which a crossplot shows a positive intercept may have accumulated under anoxic or euxinic conditions (Berner and Raiswell, 1983). Typically, sediments that accumulated under normal marine conditions show a positive correlation between S_{pyr} and C_{org} and a zero intercept on a crossplot of the two variables. In this part of the outcrop belt, the Sunbury Shale and the Cleveland and Huron members of the Ohio/New Albany Shale show different carbon–sulfur relationships. Within these cores, C_{org} content differs with stratigraphic interval. Using core D6 as an example (Fig. 2), the highest C_{org} contents are observed in the upper Cleveland and the Sunbury where C_{org} contents are typically between 10% and 15%. The lower portion of the Cleveland

ranges between 6% and 9% C_{org} . Within the Huron, the lowermost section ranges between 6% and 12% C_{org} , above the *Foerstia* zone the middle section has a slightly lower C_{org} content (typically 7–8%), and the uppermost Huron is consistently leaner with C_{org} contents around 6%. Lowest C_{org} values (below 1%) occur in parts of the Three Lick and the Bedford.

Similar trends occur in the 10-core data set. The Sunbury averages 13.9% C_T and ranges between 9.3% and 18.6%, the upper Cleveland averages 11.6% (range: 8.0–17.1%), and the lower Cleveland averages 7.3% (range: 4.8–10.0%) (Table 1). The Huron has lower overall carbon contents: C_T in the upper Huron averages 5.8% (range: 4.4–6.5%), in the middle Huron 6.5% (range: 4.8–8.4%), and in the lower Huron 6.7% (range: 0.8–12.3%). Sulfur contents vary significantly, with S_T ranging between slightly less than 2% and as much as 8%, and average S_T contents being lower for the Cleveland (average=3.0% and 2.6%, for the upper and lower subunits, respectively) than for either the Sunbury (average=3.7%) or the Huron (average=3.0%, 3.5%, and 4.5%, respectively, for the upper, middle and lower subunits) (Table 1).

Distinct differences are seen in the carbon–sulfur plots for these units (Fig. 3). Neither the Sunbury nor the Cleveland show highly significant correlations between carbon and sulfur: the correlation coefficient (r) for C_{org} versus S_T for all Cleveland samples is 0.205 (for $n=101$, correlation coefficients greater than 0.254 are significant at the 1% level); for the Sunbury, there is no correlation between C_T and S_T ($r=0.164$) (for $n=44$, correlation coefficients greater than 0.393 are significant at the 1% level). Statistical significance was determined by comparison with tables in [Snedecor and Cochran \(1989\)](#). A linear regression line drawn through these data produces an intercept along the sulfur axis between 2 and 3, but there is so much scatter in the data that not much confidence can be placed in such a line. The Huron samples ($n=103$) show a significant correlation between C_{org} and S_T ($r=0.758$, which is significant at the 1% level), and there is a positive, but low, intercept (0.8).

Another approach for determining depositional environment is that of “degree of pyritization” (DOP) as proposed by [Raiswell et al. \(1988\)](#), where DOP is the ratio of pyritic iron to total reactive iron (pyritic iron

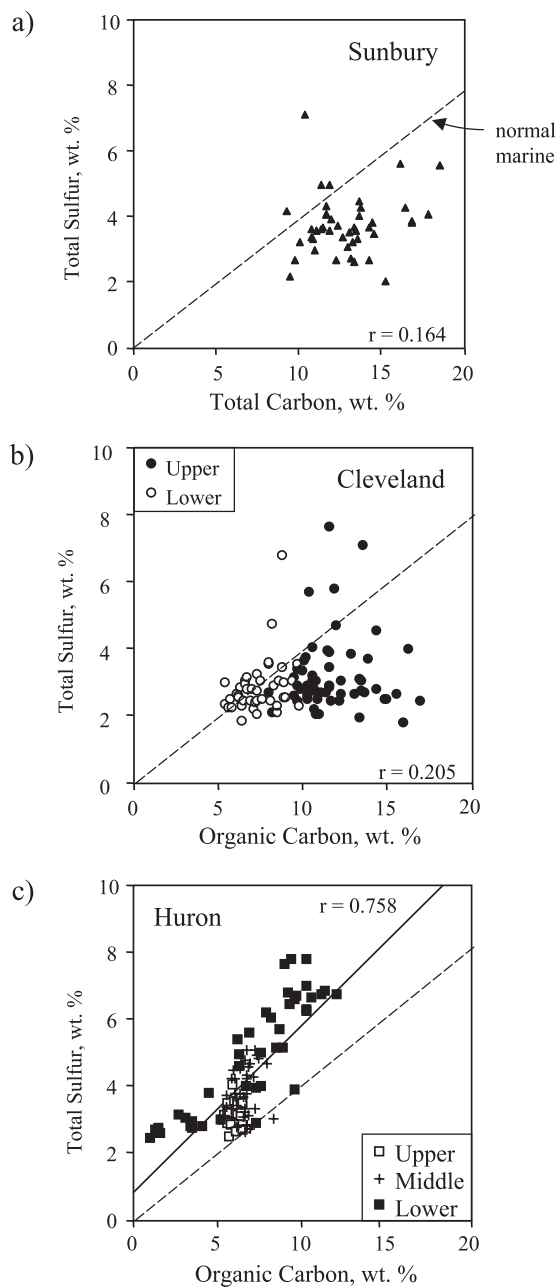


Fig. 3. Carbon–sulfur relationships. (a) Sunbury Shale, (b) Cleveland Member, and (c) Huron Member of the New Albany/Ohio shales. Solid lines are linear regression lines for data from this study; dashed line shows typical S/C ratio for normal marine sediments (based on [Berner and Raiswell, 1983](#)).

plus HCl-soluble iron). DOP_T calculated from pyritic iron/total iron (Raiswell and Berner, 1986) may be used to approximate DOP. Raiswell et al. (1988) determined that DOP values of ≤ 0.42 occurred in sediments deposited under aerobic (normal marine) conditions, and whereas there was some overlap between DOP values for “restricted” and “inhospitable” conditions (little or no oxygen present and H_2S possibly present), values in excess 0.75 indicated “inhospitable” conditions. Hence, values of 0.42 and 0.75 could approximate the boundaries between oxic and dysoxic conditions, and dysoxic and anoxic or euxinic conditions, respectively. Hatch and Leventhal (1992) suggest that intermediate DOP values (0.67–0.75) represent a less strongly stratified anoxic water column, and high DOP values (>0.75) a strongly stratified anoxic water column.

