Sea-level-driven changes in ocean chemistry at an Upper Cambrian extinction horizon

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ABSTRACT

A combined stratigraphic and isotopic study across a Late Cambrian mass-extinction horizon (Pterocephaliid-Ptychaspid biomere boundary) in cratonic and miogeoclinal sections of the western United States reveals evidence for a pattern of sea-level rise, decreasing \(^{87}\)Sr/\(^{86}\)Sr ratios, and increasing \(\delta^{13}\)C. The positive shift in \(\delta^{13}\)C, reaching maximum values a few metres above the extinction interval, is interpreted to reflect elevated primary productivity and an increase in the rate of burial of organic matter during expansion of the oxygen-minimum zone. The \(^{87}\)Sr/\(^{86}\)Sr decrease is interpreted to reflect some combination of increased sea-floor spreading rates and decreased continental weathering rates. The \(\delta^{13}\)C and \(^{87}\)Sr/\(^{86}\)Sr trends independently support the field-based hypothesis that a sea-level rise led to catastrophic oceanic overturn, possibly culminating in anoxic conditions, that ultimately proved lethal to a large fraction of the existing shelf fauna.

INTRODUCTION

Biotic crises observed in the Upper Cambrian fossil record of trilobites and brachiopods in North America (biomere boundaries; Palmer, 1965) and other continents (Henderson, 1976) are evidence of significant perturbations in the ocean-atmosphere-biosphere system. Several authors have put forth extinction models for biomorphic boundaries which postulate shelf-wide declines in temperature or dissolved oxygen (e.g., Stitt, 1975; Palmer, 1984) that may have resulted from the destabilization of a previously well-stratified Cambrian ocean (Taylor, 1977). These models are based on the paleontologic observation that iterative extinctions of diverse benthic trilobite assemblages at biomere boundaries were followed by invasions of trilobites (e.g., olenids) that were apparently adapted to deeper, cooler waters typical of outer-shelf and slope settings beneath the thermocline. Westrop and Ludvigsen (1987) pointed to the lack of physical or geochemical evidence for shelf-wide environmental changes at biomere boundaries and formulated a biographic model for the extinctions, possibly driven by sea-level rise.

Recent attempts to provide constraints on models of severe or rapid environmental change across other Phanerozoic bio-event horizons have focused on integrating evidence for secular trends in oceanic \(\delta^{13}\)C (a proxy indicator of changes in organic carbon burial rates and/or primary productivity) or \(^{87}\)Sr/\(^{86}\)Sr ratios (a proxy indicator of changes in the fluxes to seawater from continental vs. hydrothermal weathering) with geologic evidence for fluctuations in sea level or seawater chemistry (e.g., Cenomanian-Turonian boundary in Arthur et al., 1987; Permian-Triassic in Gruszczynski et al., 1992). Here, for the first time, we integrate bathymetric and isotopic data spanning a Late Cambrian biomere boundary that reveal clear evidence for a shelf-wide environmental perturbation, and serve to highlight the potential usefulness of chemostratigraphic investigations of pre-Mesozoic strata.

GEOLOGIC BACKGROUND AND METHODS

Following exposure and erosion of the North American craton during the Late Cambrian Pterocephaliid biomere, a continent-wide transgression occurred near the beginning of Elvinia Zone time that marked the onset of deposition of the Sauk III subsequence (Palmer, 1981). The Pterocephaliid-Ptychaspid biomere boundary is near the bottom of the Sauk III subsequence. It is well defined in both cratonic (Shaw and Deland, 1955; Grant, 1965) and miogeoclinal sections (Palmer, 1965) by evidence for the nonevolutionary transition between the Elvinia and Taenicephalus zones. The biomere boundary is here taken as the interval of extinction represented by the duration of the Irvingella major "faunizone" (Wilson and Frederickson, 1950) of latest Elvinia zone time (see Stitt [1975] and Palmer [1984] for views on the practical placement of the boundary).

