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Editorial

Special Issue on Neoproterozoic–Paleozoic Ocean Chemistry

This special issue is based on a theme session convened at the Annual Meeting of the Geological Society of America held in Denver, Colorado, in October 2004. The theme session brought together a diverse group of scientists interested in the chemistry of Precambrian and Paleozoic oceans and its role in climatic and evolutionary events. The contributors to this issue make use of a wide range of isotopic (Sr, C_{carb} , C_{org} , O), elemental (Mo, P, Fe, Mn), and organic (TOC) proxies to study the chemistry of Neoproterozoic and Paleozoic oceans. The contributions include stable isotopic studies working to define secular curves for regional and global correlations (Dilliard et al., Katz et al., Wynn and Read, Halverson et al.), new applications of isotopic and elemental ratios from marine facies to determine paleoatmospheric oxygen and carbon dioxide levels (Algeo and Ingall; Cramer and Saltzman), an analysis of links between the long-term carbon and sulfur cycles through the Paleozoic (Gill et al.), use of stable isotopic and trace–element ratios to determine paleo-productivity (Brand et al.), investigation of Mo–TOC relationships in Devonian black shales as a record of paleohydrographic variation (Algeo et al.), and a comparison of bulk rock and component data as seawater proxies (Batt et al.). The papers are listed in stratigraphic order from the Neoproterozoic to the Pennsylvanian.

Halverson and others propose a composite, global $^{87}\text{Sr}/^{86}\text{Sr}$ chemostratigraphy for the Neoproterozoic that is linked to a high-resolution carbon isotopic profile. Five relatively complete, partly overlapping successions with good carbon isotopic chemostratigraphy form the main structure of the curve. The main structure of the $^{87}\text{Sr}/^{86}\text{Sr}$ curve is similar to previous compilations – most of the Neoproterozoic is characterized by a systematic rise in $^{87}\text{Sr}/^{86}\text{Sr}$. Inflections in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve generally correspond to carbon cycle perturbations as measured by $\delta^{13}\text{C}$ excursions, although the relationship between C and Sr isotopic records appears to be more complex than

previously envisioned. In the Bitter Springs Stage, for example, an 8‰ decrease in $\delta^{13}\text{C}$ corresponds to a transient rise in $^{87}\text{Sr}/^{86}\text{Sr}$, contrary to a simple weathering–deposition model of linkage. At a larger scale, the data presented in their paper challenge the conventional view of the linkage between $^{87}\text{Sr}/^{86}\text{Sr}$ and global tectonic events. The composite record suggests that prolonged intervals of low $^{87}\text{Sr}/^{86}\text{Sr}$ do not correlate with intervals of continental breakup, but rather with intervals of assembly. The late Mesoproterozoic through early Neoproterozoic assembly of Rodinia is characterized by low $^{87}\text{Sr}/^{86}\text{Sr}$, while the major Neoproterozoic rise in $^{87}\text{Sr}/^{86}\text{Sr}$ is co-incident with Neoproterozoic breakup of Rodinia. The authors propose that supercontinent breakup exposes ancient continental interiors to weathering, thereby driving gradual rises in $^{87}\text{Sr}/^{86}\text{Sr}$, while continental assembly shelters ancient interiors and exposes juvenile active margins to increased weathering.

Algeo and Ingall examine secular variation in the $C_{org}:P$ ratios of organic-rich facies through the Phanerozoic. Their study units exhibit highly variable ratios, from <10:1 in the Permian Phosphoria Formation to >1000:1 in some Devonian black shales. Sedimentary $C_{org}:P$ ratios are known to be strongly influenced by benthic redox conditions: oxic conditions lead to lower ratios because organic C is lost while remineralized organic P is retained in the sediment through complexation reactions, whereas anoxic conditions lead to higher ratios because preservation of organic matter is enhanced while remineralized P diffuses out of the sediment. In this study, the authors conclude that variance in the Phanerozoic $C_{org}:P$ record is probably controlled as much by global (atmospheric pO_2) as local factors. Based on this inference, they generate a new Phanerozoic atmospheric pO_2 model that has strong similarities to existing models based on other proxies, yet differs in some potentially significant respects. In particular, the new model suggests that atmospheric pO_2 was lower

during the Early to Middle Paleozoic than previously inferred, and that Devonian atmospheric O_2 levels may have been so low (<13%) as to prevent the sustained combustion of plant material, providing an explanation for the “Devonian charcoal gap.”