Average calculated DOP_T values for the Sunbury, Cleveland and Huron do not differ by much, being 0.68, 0.61, and 0.60, respectively; however, the distributions of these values are different (Fig. 4). The range in DOP_T values for the Sunbury is between 0.57 and 0.92, for the Cleveland 0.43 to 0.83, and 0.31 to 0.86 for the Huron. Thus, there is a wider distribution of calculated DOP_T values for the Cleveland than the Sunbury, and even more so for the Huron samples. Sunbury values would be consistent with mostly anoxic or euxinic conditions although a few may indicate dysoxic conditions, or as suggested by thresholds in Hatch and Leventhal (1992), at least a less strongly stratified anoxic water column. The upper Cleveland values seem to be more indicative of anoxic conditions than those of the lower Cleveland samples. For the Huron, possibly two populations are seen for the lower Huron, one plotting in the oxic to dysoxic range, the other in the anoxic range. Middle and upper Huron samples show values consistent with dysoxic to anoxic conditions. Overall, these calculated DOP values are in agreement with those calculated for the Huron and Cleveland by Robl et al. (1989), but are lower than those determined for samples of the New Albany Shale from the Illinois Basin by Raiswell et al. (1988).

An approach based on a similar premise uses ternary Fe–S–C diagrams (Dean and Arthur, 1989; Arthur and Sageman, 1994). On such a diagram, normal marine samples plot along a line equivalent to an S/C ratio of 0.4; samples in which all of the iron

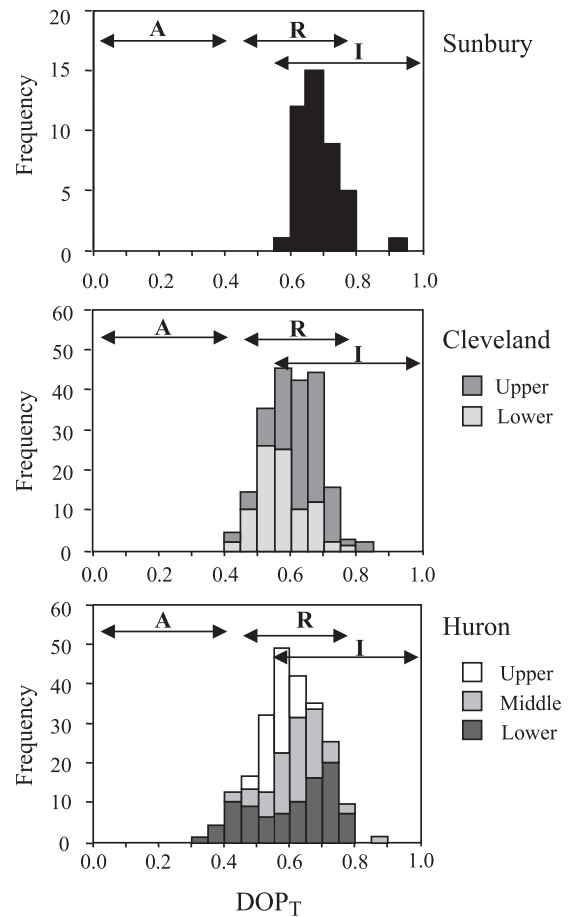


Fig. 4. Histograms showing calculated degree of pyritization (DOP_T) for the Sunbury, Cleveland, and Huron shales. A=Anaerobic; R=Restricted; I=Inhospitable (ranges from Raiswell et al., 1988).

is reactive and fixed as pyritic sulfur, data plot along the line describing a S/Fe ratio of 1.15 (based on the stoichiometry of pyrite) (see Fig. 5). Although not a direct measure of DOP, Arthur and Sageman (1994) used this technique and attained good agreement with DOP values determined by the HCl solubility method for several paleoenvironmental settings.

The Sunbury samples (Fig. 5a) plot fairly consistently along a line that intercepts the Fe/S axis at about 0.48 (i.e., 48% S and 52% Fe). If all of the iron was reactive and had been reduced and fixed in pyrite, an intercept at 0.54 would be expected (i.e., 54% S and 46% Fe). This suggests that approximately 89% (or 0.48/0.54) of the iron is in pyrite, which infers an

