Gradients in Sediment Geochemistry as a Constraint on Modeling Epeiric Sea Circulation*

Thomas J. Algeo\textsuperscript{1}, Achim Herrmann\textsuperscript{2}, and Bernd Haupt\textsuperscript{3}

Search and Discovery Article #50265 (2010)
Posted June 21, 2010

*Adapted from oral presentation at AAPG Convention, New Orleans, Louisiana, April 11-14, 2010

\textsuperscript{1}Geology, University of Cincinnati, Cincinnati, OH (thomas.algeo@uc.edu)
\textsuperscript{2}Barrett Honors College, Arizona State University, Tempe, AZ
\textsuperscript{3}Earth and Environmental Systems Institute, Pennsylvanian State University, University Park, PA

Abstract

Ancient epeiric sea deposits commonly exhibit lateral gradients in chemistry that are a reflection of spatial variation in environmental conditions. Such gradients place constraints on paleocirculation patterns and may be used to define regions of chemically distinct water masses termed "aquafacies" in which the residence time of a proxy is less than the oceanic mixing time. Tracers such as Nd isotopes and clay-mineral assemblages provide evidence of spatial variation in the provenance of the detrital fraction. Oxygen isotopes can provide information concerning spatial variation in watermass $\delta^{18}$O (e.g., as a function of salinity variation) or temperature. Carbon isotopes, although subject to more numerous controls, can provide information about spatial variation in marine primary productivity and carbon cycling. Various proxies including DOP, trace metals, and Fe\textsubscript{T}/Al have been used to discern spatial gradients in paleoredox conditions. All of these proxies provide indirect clues to paleocirculation patterns, although such information has rarely been integrated in a systematic manner, even for those few ancient epeiric seas that have been extensively studied to date, such as the Late Ordovician Mohawkian Sea.1

We are in the early stages of an integrated data-model study of the North American "Midcontinent Sea" (Middle-Late Pennsylvanian) that will investigate spatial gradients in the proxies above for the purpose of evaluating the robustness of model simulations of paleocirculation patterns. This sea provides a useful case study for internal circulation in ancient epeiric seas owing to its large area ($\sim$2.1 x 106 km\textsuperscript{2} at highstands), relatively uniform seafloor bathymetry, and pronounced lateral gradients in sediment geochemistry.
Acknowledgments

Ron Blakey (ANU), Phil Heckel (U. Iowa), James C. Hower (U. Kentucky), Barry Maynard (U. Cincinnati), Jeff Over (SUNY Geneseo), Lorenz Schwark (U. Cologne).

Selected References


Gradients in sediment geochemistry as a constraint on modeling epeiric sea circulation

Thomas Algeo, University of Cincinnati
Achim Herrmann, Arizona State University
Bernd Haupt, Pennsylvania State University
Circulation patterns in epeiric seas

Quasi-estuarine circulation (positive water balance)

A. HUDSON BAY

B. BALTIC SEA

C. QEC - basic model

D. QEC - highly stratified

E. QEC - with sill

F. high productivity

Anti-estuarine circulation (negative water balance)

G. GULF OF CARPENTARIA

H. RED SEA

I. AEC - basic model

J. AEC - with sill

K. Epicontinental Equatorial Divergence Upwelling

L. (interpreted from Parnah, 1982)

Witzke (1987)
Baltic Sea: silled anoxic basin; episodic deepwater renewal; basin-centered anoxia

Algeo et al. (GAC, 2008)
Circulation patterns in the Baltic Sea

Circulation reflected in gradients in physico-chemical variables, such as salinity

Circulation determined through tracer studies

Bendtsen et al. (2007)
Utility: Information about circulation patterns can further our understanding about controls on primary productivity, redox conditions, and other paleoceanographic parameters.
Proxies for circulation patterns in ancient epeiric seas