Carbonate strata in the study area can be divided into four distinctive facies associations. Subtidal facies include an eastern thrombolite reef, pebbly limestone facies (Snowy Range Formation; Grant, 1965), and a western shoal-water calcarenite facies (Open Door Formation; Shaw and Deland, 1955) that formed a linear shelf-margin complex near the eastern border of the Cordilleran hinge zone. The thrombolite reef facies intertongues with, and passes cratonward into, the storm-dominated, flat-pebble conglomerate facies of the intrashelf basin (Lochman-Balk, 1971). The shoal-water facies passes seaward into a sub–wave-base deep-ramp facies dominated by "blanket subtidal" wackestones (Sneakover and Barton Canyon Limestones; Brady and Rowell, 1976), remarkably uniform and laterally persistent over the eastern part of the Cordilleran miogeoclone.

We measured 23 sections in cratonic strata of Wyoming and Montana and two in miogeoclinal strata of the Great Basin (Fig. 1). Homogeneous micrites identified in

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thin section were microsampled from polished slabs by using a microscope-mounted drill assembly. Care was taken to sample micrites with no visible cements or skeletal grains, although ~10% of the samples did contain sparry calcite or skeletal material. Powders from drilling (~1 mg) were split so that half was analyzed for $\delta^{13}$C and $\delta^{18}$O and half for $^{87}$Sr/$^{86}$Sr ratios. Powders for stable isotope analyses were roasted for 1 h at 380 °C, and reacted with 100% H$_3$PO$_4$, 72 °C in a Finnigan Kiel extraction system coupled directly to a Finnigan MAT 251 mass spectrometer. Isotope ratios were corrected for $^{17}$O contribution and are reported in per mil relative to Peedee belemnite (PDB). Analytical error for $\delta^{13}$C and $\delta^{18}$O was $\pm 0.04$‰. Samples for $^{87}$Sr/$^{86}$Sr analyses were dissolved for ~5 min in 1 N acetic acid, and standard cation-exchange procedures were used to collect Sr. $^{87}$Sr/$^{86}$Sr ratios were determined on a VG Sector thermal-ionization mass spectrometer, and are normalized for mass fractionation to $^{86}$Sr/$^{88}$Sr = 0.1194. The analytical precision (2σ) for Sr analyses was in the range of 9 to 13 $\times 10^{-6}$. The NBS/SRM 987 was measured as 0.710262 ± 0.000010.

**BATHYMETRIC AND ISOTOPIC RESULTS**

**Cratonal Sections (Wyoming and Montana)**

The Pterocephaliid-Ptychaspid biomere boundary in cratonal strata overlies (within $\pm 1$ m in most sections) a drowned thrombolite reef-oid shoal complex (~3–10 m thick), which formed over a northwest-trending submarine high during the time of the *Elvinia* Zone (Fig. 2A). Thin (~30 cm) composite shell concentrations bracket the extinction interval (*I. major* and *Eooorthis* subzones; Grant, 1965) above the drowned platform. Strata deposited during the *Taenicephalus* Zone, overlying the shell concentrations, consist of open-marine nodular wackestones of the deep-ramp facies in the western half of the study area and flat-pebble wackestones of the intrashelf basin facies in the eastern half (Fig. 2B). In contrast to the shallow subtidal deposition in the region during the *Elvinia* Zone, these facies were deposited below normal wave base.

The $\delta^{13}$C values in cratral sections (Fig. 3) shift from a low of $-0.1$‰ (Gros Ventre section) in the *Elvinia* Zone to a high of +1.1‰ ~1–3 m above the extinction interval (Wind River section) near the start of the *Taenicephalus* Zone. $^{87}$Sr/$^{86}$Sr values (Wind River section) shift from 0.70925 in the *Elvinia* Zone to 0.70910 near the start of the *Taenicephalus* Zone (Fig. 4).

**Miogeoclinal Sections (Utah and Nevada)**

The Pterocephaliid-Ptychaspid biomere boundary in miogeocinal sections (Fig. 1) coincides with a distinct darkening of the uniformly predominant wackestone–lime mudstone and an apparent deepening of environments (Brady and Rowell, 1976). The darkening is most pronounced in the McGill section, where dark-gray thin-bedded lime mudstones abruptly overlie a massive unit of white lime mudstone. In the House Range, the extinction interval is bracketed by a trilobite shell concentration (*Irvingella major* coquina), which is overlain by ~50 cm of lime mud capped by an inarticulate-brachiopod shell concentration of *Taenicephalus* Zone age.