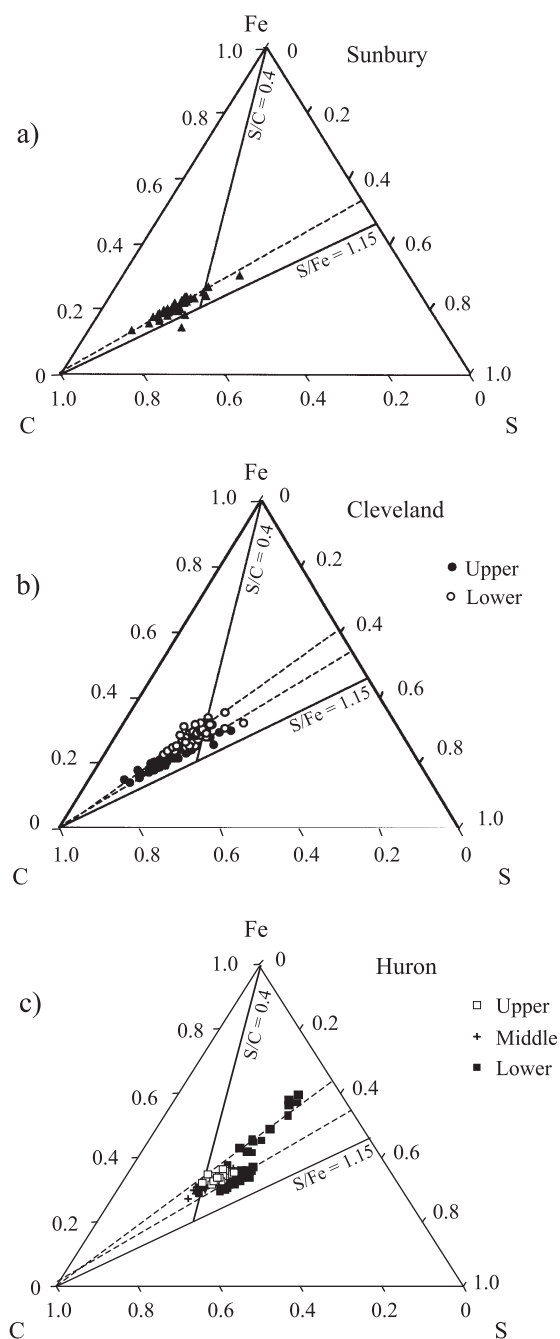


Fig. 5. Fe–S–C ternary diagrams. (a) Sunbury Shale, (b) Cleveland Member, and (c) Huron Member of the New Albany/Ohio Shales.

estimated DOP of 0.89, falling in the “inhospitable” or euxinic range (DOP>0.75) of Raiswell et al. (1988). The Cleveland samples (Fig. 5b) show more scatter and possibly indicate two separate trends: one group (mostly lower Cleveland samples) plot along a line that intersects the Fe/S axis at 0.39 (i.e., 39% S and 61% Fe), the other group (mostly upper Cleveland samples) plot along a line that intercepts the Fe/S axis at 0.46 (46% S and 54% Fe). These intercepts may infer DOP values of 0.72 and 0.85; the former would fall on the transition between dysoxic and anoxic, the latter within the anoxic range.

Huron samples (Fig. 5c) show different C–S–Fe relationships compared with the Sunbury and Cleveland samples. The middle and upper Huron samples tend to cluster around the S/C=0.4 line, but at relatively high C_{org} values. A line through the data may intersect the Fe–S axis at approximately 0.4, suggesting a DOP of around 0.74, placing these at the border of anoxic and dysoxic conditions. The lower Huron samples show two populations (as was suggested in the histogram in Fig. 4), with one group plotting along a line that intercepts the Fe/S axis at 0.37, the other at 0.45, inferring DOP values of 0.68 and 0.83, respectively. The former group would fall in the dysoxic range, but some of these data actually plot in an area similar to those for marginally oxic samples from the Stark Shale (Arthur and Sageman, 1994).

3.2. Trace elements

Analysis of trace-element data for these cores shows that all three shale units show different levels of enrichment. Enrichment factors (EF) were determined by normalizing each trace element to Al, which is assumed to represent the detrital influx, and comparing these ratios to those of a normal shale. This approach has been used by several authors to evaluate trace-element enrichments in modern and ancient sediments (e.g., Calvert and Pedersen, 1993). The enrichment factor (EF) is equal to $(\text{Element}/\text{Al})_{\text{shale}} / (\text{Element}/\text{Al})_{\text{normal}}$, where the ratio in the numerator is that for the shale in question, and the ratio in the denominator is that for a “typical” shale (using data from Wedepohl, 1971). Based on EF values, the magnitude of enrichment differs, with Mo showing the highest levels of enrichment and Cr and Co the least; the approximate order of enrichment relative to a typical

shale is Mo>Pb>Zn>V>Ni>Cu>Cr>Co (Table 2). The Sunbury generally shows the highest levels of enrichment, followed by the Cleveland, with the Huron showing the lowest enrichment factors.

Molybdenum has been suggested as an indicator of anoxic conditions (e.g., Dean et al., 1997) and higher levels of Mo have been reported for areas of anoxic basins that are more permanently anoxic (Francois, 1988). Molybdenum contents for these samples range from less than 20 ppm to about 550 ppm (Table 1). Lowest Mo contents are seen in parts of the Huron (<100 ppm) and the lower part of the Cleveland, and highest values (200–550 ppm) in the Sunbury Shale. For a large part of the data set there is a strong relationship between Mo and C_{org} (Fig. 6), although at high Mo contents (>200 ppm) there is considerable scatter in the data. At higher carbon contents (>10%),

two groups emerge, one with high Mo contents (the Sunbury) and one with considerably lower Mo contents (the upper part of the Cleveland Member). There are significant correlation coefficients between Mo and C_T , $r=0.605$ for the Sunbury ($n=44$), and between Mo and C_{org} , $r=0.906$ for the Huron samples ($n=224$), both significant at the 1% level. For the lower part of the Cleveland, the correlation coefficient is 0.370 ($n=88$) (significant at the 5% level), for the upper part 0.098 ($n=115$) (insignificant).

