

Can marine anoxic events draw down the trace element inventory of seawater?

Thomas J. Algeo Department of Geology, University of Cincinnati, Cincinnati, Ohio 45221-0013, USA

ABSTRACT

The trace element inventory of seawater is likely to have varied in the past owing to changes in the proportion of oxic-suboxic versus anoxic marine facies. Because only ~0.3% of the modern global seafloor is subject to benthic anoxia, removal of redox-sensitive trace elements from seawater is largely mediated by oxic-suboxic facies. This results in higher concentrations and longer residence times for such elements in seawater compared with strongly anoxic paleoseas such as those of the Late Devonian. Reservoir modeling of Mo in Late Devonian seawater suggests that its concentration could have been reduced to ~30%–50% of the present-day value. Chemostratigraphic data from Upper Devonian black shales of the Central Appalachian Basin provide empirical evidence of such depletion: sedimentary Mo concentrations decline within the Cleveland Shale despite intensified benthic anoxia, as proxied by degree of pyritization. Mo may have been depleted in penecontemporaneous seawater as a consequence of elevated burial fluxes associated with black shale deposition at time scales of 10^5 to $>10^6$ yr.

Keywords: molybdenum, biogeochemical cycles, paleoceanography, Devonian, black shale, Appalachian Basin.

INTRODUCTION

The global ocean is a major geochemical reservoir that mediates the transfer of many chemical species between the exosphere (i.e., hydrosphere + biosphere + atmosphere) and the lithosphere. Although secular variation in the major element chemistry of seawater has been documented (e.g., Holland, 1984; Hardie, 1996; Lowenstein et al., 2003), evidence for secular variation in its trace element inventory is limited (e.g., Emerson and Huested, 1991). Understanding such variation is important because certain trace elements play essential roles in biogeochemical processes, e.g., Mo and/or V are present in nitrogenase, an enzyme used by nitrogen-fixing bacteria, and Cu and Zn are components of many enzymes and proteins (Kieffer, 1991; Anbar, 2004). A paleocean containing significantly lower concentrations of such trace elements might have seriously perturbed biogeochemical cycles (Anbar and Knoll, 2002).

One of the most important influences on the trace element inventory of seawater through time probably has been black shale deposition. Certain redox-sensitive trace elements (e.g., Mo, Pb, U, V, Zn) exhibit significantly higher rates of transfer to the sediment at lower redox potentials as a consequence of uptake by organic matter or authigenic minerals (Morford and Emerson, 1999). Large quantities of such trace elements can become sequestered in organic-rich deposits during marine anoxic events, i.e., protracted episodes of widespread benthic anoxia such as that of the Late Devonian, potentially leading to a substantial drawdown of their seawater concentrations compared with those of a well-oxygenated ocean. The Late Devonian may have been an epoch particularly susceptible to such changes in seawater chemistry owing to extensive black shale deposition during an interval of ~15 m.y. (Ulmishek and Klemme, 1990). This contribution (1) evaluates the potential for drawdown of the trace element inventory of Late Devonian seawater using a reservoir model, and (2) presents chemo-

TABLE 1. BUDGETS OF REDOX-SENSITIVE TRACE ELEMENTS IN MODERN SEAWATER

Trace element*	Mass, $M^†$ (10^{12} kg)	Source flux, f_Q (10^6 kg yr $^{-1}$)	Residence time, $\tau^§$ (10^3 yr)	Black Sea/global burial flux ratio
Mo	13.3	18.2	731	0.034
U	4.40	10.9	402	0.016
V	2.69	56.0	48.1	0.011
Zn	0.69	25.0	27.7	~0
Pb	0.00062	12.9	0.048	~0

*Data sources: Mo, U and V—Morford and Emerson (1999); Zn—Chester (1990); Pb—Henderson and Maier-Reimer (2002); n.b.—anthropogenic fluxes not included.

$†$ Calculated based on a seawater mass of 1.32×10^{21} kg.