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1. GSA Data Repository item 9546, isotopic data for the four sections, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301.
The δ^{13}C values (Fig. 3) within the Elvinia Zone are between 0‰ and +1‰; the highest values are recorded near the top of the zone. Values for δ^{13}C within the <1-m-thick extinction interval (I. major faunizone) show a wide range, from a low of −0.3‰ to a high of 1‰ at the top in the intensively sampled (centimetre scale) House Range section. The δ^{13}C values reach a maximum 1–3 m above the extinction interval (+2.8‰, House Range; +1.9‰, McGill).

**DISCUSSION AND CONCLUSIONS**

The drowning unconformity that was formed coeval with or before the time of the Pterocephaliid-Ptychaspid biomere boundary in northwestern Wyoming (Fig. 2) is evidence for a rise in relative sea level that was rapid enough to exceed the growth potential of the carbonate platform (Schlager, 1991). Changes in ocean chemistry (discussed below) likely played a role in the drowning event by reducing the growth potential of the platform, or may even have been the sole cause. However, a definitive role for regional (eustatic?) sea-level change in the formation of this drowning unconformity is suggested by the work of Rausch and Unfer (1964) on nearshore sandstones in the upper Mississippi valley. This work revealed a distinct shift in sand populations toward finer grain sizes precisely at the Pterocephaliid-Ptychaspid biomere boundary (Ironont-Goodenough cycle boundary) that Rausch and Unfer interpreted to reflect transgression.

The expression of this drowning unconformity or marine flooding surface that we have recognized in Wyoming, which may be a type-2 sequence boundary (Van Wagoner et al., 1987) or genetic sequence boundary (Galloway, 1989), is cryptic in miogeoclastic sections of the Great Basin (Oslager and Read, 1993). This probably reflects the lack of facies belts sensitive to sea-level changes on the broad, low-relief ramp that characterized the miogeocline at that time (Brady and Rowell, 1976). However, relative deepening of environments in the McGill and House Range sections (Brady and Rowell, 1976), combined with a similar pattern in outer-shelf settings of Nevada (Taylor, 1985), is consistent with (an increase in the rate of) sea-level rise at or preceding the extinction interval.

Further evidence suggesting a sea-level rise across the biomere boundary is the presence of distinctive shell concentrations, which bracket the extinction interval in cratranal and miogeoclastic sections. The trilobite (Irvingella major) coquina (and brachiopod (Eoorthis coquina) shell concentrations are remarkably widespread across the North American craton (Wilson and Frederickson, 1950; Grant, 1965; Lochman-Balk, 1971); we interpret these deposits as a transgressive lag and condensed section (cf. Kidwell, 1991), respectively, that formed during the transgressive systems tract and maximum-flooding interval. In addition, or alternatively, the coquinoid abundances of these taxa may reflect a relaxation of population pressures on certain opportunistic taxa as a result of changes in ocean chemistry and ecology (e.g., Stitt, 1975).

Several authors have linked transgressive pulses to oceanographic changes (e.g., intensification of formation of warm saline bottom waters and increased net rates of overturn of nutrient-enriched deep waters), which should have resulted in greatly enhanced primary productivity and burial of organic carbon (observed as a δ^{13}C increase), possibly culminating in anoxic conditions (e.g., Arthur et al., 1987; Joachimski and Buggisch, 1993). We interpret the positive δ^{13}C shift across the top of the Pterocephaliid-Ptychaspid biomere boundary (Fig. 3) to reflect similar oceanographic changes from a generally stratified ocean to a mixed ocean driven by sea-level rise. Distinct darkening of strata in miogeoclastic sections (House Range and McGill sections) is consistent with increased organic carbon burial across the biomere boundary and may indicate anoxic conditions.