Trace-element indices Ni/Co, V/Cr, and V/(V+Ni) have been used in other studies to evaluate paleoredox conditions (e.g., Hatch and Leventhal, 1992; Jones and Manning, 1994). Jones and Manning (1994) suggested that Ni/Co ratios <5 inferred oxic conditions, 5–7 dysoxic conditions, and >7 suboxic to anoxic conditions. They also used V/Cr ratios of <2

Table 2
Enrichment factors (EF) for selected trace elements in the Sunbury, Cleveland, and Huron shales

Element	Average ^{a,b} Shale	Average ^{b,c} Black Shale	Sunbury ($n=44$)	Upper Cleveland ($n=115$)	Lower Cleveland ($n=88$)	Upper Huron ($n=60$)	Middle Huron ($n=73$)	Lower Huron ($n=91$)
Co (ppm)	19	10	24	19	20	25	25	30
(Co/Al) *10 ⁴	2.1	1.4	2.9	2.4	2.4	2.6	3.1	3.4
EF		0.7	1.4	1.1	1.1	1.2	1.4	1.6
Cr (ppm)	90	100	178	198	113	99	84	90
(Cr/Al) *10 ⁴	10.2	14.3	21.6	24.7	13.3	10.5	10.4	10.3
EF		1.4	2.1	2.4	1.3	1.0	1.0	1.0
Cu (ppm)	45	70	132	121	68	59	64	75
(Cu/Al) *10 ⁴	5.1	10.0	16.0	15.1	8.0	6.2	8.0	8.5
EF		2.0	3.1	3.0	1.6	1.2	1.6	1.7
Mo (ppm)	2.6	10	297	82	132	87	88	95
(Mo/Al) *10 ⁴	0.3	1.4	36.0	10.2	15.5	9.2	10.8	10.8
EF		4.9	122.4	34.8	52.6	31.3	36.7	36.8
Ni (ppm)	68	50	282	144	113	105	83	90
(Ni/Al) *10 ⁴	7.7	7.1	34.2	18.0	13.3	11.1	10.3	10.3
EF		0.9	4.4	2.3	1.7	1.4	1.3	1.3
Pb (ppm)	20	20	234	89	73	81	82	114
(Pb/Al) *10 ⁴	2.3	2.9	28.4	11.1	8.6	8.6	10.2	13.0
EF		1.3	12.5	4.9	3.8	3.8	4.5	5.7
V (ppm)	130	150	1166	843	463	265	202	193
(V/Al) *10 ⁴	14.7	21.4	141.3	105.1	54.7	28.0	25.1	22.0
EF		1.5	9.6	7.1	3.7	1.9	1.7	1.5
Zn (ppm)	95	300	1154	539	261	157	161	240
(Zn/Al) *10 ⁴	10.7	42.9	139.9	67.2	30.8	16.6	20.0	27.3
EF		4.0	13.0	6.3	2.9	1.5	1.9	2.5

Mean Al contents (%; 550 °C ash): Sunbury: 8.25%; Upper Cleveland: 8.02%; Lower Cleveland: 8.47%; Upper Huron: 9.45%; Middle Huron: 8.05%; Lower Huron: 8.78%. Trace element data reported as ppm, 550 °C ash.

^a Average shale data from Wedepohl (1971).

^b Mean Al content for average shale: 8.84% (Wedepohl, 1971); mean Al content for average black shale: 7.00% (Vine and Tourtelot, 1970).

^c Average black shale data from Vine and Tourtelot (1970).

to infer oxic conditions, 2–4.25 for dysoxic conditions, and >4.25 for suboxic to anoxic conditions. Lewan (1984) demonstrated that $V/(V+Ni)$ for OM that accumulated under euxinic conditions should be greater than 0.5. Hatch and Leventhal (1992) compared $V/(V+Ni)$ ratios to other geochemical redox indicators, including degree of pyritization, and suggested ratios greater than 0.84 for euxinic conditions, 0.54–0.82 for anoxic waters, and 0.46–0.60 for dysoxic conditions. The three units and their subunits show different trace element ratios (Table 1, Fig. 7). For each of the indices used, the Sunbury shows high overall values and data plot within the anoxic or euxinic fields. The upper Cleveland samples consistently show higher values than do the lower Cleveland. Ni/Co values indicate predominantly anoxic to dysoxic conditions for the upper Cleveland and dysoxic to oxic environments for the lower Cleveland samples. V/Cr values show similar differences, and whereas there is more spread in these values, values are weighted towards anoxic conditions for the upper Cleveland, and towards dysoxic conditions for the lower Cleveland. There is not good agreement between these two environmental indicators and $V/(V+Ni)$; this latter ratio infers euxinic to anoxic conditions for the Cleveland, but does suggest less extreme conditions for the lower Cleveland than the upper part of the unit. For the Huron Member, oxic to dysoxic conditions are suggested by Ni/Co and V/Cr ratios, with some indications that conditions may have shifted to lower oxygen regimes between accumulation of the lower part and the upper part of the unit. $V/(V+Ni)$ ratios show a similar shift up-section towards lower oxygen regimes, but as was observed for the Cleveland samples, this ratio infers lower oxygen bottom-water conditions (anoxic) than does either Ni/Co or V/Cr.

4. Discussion

4.1. Inferences from carbon–sulfur–iron relationships

Berner and Raiswell (1983) have shown that in normal marine sediments (under oxygenated conditions), pyrite production occurs below the sediment–water interface and is limited by organic carbon availability; thus, C_{org} and S_{pyr} show a strong positive

correlation and on a plot of C_{org} versus S_{pyr} , a line drawn through the data passes through the origin. For euxinic environments, pyrite formation is controlled primarily by iron availability, and a plot of C_{org} versus S_{pyr} shows a non-zero sulfur intercept (thus higher pyritic sulfur contents are associated with low organic carbon contents) (Berner and Raiswell, 1983). This positive intercept represents pyrite formation within the water column and at the sediment–water interface under euxinic conditions, a process that is independent of the amount of organic carbon deposited in the sediment (Lyons and Berner, 1992). Sediments deposited under euxinic conditions may show no relationship between C_{org} and S_{pyr} (a zero slope on a linear regression line through the data), or there may be some relationship between the two (a positive slope) (but plots for both scenarios will have a non-zero sulfur intercept). A positive slope could suggest some contribution due to carbon-limited, early diagenetic pyrite formation in addition to syngenetic pyrite formation; alternatively, it may represent syngenetic pyrite formation under iron-limited conditions, but where there is some relationship between organic carbon and reactive iron deposition (Lyons and Berner, 1992).