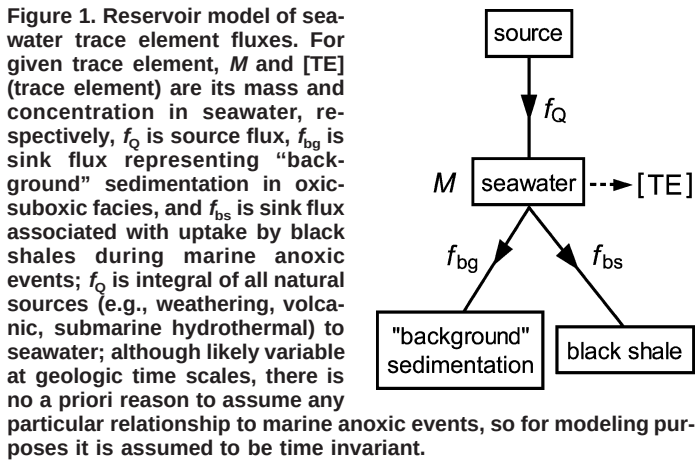
$§$ Calculated as M/f_Q ; see Meybeck (1988) for discussion of uncertainties in river flux data.

stratigraphic evidence for such changes from the Upper Devonian black shale succession of the Central Appalachian Basin.

MODERN SEAWATER TRACE ELEMENT BUDGETS

Redox-sensitive trace elements exhibit widely varying masses and residence times in modern seawater owing to differences in their source fluxes and removal processes (Table 1). The modern ocean may have a quasi-steady-state trace element inventory owing to dominance of oxic and suboxic facies during the past million years. At present, permanent (i.e., nonseasonal) benthic anoxia is found in only a few restricted ocean basins, fjords, and estuaries, accounting for ~0.3% of total seafloor area (Bertine and Turekian, 1973). This value probably has not been exceeded during the Quaternary, because the largest modern anoxic basins were either nonmarine (e.g., Black Sea) or better oxygenated (e.g., Cariaco Basin) during Pleistocene glacial stages (Jones and Gagnon, 1993; Yarincik et al., 2000). Limited uptake of redox-sensitive trace elements by anoxic facies during the Quaternary has resulted in comparatively high concentrations and long residence times of such elements in modern seawater.

Despite their present areal insignificance, anoxic facies potentially can play a disproportionately large role in the trace element budget of seawater. Global fluxes to anoxic facies can be approximated by flux estimates for the Black Sea, which accounts for approximately two-thirds of modern anoxic seafloor. Trace element enrichment occurs in surface sediments below the chemocline (~100–150 m water depth) over an area of ~330,000 km 2 (Murray, 1991). Marine-influenced sedimentation commenced ca. 7540 yr B.P., resulting in deposition of a surface layer (units I and II) with an average thickness of ~70 cm (Jones and Gagnon, 1993). Its volume is thus $\sim 2.3 \times 10^{11}$ m 3 and its average accumulation rate is $\sim 3.1 \times 10^7$ m 3 yr $^{-1}$. The surface layer has a high porosity (~70%–90%) and low dry bulk density (~300–500 kg m $^{-3}$; Keller, 1974), yielding a sediment mass flux of $\sim 1.2 \times 10^{10}$ kg yr $^{-1}$. Subtracting a detrital component (Table 1), the authigenic fraction of trace elements in this layer is ~50 ppm Mo, ~14 ppm U, ~50 ppm V, and ~0 ppm Zn and Pb (Hirst, 1974; Lyons, 1992; Colodner et al., 1995). Multiplying these values by the sediment mass flux, the burial fluxes of authigenic Mo and V are each $\sim 0.61 \times 10^6$ kg yr $^{-1}$ and that of authigenic U is $\sim 0.17 \times 10^6$ kg yr $^{-1}$. Thus, the Holocene Black Sea accounts for <4% of the global burial flux of Mo and <2% of that of other redox-sensitive trace elements (Table 1). This implies that oxic-suboxic facies dominate trace element sink fluxes



globally, and that the modern ocean may be a suitable analog for well-oxygenated paleoceans.