The carbon isotope stratigraphy (Fig. 3) suggests a possible chronology for this oceanographic perturbation. Maximum δ^{13}C values were clearly reached at a point after (1–3 m or <10^9 yr) the onset of sea-level rise and faunal turnover. This may reflect the fact that the earliest pulses of upwelling of cold, nutrient-rich deep waters may have actually inhibited surface-water productivity, possibly due to toxic metal concentrations (Wilke et al., 1990), and initiated rapid turnover of benthic faunas. In this initial stage, the surface ocean should have periodically recorded negative δ^{13}C shifts due to influxes of δ^{13}C-enriched deep waters and the lowered δ^{13}C demand of the primary producers (the so-called Strangelove ocean condition; Hsu et al., 1985). In fact, the δ^{13}C stratigraphy for the intensively sampled House Range section indicates that the lowest values were recorded during the initial stage of faunal turnover (~0.3‰ in the I. major faunizone; Fig. 3). An additional feature of the curves—generally higher δ^{13}C values in miogeoclastic sections for both the Elvinia and Taenicephalus Zones—may reflect higher local productivity in surface waters, consistent with the apparently higher organic carbon content of these strata, most notably in the Taenicephalus Zone.

The field-based hypothesis of a eustatic sea-level rise coeval with or before the time of the Pterocephaliid-Ptychaspid biomere boundary is supported independently by decreasing 87Sr/86Sr ratios in the Wind River section (Fig. 4). This decreasing trend likely reflects some combination of an increase in the flux of relatively nonradiogenic strontium to the oceans as a result of increased rates of sea-floor spreading or a decrease in the flux of relatively radiogenic strontium as a result of decreased continental weathering rates (Elderfield, 1986). A decreased continental Sr flux would result from flooding of cratral interiors during sea-level rise. Furthermore, Jones et al. (1994) and Ingram et al. (1994) concluded that a 87Sr/86Sr decrease across the Cenomanian-Turonian boundary, similar in timing and magnitude (~0.0002) to our Late Cambrian change, likely represents a pulse of hydrothermal activity. This postulated volcano-tectonic event was associated with, and may even have resulted in, an apparent eustatic sea-level rise across the Cenomanian-Turonian boundary (Arthur et al., 1987). It thus seems possible that the 87Sr/86Sr decrease and sea-level rise across the biomere boundary may reflect a pulse of sea-floor hydrothermal activity. An alternative explanation of the Sr data—that the 87Sr/86Sr decrease reflects catastrophic mixing of the large, relatively nonradiogenic deep-water reservoir with a small, relatively radiogenic shelf reservoir (Gruszczynski et al., 1992)—seems unlikely because of the long residence time of Sr in the oceans (Elderfield, 1986; Jones et al., 1994). The different time scales of interaction of the above factors and poor geologic
constraints on controlling variables (e.g., rates of sea-floor spreading or rates and δSr/86Sr of the continental weathering flux) preclude a unique interpretation of the Sr data at this time.

Our data provide the first evidence for a shelf-wide environmental perturbation at a biomere boundary and seem to support previous models for faunal turnover (Stitt, 1975; Palmer, 1984) that involve the destabilization of a previously well stratified Cambrian ocean. We have postulated that the trigger for this event may have been a eustatic sea-level rise (geochemical evidence for a meteor impact, which might also be postulated as a trigger, has not been found [Palmer, 1984]). Following destabilization and the initial phase of extinctions (the “crisis interval” of Palmer, 1984), a sharp increase in δ13C occurred. If the δ13C increase coincided with increased productivity, due to overturn of nutrients (e.g., Arthur et al., 1987; this paper), then anoxia probably played a role in subsequent faunal turnover. Alternatively, if the δ13C increase coincided with decreased productivity, due to loss of nutrients to an expanded organic carbon reservoir on the shelves during sea-level rise (e.g., Broeker, 1982; Paul and Mitchell, 1994), then famine may have been a factor (Paul and Mitchell, 1994).

Although we are unaware of any sea-level curves produced for other shelves where the biomere boundary has been recognized, a hint of the positive δ13C excursion has been observed in Kazakhstan (R. L. Ripperdan, 1995, personal commun.), coincident with or following faunal turnover at the base of the Pseudagnostus pseudangustilobus Zone (Sackian-Malykaraatauan transition; Ergaliev, 1981). It thus seems likely that the Stereocellular-Ptychaspis biomere boundary discussed here reflects a global perturbation of the ocean-atmosphere-biosphere system.

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