For the Sunbury and the Cleveland, there is little correlation between sulfur and carbon (Fig. 3a,b). If a linear regression line was drawn through the data, a positive intercept between 2 and 3 would result (however, there is considerable scatter in the data). The Huron shows a low positive intercept (0.8) and a positive correlation between sulfur and carbon (Fig. 3c). Based on the work of Berner and Raiswell (1983) and others, the S/C relationships shown here may suggest anoxic to euxinic conditions existed during Sunbury and Cleveland accumulation (no correlation and positive intercepts). Conditions during Huron accumulation probably were different; although the points do plot above the normal marine line as a result of higher sulfur contents, the positive correlation and small positive intercept for the Huron data may indicate that Huron conditions were not persistently anoxic, and possibly closer to normal marine at times. For example, data for the lower Huron from a single core (D6) not only show a positive correlation, but also a linear regression line that passes through the origin (Rimmer et al., review).

These interpretations would be consistent with environments of deposition inferred by DOP_T . Com-

paring the DOP_T distributions with previously established thresholds presented in Raiswell et al. (1988), primarily anoxic or euxinic conditions are suggested for the Sunbury, anoxic to dysoxic conditions for the Cleveland, with the upper part of the Cleveland showing a greater predominance of values in the anoxic range compared to more dysoxic values for the lower part of the unit; and highly variable conditions ranging from anoxic to oxic for the Huron. In the case of the Huron, parts of the lower Huron have some DOP_T values that suggest oxic conditions, which would be consistent with observations of burrowing in the lower parts of the unit. Middle and upper Huron samples are inferred to be dysoxic to anoxic. Conditions inferred from DOP_T are consistent with those suggested by the Fe–S–C ternary diagrams using the approach of Dean and Arthur (1989) and Arthur and Sageman (1994): anoxic to euxinic conditions for the Sunbury and Upper Cleveland; anoxic to dysoxic for the lower Cleveland; and anoxic, dysoxic and even marginally oxic for the Huron (Fig. 5).

4.2. Inferences from trace-element enrichments and redox indices

In black shales such as these, metals are incorporated via syngenetic mineralization associated with both sulfides, either as a discrete sulfide phase or as a trace component of pyrite, and organic matter (Pratt and Davis, 1992; Wignall, 1994). Factors influencing metal contents may include redox conditions, OM type, sediment accumulation rates, and diagenetic and later mineralization processes (Pratt and Davis, 1992). For Devonian black shale samples from the Illinois Basin, Ripley et al. (1990) noted significant enrichments in Cu, Pb, Zn, Ni, Cd, Mo, and V in high C_{org} zones. They proposed that within a stratified water column metals adsorbed, either electrostatically or via oxygen functional groups, onto woody (terrestrial) OM and thereby were transported down and incorporated into the sediment. Subsequent OM decomposition of labile marine OM led to desorption of the metals and formation of sulfide minerals and possibly V-bearing clays.

For the trace elements studied here, significant enrichments are seen for Mo and Pb in all units. For V and Zn, high enrichments factors (EF) are noted for

the Sunbury and Cleveland samples, but less so for other units; Ni and Cu show enrichments in the Sunbury and upper Cleveland. Other elements, such as Co and Cr do not show significant enrichments in any units. If incorporation of these elements, especially Mo, V, and Zn, is thought to be redox sensitive, EFs seen here would be consistent with the low oxygen bottom-water conditions suggested by C–S–Fe data for the Sunbury and Cleveland. Based on environments inferred by C–S–Fe data for the Huron, lower trace-element concentrations may be expected for the Huron. With the exception of Mo and Pb, EF values for the Huron are typically less than 2.0.

Molybdenum may be considered the best diagnostic element for sediment deposition under seawater sulfate-reducing conditions (Dean et al., 1997). Mo concentrations are strongly enriched in modern reducing sediments where free H_2S is present, with Black Sea reduced sediments containing 2–40 ppm and Saanich Inlet sediments 50–125 ppm (Crusius et al., 1996). Such levels are considerably higher than the average Mo concentrations in normal shales (2.6 ppm) (Wedepohl, 1971) and in black shales (10 ppm) (Vine and Tourtelot, 1970) (Table 2). Despite the relatively low average value reported for black shales, extremely high Mo concentrations have been observed, with some Pennsylvanian-age marine black shales containing in excess of 1000 ppm (Coveney and Martin, 1983; Coveney and Glascock, 1989).

The actual site and mechanisms for Mo enrichment is debated, with Calvert and Pedersen (1993) pointing out that the enrichment can occur both in anoxic surface sediments or in subsurface anoxic sediments (i.e., those accumulating below an oxic surface). Crusius et al. (1996) note a lack of Mo enrichment in materials from sediment traps within sulfidic basins and suggest also that the enrichment occurs at or below the sediment–water interface rather than within the water column. Others have suggested that higher levels of Mo may occur in areas of anoxic basins that are more permanently anoxic (Francois, 1988). One reason there is debate over the mechanisms involved in Mo enrichment is that, whereas some larger, identifiable molybdenum sulfide forms may occur much of the molybdenum in black shales and sediments deposited in euxinic environments is submicron, dispersed, and of uncertain form (Helz et al., 1996). Under anoxic conditions, Mo may be fixed by

sulfide precipitation (Bertine, 1972), may become associated with the organic matter (Pilipchuk and Volkov, 1974), or may be scavenged by Fe oxides or humic materials (Helz et al., 1996). Close associations with C_{org} have been reported (e.g., Vine and Tourtelot, 1970), possibly with humic (terrestrial) OM (e.g., Coveney et al., 1991), and with sulfides, especially pyrite (Huerta-Diaz and Morse, 1992). Ripley et al. (1990) suggest as much as 85% of the Mo in New Albany Shale samples from the Illinois Basin is associated with sulfide and selenide minerals.