MODELING OF TRACE ELEMENT PALEOFLUXES

Possible changes in the trace element inventory of paleoseawater can be investigated using reservoir theory (Rodhe, 1992). The mass M of a given trace element in seawater can be modeled as a function of (1) a time-invariant source flux, f_Q , and (2) two first-order sink fluxes, one representing "background" sedimentation in oxic-suboxic facies, f_{bg} , and the other uptake by black shales during marine anoxic events, f_{bs} (Fig. 1). From the initial steady-state condition representing a well-oxygenated ocean (i.e., with $f_{bg} = f_Q$ and $f_{bs} = 0$), onset of a marine anoxic event activates the black shale sink, decreasing the trace element concentration, $[TE]$ (a linear function of mass, M), and residence time, τ , of a trace element in seawater (Fig. 2A). The system asymptotically approaches a new steady state with a concentration, $[TE]_{eq}$, and residence time, τ_{eq} , given by:

$$[TE]_{eq} = [TE]_0 \times f_{bg} / (f_{bg} + f_{bs}) \quad (1)$$

and

$$\tau_{eq} = \tau_0 \times f_{bg} / (f_{bg} + f_{bs}), \quad (2)$$

where $[TE]_0$ and τ_0 are the initial concentration and residence time of a trace element in seawater. The response time of the system (or $1/e$ -folding time), τ' , representing the time scale of adjustment to an external perturbation (Rodhe, 1992), is equal to the new steady-state residence time, τ_{eq} (equation 2). Thus, the system can be fully characterized by three parameters: (1) M_0 , the initial trace element mass in seawater, (2) f_Q , the source flux, and (3) f_{bs} , the black shale sink flux. In estimating trace element paleofluxes, M_0 and f_Q are based on modern seawater budgets (Table 1) and f_{bs} is calculated from sediment mass and trace element concentration data for ancient black shales (e.g., Table 2). The procedure used to calculate f_{bs} is the same as that for the Holocene Black Sea example here, i.e., determination of (1) sediment mass from formation dimension and density data; (2) sediment flux from sediment mass and formation duration; and (3) trace element flux from sediment flux and authigenic (i.e., total minus detrital) trace element concentrations.

The ~15 m.y. Late Devonian marine anoxic event deposited sediments containing 5–20 wt% of mainly type II organic matter widely across North America and in intracratonic basins of Russia, South America, northern Africa, and China (Ulmishek and Klemme, 1990). To assess the effects of these deposits on penecontemporaneous seawater chemistry, sediment mass and trace element concentration data