Gill and others investigate the paired record of carbon and sulfur isotopes at multiple horizons in the Paleozoic to determine the links between these two systems. Large positive carbon and sulfur isotopic shifts at the Late Cambrian SPICE event indicate a large-scale carbon burial event coinciding with increased pyrite burial. Throughout the remainder of the Paleozoic the carbon and sulfur records are not coupled, which the authors suggest reflects decreasing sensitivity of the seawater sulfur isotopic record to flux changes as the marine sulfate concentrations increased. The authors suggest the Paleozoic ocean was transitional between the Proterozoic ocean of rapid isotopic variability and low sulfate concentration and the more stable and relatively sulfate-rich Mesozoic and Cenozoic oceans. The authors also suggest the emergence and evolution of terrestrial ecosystems in the middle and late Paleozoic produced a new locus of organic carbon burial that helped to decouple the carbon and sulfur isotopic records as this burial occurred in sulfate-limited environments and in the absence of significant pyrite burial.

Dilliard and others present a high-resolution C-isotopic record for Lower Cambrian rocks of the Selwyn Basin, Northwest Territories, Canada. Carbon isotopic data in this study are correlated across the entire carbonate platform from peritidal settings in the east to deep marine settings in the west with biostratigraphy and sequence stratigraphy. Eight carbon isotopic “cycles” provide a much high-resolution of correlation than traditional trilobite biostratigraphy and compliment the sequence stratigraphy. The secular curve in this study is very similar to and compliments a composite carbon isotope curve from Siberia (Brasier and Sukhov, 1998). The shape of the Sekwi Formation secular variation curves are similar across the platform but the variations in the amplitude of fluctuations associated with each of the cycles is attributed to local tectonic, eustatic and diagenetic processes. A large negative $\delta^{13}C$ excursion coinciding with a regional drowning event that occurs just below the Early–Middle Cambrian boundary is likely correlative to a similar event recorded elsewhere along the western Laurentian margin. This study indicates that high-resolution carbon isotope chemostratigraphy can be a powerful stratigraphic tool for deciphering local, regional and global events.

Cramer and Saltzman investigate controls on the Early Silurian (Wenlock) Ireviken Event, which accom-

panied a transition from a cool to a warm climate state. Although positive carbonate $\delta^{13}C$ excursions such as that of the Ireviken Event are commonly attributed to increased organic C burial, leading to a decline in atmospheric pCO_2 , the present study invokes a different scenario. By generating paired carbonate and organic carbon $\delta^{13}C$ analyses for marine carbonates of the Wayne Formation of central Tennessee, the authors show that the Ireviken Event was accompanied by a ~6‰ decrease in $\delta^{13}C_{(carbonate-organic)}$, suggesting a concurrent *increase* in atmospheric pCO_2 . This suggests that changes in atmospheric pCO_2 were the principal forcing factor and may have triggered a shift in deep-water formation from high to low latitudes, leading to enhanced deep-ocean anoxia and increased organic C burial. Because paired $\delta^{13}C_{carb}-\delta^{13}C_{org}$ analyses have been generated for relatively few C-isotopic events, this study may necessitate reconsideration of the significance of other events of this type.

Algeo and others examine Mo–TOC relationships in organic-rich facies of Middle Devonian to Early Carboniferous age from the North American craton. Most of their study units exhibit significant Mo–TOC covariation, yielding regression-line slopes (m) ranging from ~2 to 65 ($\times 10^{-4}$). This range is similar to that encountered in a recent study of four modern anoxic silled basins, in which m varied from 4.5 to 45 ($\times 10^{-4}$) (Algeo and Lyons, 2006). In that study, it was demonstrated that sedimentary Mo concentrations are a function of the availability of dissolved Mo as well as organic host phases, and that m is thus closely linked to the degree of restriction of the subpynoclinical water-mass, as reflected in aqueous Mo concentrations ($[Mo]_{aq}$) and deepwater renewal times (τ_{dw}). In the present study, this insight is applied to an analysis of hydrographic conditions in silled cratonic–interior basins of the Devonian–Carboniferous North America Seaway. Systematic patterns of geographic and stratigraphic variation in m suggest control of Mo–TOC relationships by slowly evolving water-mass characteristics of the seaway. Based on modern analogs, m values in the Devonian–Carboniferous study units suggest aqueous Mo concentrations ranging from <20% to >70% that of modern seawater, and deepwater renewal times ranging from <100 years to >1000 years. This study demonstrates that sedimentary Mo–TOC data have considerable potential for analysis of paleohydrographic conditions in anoxic marine facies.