Despite the uncertainties surrounding the mechanism of Mo enrichment, the Mo levels observed in these samples may provide some clues to redox conditions that accompanied sediment accumulation. A crossplot for Mo and C_{org} (Fig. 6) shows a strong coupling between the two elements. Above 200 ppm Mo, there is more scatter in the data, with Sunbury samples having Mo contents as high as 550 ppm. Coupling between C_{org} and Mo in the Oatka Creek of New York (Middle Devonian) has been attributed to scavenging of Mo by OM as it settled through a sulfidic water column (Werne et al., 2002). The strong correlation between the two ($r=0.605$) and high Mo contents (200–550 ppm) for the Sunbury observed in this study would certainly be consistent with this model. In addition, following the argument of Francois (1988), the high Mo contents seen in the Sunbury

may indicate persistent anoxia. However, a stronger correlation is observed between Mo and C_{org} for the Huron ($r=0.906$), but Mo contents stay relative low (less than 200 ppm and mostly <150 ppm). In an analysis of shales from the Midcontinent, Schultz and Coveney (1992) describe Heebner-type shales as having Mo contents up to 200 ppm, and DOP values between 0.27 and 0.35 that suggest oxic to dysoxic conditions. Piper (1994) compared several trace-element ratios (Cd:Cu, Zn:Ni:Mo, and Mo:Cu) with planktonic values for those same sediments and concurred that they most likely accumulated in the near absence of sulfate-reducing bottom waters. By comparison, therefore, we may infer that Mo contents of up to 200 ppm may not be inconsistent with more oxygenated bottom-water conditions. Certainly this interpretation, one of dysoxic and possibly only intermittent anoxic conditions during Huron and lower Cleveland accumulation would concur with carbon–iron–sulfur indications. However, under these conditions a strong coupling between Mo and C_{org} exists. The upper Cleveland samples are somewhat problematic; they show no correlation between C_{org} and Mo. However, this lack of correlation results from a few higher Mo (~ 6) samples away from the major trend in Mo– C_{org} for this unit. Except for these few data points, there is a significant relationship for the majority of the upper Cleveland samples.

Ni/Co has been used as an indicator of oxygen levels (Dypvik, 1984) as has V/Cr (Dill, 1986). Both were used later by Jones and Manning (1994) in a study of the utility of these parameters in the interpretation of Upper Jurassic to Lower Cretaceous sediments in Europe. Hatch and Leventhal (1992) looked at V/(V+Ni) ratios in Pennsylvanian-age shales and related this to depositional environment. Both Ni and V occur in highly stable tetrapyrrole structures (such as porphyrin) originally derived from chlorophyll and preferentially preserved under anaerobic conditions (Lewan and Maynard, 1982). Organic matter that has been exposed to aerobic conditions for an extended time will have a low tetrapyrrole content, and hence low Ni and V contents. Lewan (1984) suggested that because of the strong bonds between these elements and high molecular weight organics, the proportionality of vanadium and nickel in crude oils remains unchanged by thermal maturation, migration, or other alteration processes, and as such

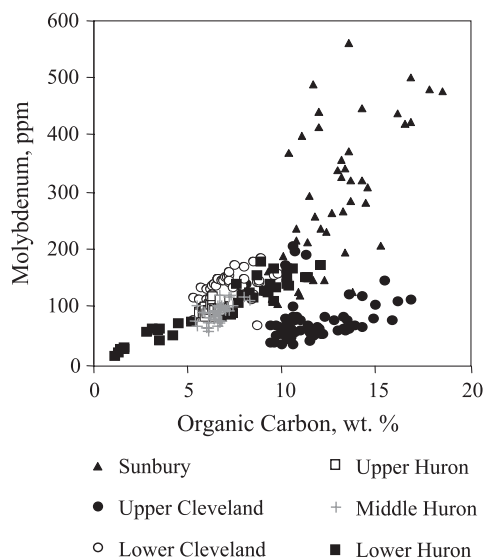


Fig. 6. Crossplot of Mo (ppm) and C_{org} (wt.%).

records environmental conditions at the time of deposition. V also may occur adsorbed onto clay minerals, an association that probably results following burial

(Breit and Wanty, 1991). Cr is thought to be associated only with the detrital fraction (Dill, 1986), is not influenced by redox conditions, and thus high V/Cr