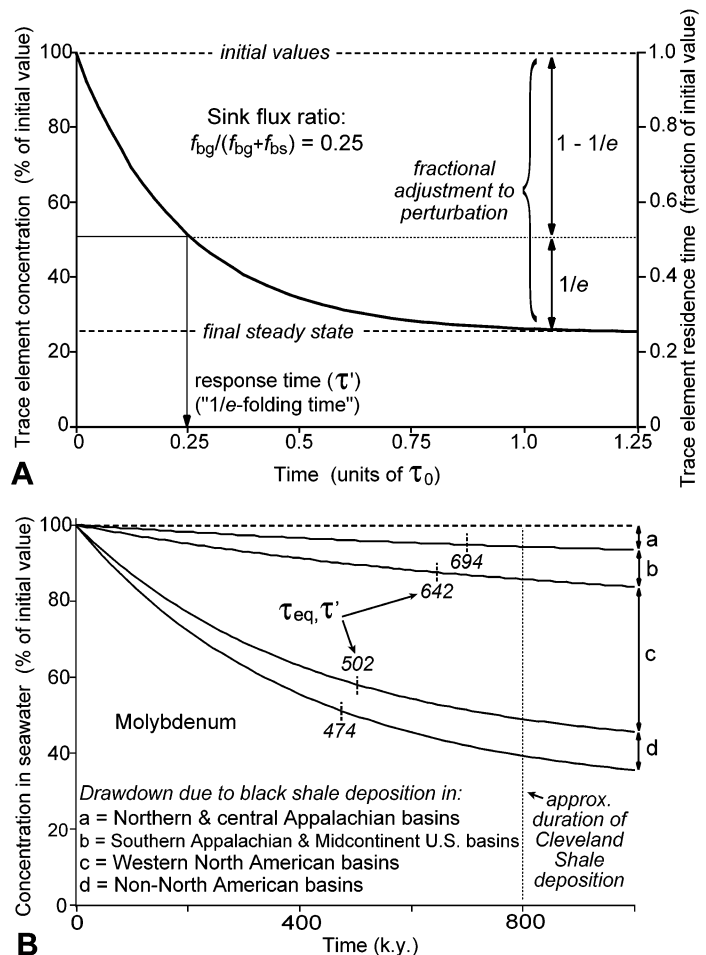


Figure 2. A: Evolution of trace element concentrations, $[TE]$, and residence times, τ , in seawater resulting from onset of marine anoxic event. $[TE]$ and τ asymptotically approach new steady-state values at rate determined by response time of system, τ' , and sink flux ratio, $f_{bg}/(f_{bg} + f_{bs})$. **B:** Drawdown of dissolved Mo in Late Devonian seawater resulting from Mo burial flux to Cleveland Shale of Central Appalachian Basin (a; Table 2) and global stratigraphic equivalents (b–d; n.b., curves are cumulative). Vertical dashed lines show new steady-state residence times, τ_{eq} , for Mo in seawater and system response times, τ' (equation 2; values in k.y.). Uncertainties in burial flux estimates, f_{bs} , are function of (1) availability of stratigraphic and geochemical data by region: $\pm 30\%$ for a and b, $\pm 2\times$ for c, no estimate for d; and (2) accuracy of time estimates: $\sim 800(\pm 2\times)$ k.y. for Cleveland Shale, which represents *expansa* and *praesulcata* zones of late Famennian Stage (Ettensohn et al., 1989).

TABLE 2. TRACE ELEMENT BURIAL FLUXES, UPPER DEVONIAN CLEVELAND SHALE

Trace element	Avg. concentration (total/authigenic)* (ppm)	Total mass† (10 ¹² kg)	Black shale sink flux f_{bs} ‡ (10 ⁶ kg yr ⁻¹)	Sink flux ratio $f_{bs}/(f_{bg} + f_{bs})$ §	Response time τ' (10 ³ yr)
Mo	170/167	0.77	0.96	0.050	694
U	15/11	0.05	0.16	0.006	400
V	500/370	1.71	2.14	0.037	46.3
Zn	350/255	1.18	1.47	0.056	26.1
Pb	50/30	0.14	0.17	0.013	0.047

*From Robl et al. (1984) and Jaminski (1997); detrital concentrations from Drever (1997).

†Trace element mass calculated as the product of formation mass and authigenic trace element concentration; formation mass (4.62×10^{15} kg) based on formation volume (1.78×10^{12} m³) from de Witt et al. (1993) and formation density (2600 kg m⁻³) from Schmoker (1979).

‡Calculated as total mass divided by formation duration (~0.8 m.y.; see Fig. 2 caption).

§"Background" sink flux, f_{bg} , is equal to source flux, f_Q (Table 1).