<table>
<thead>
<tr>
<th>Elemental</th>
<th>Isotopic</th>
<th>Other Proxies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trace metals (Mo, U, etc.) REEs</td>
<td>$\delta^{13}C_{\text{carb}}$</td>
<td>Mineral assemblages</td>
</tr>
<tr>
<td></td>
<td>$\delta^{13}C_{\text{org}}$</td>
<td>Organic fraction</td>
</tr>
<tr>
<td></td>
<td>$\delta^{18}O$</td>
<td>(maceral types, biomarkers,</td>
</tr>
<tr>
<td></td>
<td>$\delta^{15}N$</td>
<td>Rock Eval parameters)</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$Nd</td>
<td></td>
</tr>
</tbody>
</table>
Spatial variation in proxy residence time

RESIDENCE TIMES: SEAWATER VS. RESTRICTED BASINS

Seawater,  \( \tau \sim 750,000 \text{ yr} \)
Cariaco Basin, \( \tau \sim 320,000 \text{ yr} \)
Black Sea, \( \tau \sim 80,000 \text{ yr} \)
Saanich Inlet, \( \tau \sim 15,000 \text{ yr} \)
Framvaren Fjord, \( \tau \sim 1,000 \text{ yr} \)

Aqueous Mo residence times (of deep water for restricted basins)

Key factor:
Proxy residence time versus watermass mixing time
Late Ordovician Mohawkian Sea (~454 Ma)

Fanton and Holmden (2007)

Maps: Ron Blakey
“Aquafacies” – Chemically distinct watermasses

Sources: Holmden et al. (1998), Fanton and Holmden (2007)

Discriminant plot

Nd isotopes

C isotopes

Midcontinent Aquafacies

Taconic Aquafacies

Southern Aquafacies

Jessamine-Nashville domes

Sebree Trough

Kolata et al. (2001)

Discriminant plot

\[ \delta^{13}C = 0\% \text{ to } 2\% \]

\[ \epsilon_{Nd} \text{ contour lines} \]

\[ \delta^{13}C \text{ contour lines} \]

Sm/Nd (atom)

MFR conodonts

AFR conodonts

Metalliferous crusts
Late Pennsylvanian
Midcontinent Sea

Missourian Stage
Hushpuckney Shale

Global paleogeography
~300 Ma
Bathymetry of Late Pennsylvanian Midcontinent Sea

Relatively shallow depths (<100 m)

Muted bottom topography

Large latitudinal (~0 to 20°N) and climatic ranges

Wells et al. “Numerical Modeling of Tides in the Late Pennsylvanian Midcontinent Seaway of North America with Implications for Hydrography And Sedimentation” (JSR, 2007)
Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation

T.J. Algeo a,b, N. Tribovillard b

a Department of Geology, University of Cincinnati, Cincinnati, Ohio 45221-0013, USA
b Université Lille 1, Laboratoire Géosystèmes, UMR CNRS 8157, bâtiment SNS, 59655 Villeneuve d’Ascq cedex, France


Algeo, T.J. & Maynard, J.B., 2008, Trace metal covariation as a guide to water-mass conditions in ancient anoxic marine environments. Geosphere. v. 4; no. 5; p. 872-887.


Paleoceanographic profiles – connections to global ocean

Algeo et al. (2008); Algeo & Heckel (2008)
Nitrogen isotopic evidence for lateral advection of O₂-deficient watermasses from the Eastern Tropical Panthalassic Ocean to the LPMS
Modern: oxygen-deficient intermediate waters in the modern eastern tropical Pacific Ocean rise to <100 m at latitudes of 5-12ºS and 5-20ºN. Advection into the Gulf of California contributes to benthic anoxia in that sea.

Trade winds enhance productivity through upwelling of nutrient-rich intermediate waters.

Intermediate waters are oxygen-deficient owing to “cul-de-sac” effect, only weakly connected to subtropical gyres.
Nd isotopes as a tracer in the LPMS

Uniform $\varepsilon_{Nd}$ across the LPMS, indicating good watermass exchange

Algeo & Heckel (2008)
Clay mineral assemblages as a tracer in the LPMS

Smectite from S = stronger chemical weathering; illite from N = stronger physical weathering

Algeo & Heckel (2008)

Temperate weathering

Tropical weathering
Organic macerals as a tracer in the LPMS

Vitrinite from LPMS interior coal swamps, possibly transported NW by CCW gyre
Inferred circulation patterns in the LPMS
Conclusions:

(1) Internal circulation patterns can be reconstructed in ancient epeiric seas using a variety of proxies

(2) Such reconstructions can be useful in understanding controls on primary productivity, redox conditions, and other paleoceanographic variables

(3) Such reconstructions can provide boundary conditions for paleoceanographic modeling studies, the results of which can provide information about controls on paleocirculation.