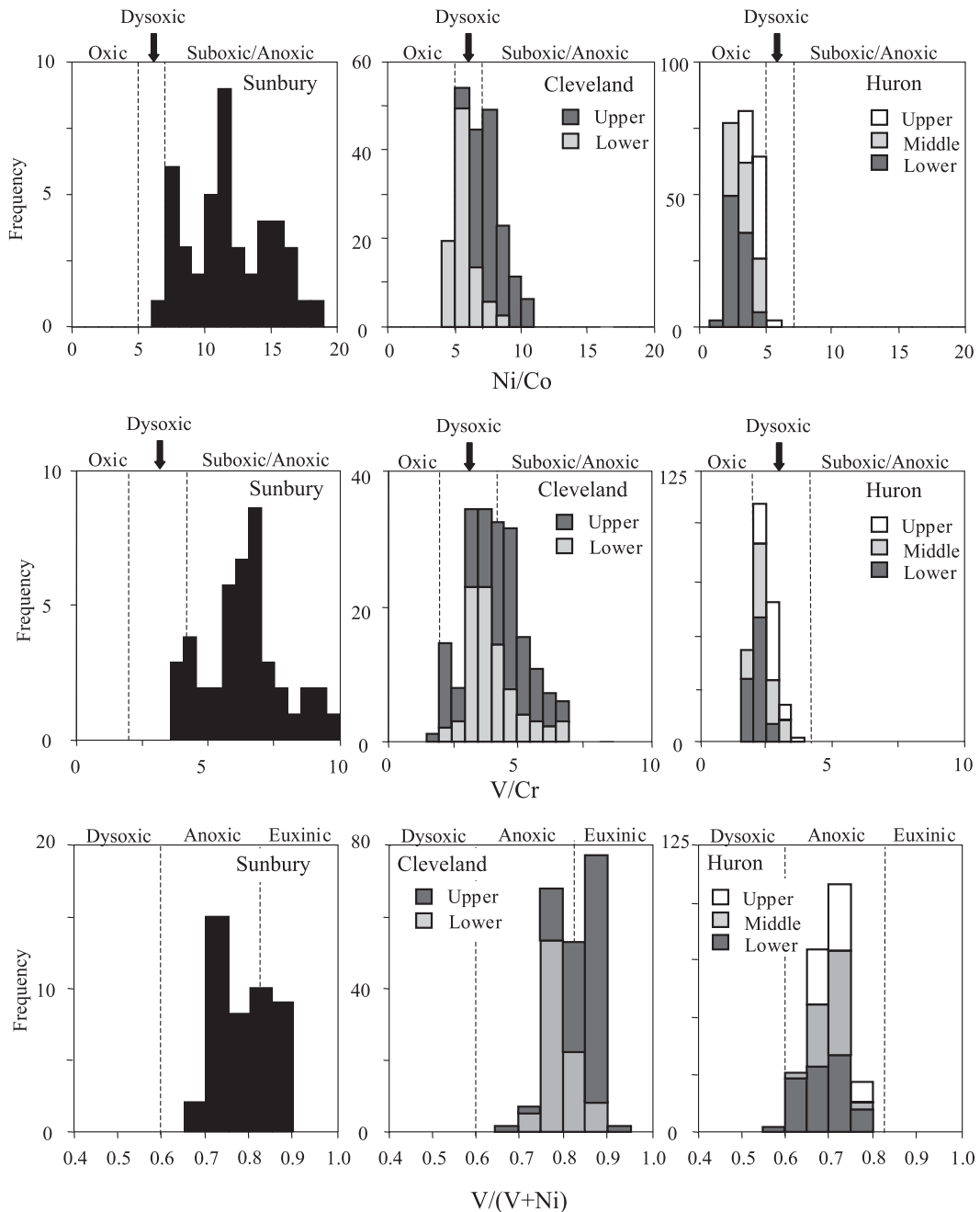


Fig. 7. Histograms for paleoredox proxies Ni/Co, V/Cr, and V/(V+Ni). Ranges for inferred bottom-water conditions for V/Cr and Ni/Co are from Jones and Manning (1994); ranges for V/(V+Ni) are from Hatch and Leventhal (1992).

values (>2) are thought to indicate anoxic conditions. Both Ni and Co occur in pyrite, but high Ni/Co ratios are thought to be associated with anoxic conditions (Jones and Manning, 1994).

In the present study, we see fairly good agreement in the interpretations of redox conditions using thresholds established by Jones and Manning (1994) for Ni/Co and V/Cr (Figs. 7 and 8a). However, $V/(V+Ni)$ ratios predict lower oxygen conditions than either Ni/Co or V/Cr for all but the Sunbury samples, for which there seems to be better agreement among predictions based on all of the ratios. In fact, for most of the Huron samples, $V/(V+Ni)$ predicts anoxic redox conditions, whereas Ni/Co (Fig. 8b) and V/Cr predict oxidic to dysoxic. There seems to be a coupling of Mo with Ni/Co suggesting similar controls on accumulation (Fig. 8c), with both suggesting anoxic to euxinic conditions for the Sunbury. Earlier, the possibility was raised that Mo contents below 200 ppm were not inconsistent with anoxic to dysoxic conditions. Fig. 8c shows the Huron and lower Cleveland samples, which have Mo contents <200 ppm, plot within oxidic to dysoxic ranges as indicated by Ni/Co ratios.

Although it may be problematical to compare these ratios directly to thresholds suggested in previous studies, these data do show variability between units that would be consistent with deposition under different paleoenvironmental conditions as was suggested by the C–S–Fe data. Thus, it may be reasonable to use these ratios in a *relative* sense, i.e., using differences in the ratios within a data set to suggest variable redox conditions, but specific thresholds developed for different geological formations should be applied cautiously. For example, strict application of Hatch and Leventhal's (1992) ratios developed for the Pennsylvanian (Missourian) Stark Shale Member would infer anoxic to euxinic environments for all of these units, which would be inconsistent with other redox indicators studied herein and sedimentological evidence (e.g., burrowing in the lower Huron). Differences between basins of different geologic age and geographic settings, such as influx of nutrients and trace elements from riverine sources, types and rela-