Katz and others investigate controls on the stratigraphic architecture and evolution of the early Mississippian Madison Ramp in southeastern Wyoming and southwestern Montana through coupled C- and Sr-

isotopic analyses of marine carbonates of the Madison Limestone. This study develops a high-resolution, surface-to-subsurface sequence stratigraphic framework based on eight localities representing an inner- to outer-ramp transect. The Kinderhookian–lower Osagean succession is characterized by a 2nd-order eustatic T–R cycle with a maximum flooding surface near the stage transition, upon which a series of 3rd-order eustatic fluctuations are superimposed. High-stands are characterized by maximum $\delta^{13}\text{C}$ values and least radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values, reflecting increased marine productivity and burial of organic matter in conjunction with decreased continental weathering rates as a consequence of flooding of previously exposed land masses. Maximum flooding surfaces exhibit geographic variation in $\delta^{13}\text{C}$, with more ^{13}C -depleted values toward the inner ramp, reflecting increased water-mass restriction proximal to land. The C-isotope record of the Madison Ramp correlates with those of lower Mississippian successions in Belgium and the Urals but yields significantly higher $\delta^{13}\text{C}$ values, suggesting that both global and local processes influenced the C-isotopic composition of early Mississippian seawater dissolved inorganic carbon (DIC).

Wynn and Read investigate the C- and O-isotopic composition of Mississippian (Chesterian) carbonate muds deposited on the ramp slope of a rapidly subsiding foreland basin in Virginia. The isotopic composition of the study units varies at the scale of the 4th-order sequences that dominate the adjacent platform succession, yet the C-isotopic signal of the study units was not significantly reset by the regional meteoric aquifer system that affected the platform. Within each 4th-order sequence, $\delta^{13}\text{C}$ values decrease by $\sim 1\text{‰}$ to 2‰ at the maximum flooding surface relative to underlying low-stand beds, followed by a positive shift upward in the high-stand-regressive phase before becoming more negative toward 4th-order correlative conformities. Meteoric diagenesis might account for ^{13}C -depleted values beneath sequence boundaries, but it cannot account for the observed shifts evident throughout the sequences. Enrichment in ^{13}C associated with the high-stand-regressive phases is attributed to increased productivity during glacial stages, possibly as a result of improved ocean circulation coupled with shallowing. Isotopic evidence of 4th-order glacio-eustasy suggests that Gondwanan glaciation was already extensive by the Late Mississippian. The O-isotope record of the study units was strongly influenced by burial diagenesis.

Brand and others determined stable and trace element chemistry of well-preserved brachiopods from stratigraphically well-constrained latest Mississippian

and earliest Pennsylvanian strata of the southern Great Basin to determine the link between bathymetry and productivity. $\delta^{18}\text{O}$ values increase from the Mississippian–Pennsylvanian in conjunction with sedimentologic data indicating that water depth increased during this period. Fe/Mn ratios during this period indicate decreasing productivity during the deepening, however, $\delta^{13}\text{C}$ isotopes on coeval samples are invariant during this period indicating that like in the modern oceans they do not robustly record long-term productivity changes. The source of the Fe recorded in these rocks is postulated to be the Antler Orogenic Highlands to the west of the latest Mississippian–Pennsylvanian carbonate shelf. This study indicates that stable isotopes of well-preserved samples record temperature decreases due to sea level rises and that multiple geochemical proxies are necessary to understand the record of productivity associated with these rises.

Batt and others present a continuous, high-resolution carbon isotope record of mid-Carboniferous (Chesterian) carbonates in the Antler foreland basin of Idaho. They examine in detail the preservation and reliability of bulk carbonate and other components as reliable proxy records for seawater carbon isotopes. The authors observed little variability in the carbon isotope values of bulk carbonates and micrites, which holds true for the wide range of lithofacies examined in this study. The analyzed brachiopod carbon and oxygen isotope values are higher than average bulk carbonate and micrite, but show considerable isotopic variability by taxa and ultrastructure. Based on the overlap in carbon isotope values of brachiopod secondary shell layers, bulk carbonates, microdrilled matrix, and marine cements, the authors propose that bulk carbonate-derived curves may be reasonably used to delineate ambient seawater trends in their study. This new curve fills the ‘Chesterian gap’ seen in previous work in the western United States and reveals several previously unrecognized carbon isotope shifts. The observed changes in the nature of the carbon isotope fluctuations, together with a significant shift across the mid-Carboniferous boundary, reveals changes in carbon cycling as the Earth transitioned to an icehouse climate of the late Paleozoic.

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Michael C. Pope

*School of Earth and Environmental Sciences,
Washington State University, Pullman, WA 99164, USA*

E-mail address: mcpope@wsu.edu.

Corresponding author.

Thomas J. Algeo

*Department of Geology, University of Cincinnati,
Cincinnati, OH 45221, USA*

E-mail address: algeot@email.uc.edu.

Matt Saltzman

*Department of Geological Sciences,
Ohio State University, Columbus, OH 43210, USA*

E-mail address: saltzman.11@osu.edu.

Julie K. Bartley

*Department of Geosciences, University of West Georgia,
Carrollton, GA 30118, USA*

E-mail address: jbartley@westga.edu.

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