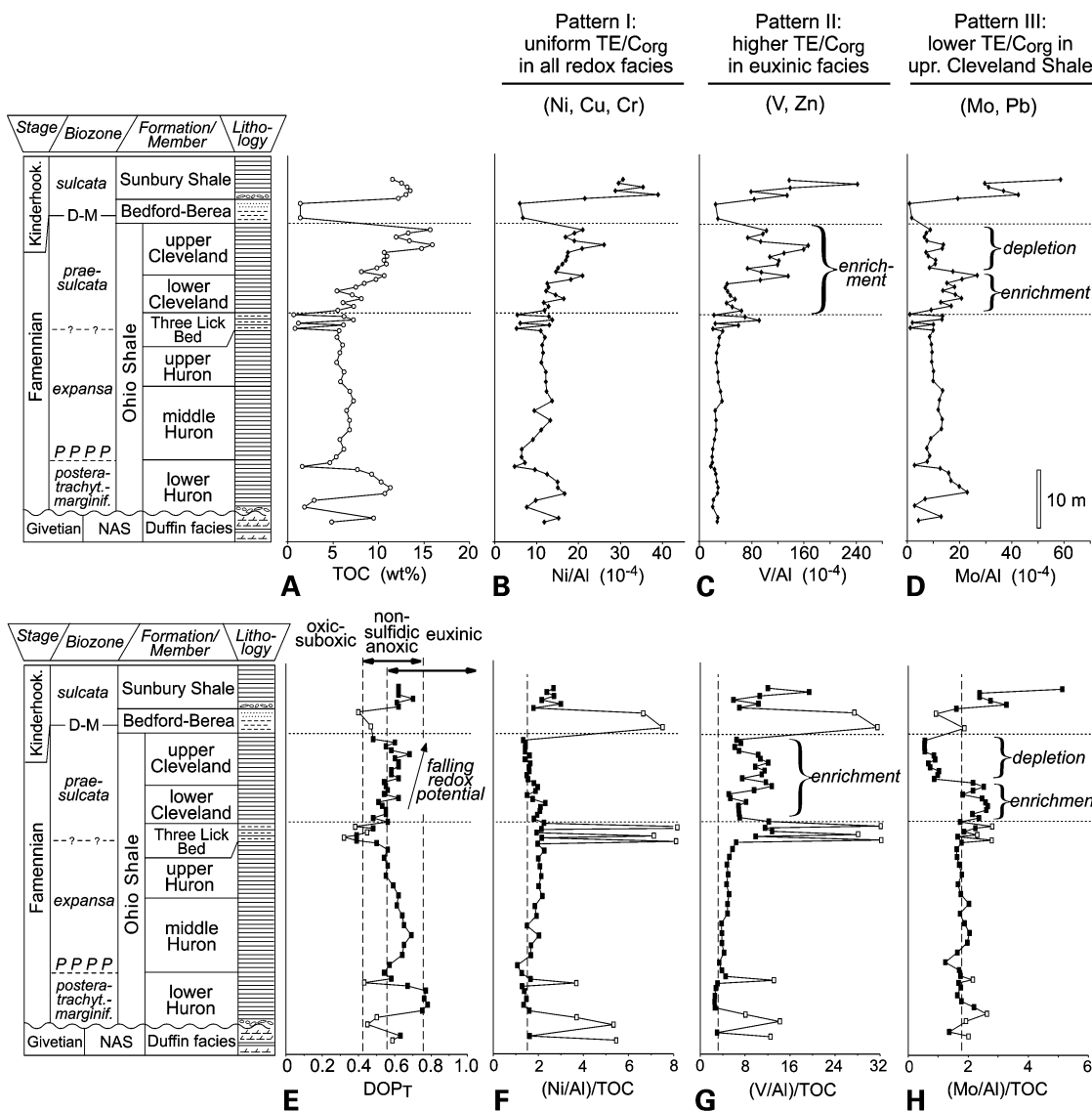


Figure 3. Chemostratigraphic data from Upper Devonian–Lower Mississippian black shale succession of Central Appalachian Basin. **A:** Total organic carbon, TOC. **B–D:** Trace elements, TE. **E:** Degree of pyritization, DOP_T. **F–H:** TOC-normalized trace elements. DOP_T (paleoredox proxy) is based on total Fe rather than reactive Fe; Jaminski (1997) determined a mean difference between DOP and DOP_T in these units of -0.02 ($r = 0.76$; $n = 12$), so DOP_T is robust estimator of true DOP (Raiswell et al., 1988); redox thresholds are from Rimmer (2004). Open symbols in E–H represent TOC-poor siltstone units; TOC-normalized trace element concentrations are not comparable to those from black shale intervals. NAS—New Albany Shale; PPP—*Protosavina* (biostratigraphic marker; Ettensohn et al., 1989); D-M—Devonian–Mississippian boundary. Data are from Kentucky Geological Survey core D-4, Bath County, Kentucky (Robl et al., 1984).