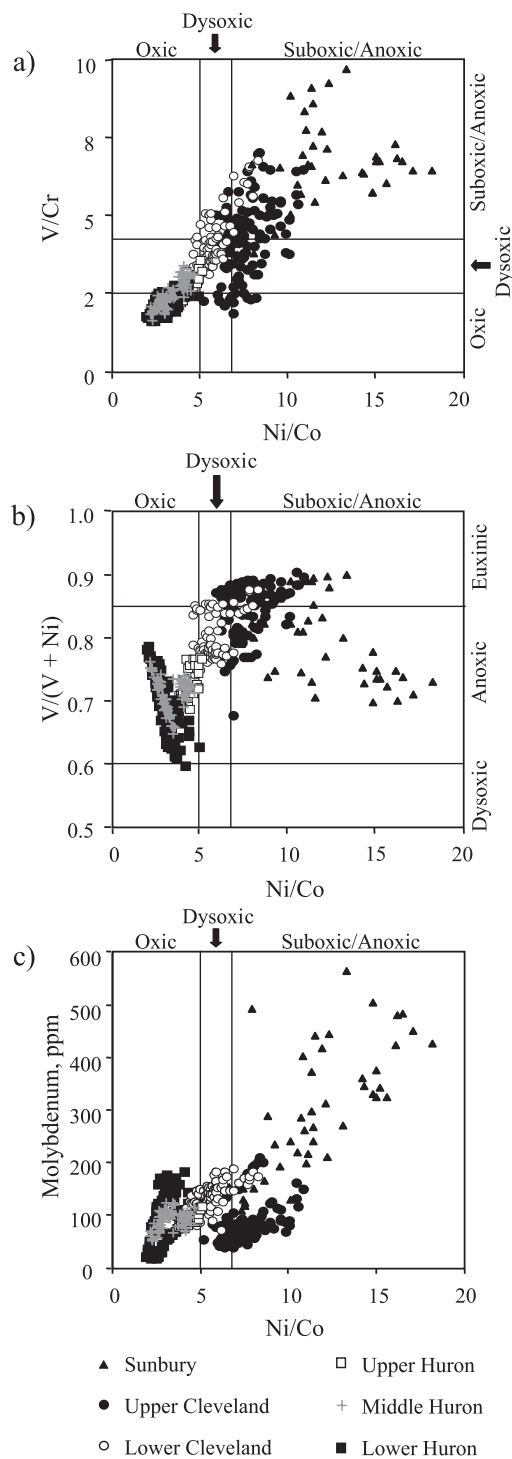


Fig. 8. Crossplots of trace-element ratios used as paleoredox proxies. (a) V/Cr vs. Ni/Co; (b) $V/(V+Ni)$ vs. Ni/Co; and (c) Mo vs. Ni/Co. Ranges for V/Cr and Ni/Co are from Jones and Manning (1994); ranges for $V/(V+Ni)$ are from Hatch and Leventhal (1992).

tive amounts of OM, degrees of oceanic mixing, and so on, would probably limit the application of these strict thresholds from one study to another.

4.3. Potential role of anoxia in organic carbon accumulation

One reason redox indicators were examined was to evaluate the role of anoxia in OM accumulation. Conditions inferred by this study indicate that for certain units, especially the Sunbury and possibly the upper Cleveland, the overwhelming majority of redox indicators suggest persistent anoxic and possibly euxinic conditions. Thus, in these two units at least, low-oxygen bottom waters and possibly even sulfidic bottom waters likely were a controlling factor in OM accumulation. Anoxic and intermittently dysoxic conditions probably enhanced accumulation of OM in parts of the lower Cleveland and the Huron. However, if redox conditions were the only factor in OM accumulation in these sediments, and if it is assumed that post-depositional and diagenetic changes have not significantly altered shale composition, strong correlations between redox-sensitive elements or ratios and C_{org} may be anticipated. It may be difficult to rule out the possibility of post-depositional alteration, but different relationships between C_{org} and a redox-sensitive element in adjacent units, units that most likely have experienced similar tectonic and basinal fluid influences, may suggest differing roles of anoxia during OM accumulation.

For example, if Ni/Co indicates redox conditions, then strong correlations may be expected between this ratio and C_{org} as is seen for the Cleveland and Sunbury samples; such a relationship does not occur in the Huron, where Ni/Co values suggest less reducing bottom conditions (Fig. 9). There may be several explanations for such observations. The elemental concentrations or ratios, in fact, may not be accurate indicators of redox conditions at the time of sediment accumulation; there may have been selective changes in elemental composition during diagenesis; or the lack of coupling between an element or ratio and C_{org} for a unit or subunit may imply that redox conditions were not the sole or even primary control on OM accumulation for that interval. Other factors, such as productivity or changes in the type of OM accumulating in the basin, also may have influenced seques-

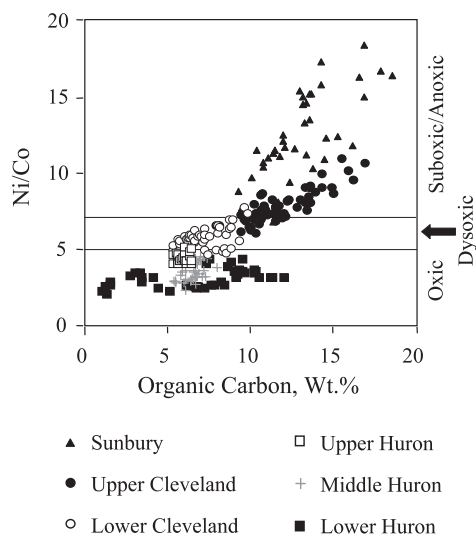


Fig. 9. Crossplot of Ni/Co and C_{org} (wt. %).

tration of OM. Thus, an examination of crossplots of C_{org} and redox sensitive elements may provide clues as to the role of anoxia in OM accumulation.

5. Conclusions

Based on this analysis of geochemical redox indicators for the Devonian–Mississippian black shales of central Kentucky, the following may be concluded:

1. Carbon–sulfur–iron relationships suggest that conditions during accumulation of the Sunbury and upper Cleveland were anoxic, and possibly euxinic in the case of the Sunbury. The lower Cleveland seems to have accumulated under conditions that were not as extreme as those experienced during deposition of the upper Cleveland, being anoxic at times but probably with intermittent dysoxia. The Huron accumulated under the most variable conditions, with the lower part of the Huron accumulating under anoxic though marginally oxic conditions.
2. Redox-sensitive elements (especially Mo) and trace-element redox indices (especially Ni/Co and V/Cr) suggest similar environments to those inferred by carbon, sulfur, and iron relationships. However, there is not complete agreement between

different redox trace-element ratios. Therefore, it is suggested that *absolute* thresholds established in other studies should be applied carefully, but that ratios may provide information on *relative differences* in redox conditions.

- Relationships between C_{org} and an element such as Mo or a ratio such as Ni/Co may provide clues as to whether redox conditions were the *primary* control on OM accumulation. Lack of a good correlation between two parameters likely reflects different processes or conditions were responsible for accumulation of the OM and the element(s) in question, assuming that relationships have not been altered by post-depositional processes.

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