Acknowledgments: Ron Blakey (ANU), Phil Heckel (U. Iowa), James C. Hower (U. Kentucky), Barry Maynard (U. Cincinnati), Jeff Over (SUNY Geneseo), Lorenz Schwark (U. Cologne)

Research support: U.S. National Science Foundation (EAR-0310072, EAR-0618003, and EAR-0745574) and the University of Cincinnati Research Council
The North American Late Devonian Seaway: a series of restricted cratonic-interior basins

Algeo et al. (2007)
Analysis of Mo-TOC covariation → paleohydrographic conditions

Late Devonian Ohio Shale, Ohio

Algeo et al. (2007)
Significance: $m$ shows a strong relationship to both deepwater aqueous Mo concentration and deepwater renewal age; hence, it has predictive value for these parameters in paleomarine systems.

**Left Diagram:**

- $r^2 = 0.96$
- $p(\alpha) \sim 0.01$
- Deepwater [Mo]$_{aq}$ vs. sediment Mo/TOC.

**Right Diagram:**

- $r^2 = 0.90$
- $p(\alpha) \sim 0.01$
- Deepwater age vs. renewal time.

[Mo]$_{sed}$ is determined by the concentration of both TOC in the sediment and Mo in the watermass:

$$[\text{Mo}]_{\text{sed}} \equiv [\text{TOC}]_{\text{sed}} \cdot [\text{Mo}]_{\text{aq}} \Rightarrow [\text{Mo}/\text{TOC}]_{\text{sed}} \equiv [\text{Mo}]_{\text{aq}}$$
Astronomical tide and semidiurnal boundary tide (2 m range)

Tidal range in cm, contours at 10 and 20 cm, then at 20 cm intervals to 200 cm

---

Wells et al. (2007)
The Late Pennsylvanian Midcontinent Sea had a deepwater connection to the Panthalassic Ocean through the Permian Basin Seaway, hence, probably unrestricted deepwater circulation. Major differences in bathymetry, circulation & hydrographic conditions.
Late Pennsylvanian Midcontinent Sea:
Strong trace-metal covariation →
constant watermass chemistry indicative
unrestricted deepwater renewal

Late Devonian Seaway:
Divergent trace-metal concentration patterns
→ evolution of watermass chemistry
indicative of restricted deepwater renewal

Upper Pennsylvanian, Midcontinent USA
Dominant control: Benthic redox variation

Upper Devonian, Appalachian Basin
Dominant control: Degree of deepwater restriction
Panchuk et al. (2006)
Panchuk et al. (2006)
Chemically distinct watermasses

$\delta^{13}C_{org}$

Panchuk et al. (2006)
Kolata et al. (2001)
Paleoceanographic modeling of Mohawkian Sea

Panchuk et al. (2005)

Boundary conditions

Paleogeography

Model results

Paleoceanographic modeling of Mohawkian Sea

Panchuk et al. (2005)
Highstand / lowstand cycles → changes in epeiric sea circulation

Fanton and Holmden (2007)

<table>
<thead>
<tr>
<th>Event</th>
<th>TOC</th>
<th>$\delta^{13}$C$_{\text{carb}}$</th>
<th>$\delta^{13}$C$_{\text{org}}$</th>
<th>Sea level</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon_{\text{Nd}}$</td>
</tr>
<tr>
<td>C6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Highstand / lowstand cycles → changes in epeiric sea circulation

**A** Sea level lowstand

- Arch and Shield
- Sebree Trough
- Taconic Highlands

**B** Sea level highstand

- Fresh water runoff
- Upwelling $C_{org}$-burial

Legend:
- **Land** (low relief)
- $\delta^{13}C = 0\%$ to $2\%$
- **Sebree Trough**
- **Shale**
- $\delta^{13}C = 0\%$ to $-2\%$
- **Pycnocline**

Fanton and Holmden (2007)

Positive isotope shift recorded in sediments