for North American black shales were compiled from the literature and used to calculate trace element burial fluxes, f_{bs} (e.g., Table 2). For example, burial fluxes associated with the Cleveland Member of the Ohio Shale in the Central Appalachian Basin were sufficient to draw down Mo, V, and Zn in Late Devonian seawater by $\sim 3\%$ – 6% of their initial concentrations (Table 2), an effect somewhat larger than that of the Holocene Black Sea (Table 1) and sustained for a far longer time (~ 800 k.y. vs. < 8 k.y.). Further, this formation represents only a fraction ($\sim 10\%$ – 15%) of global trace element fluxes to Late Devonian anoxic facies: even larger fluxes were associated with stratigraphic equivalents in Midcontinent North America (i.e., portions of the Chattanooga, New Albany, Woodford, and Bakken Shales; Ulmishek and Klemme, 1990; de Witt et al., 1993) and in western Canadian basins (i.e., portions of the Exshaw, Besa River, and Ford Lake Formations; Douglas et al., 1970; Gabrielse and Yorath, 1992). The global burial flux of Mo may have depleted Late Devonian seawater by $\sim 50\%$ – 70% of its initial inventory and decreased the residence time of Mo in seawater from ~ 731 k.y. to ~ 474 k.y. (Fig. 2B). That the response time of the seawater Mo cycle was probably shorter than the duration of Cleveland Shale deposition (~ 800 k.y.) is consistent with observations of Mo depletion within this unit (see following).

EVIDENCE OF TRACE ELEMENT DRAWDOWN IN LATE DEVONIAN SEAWATER

The foregoing analysis suggests that anoxic sedimentation had the potential to draw down the trace element inventory of Late Devonian seawater, but is there empirical evidence for such a process? The Upper Devonian–Lower Mississippian black shale succession of the Central Appalachian Basin may provide such evidence (Fig. 3). These shales contain 5–16 wt% organic matter (Fig. 3A) and were deposited under redox conditions ranging from suboxic to euxinic, with lower redox potentials most characteristic of the Cleveland and Sunbury Shales (Fig. 3E; Robl et al., 1984; Rimmer, 2004). Redox-sensitive trace elements in these shales generally covary with organic carbon in one of two patterns: (I) simple linear covariation in all redox facies (e.g., Ni, Cu, Cr; Fig. 3B), and (II) linear covariation with total organic carbon (TOC) in noneuxinic facies and preferential enrichment in euxinic facies (e.g., V, Zn; Fig. 3C). A third pattern is found only in the upper Cleveland Shale, and then only for Mo and Pb: (III) declining concentrations despite correlative increases in TOC, degree of pyritization (DOP_T), and other redox-sensitive trace elements (Fig. 3D). Visualization of all three patterns is facilitated by normalization of TE concentrations to TOC: pattern I yields a nearly uniform TE/C_{org} ratio

(Fig. 3F), and patterns II and III result in increasing and decreasing TE/C_{org} ratios, respectively (Figs. 3G–3H).

The most satisfactory explanation for declining Mo concentrations in the upper Cleveland Shale appears to be drawdown of dissolved Mo in Late Devonian seawater owing to massive uptake by anoxic sediments at time scales of 10⁵ to >10⁶ yr. A local redox control (e.g., Morford and Emerson, 1999) can be discounted because of correlative increases in redox proxies such as DOP_T. Other factors, e.g., a change in source flux related to the composition of rocks undergoing weathering, are speculative and improbably coincidental (e.g., why should the Mo weathering flux diminish suddenly near the end of a multimillion-year marine anoxic event?). Another observation in support of the seawater drawdown hypothesis is the rebound of Mo concentrations in the Early Mississippian Sunbury Shale, quite likely as the result of erosion and remobilization of material from earlier-deposited black shales coincident with a major sea-level fall across the Devonian-Carboniferous boundary, recorded as lowstand deposits of the Bedford-Berea sequence (Pashin and Ettensohn, 1995). Although the same processes might have controlled changes in the Pb burial flux (Fig. 3D), the residence time of this element in seawater is so short (~48 yr; Table 1) that spatial variability of dissolved Pb in Late Devonian seawater cannot be ruled out.

ACKNOWLEDGMENTS

I thank Thomas Robl and Susan Rimmer for sharing Devonian shale data generated by the Institute for Mining and Minerals Research (now the Center for Applied Energy Research) of the University of Kentucky; Timothy Lyons for sharing Black Sea sediment data; Timothy Phillips for drafting services; and Ariel Anbar, Timothy Lowenstein, and Robert Raiswell for constructive reviews of the manuscript.

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Manuscript received 14 June 2004

Revised manuscript received 25 August 2004

Manuscript accepted 31 August 2004

Printed in USA