ORGANIC CARBON BURIAL AND PHOSPHOGENESIS IN THE ANTLER FORELAND BASIN: AN OUT-OF-PHASE RELATIONSHIP DURING THE LOWER MISSISSIPPIAN

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ABSTRACT: Stratigraphic analysis of Lower Mississippian successions at four localities in Utah and Wyoming establish the relative timing of a large carbon isotope excursion (\(\delta^{13}C\) \(\approx +7\%e\)) and episode of regional phosphogenesis in the Antler foreland basin and adjacent shelf (Delle Phosphatic Member). The \(\delta^{13}C\) excursion, which appears global in scope, is marked by peak values of \(+7.3\%e\) in western Wyoming, which are among the heaviest known from Phanerozoic successions. The isotope excursion is well dated to the late Kinderhookian \(S. isosticha\) and early Osagean lower \(G. typicus\) zones and precedes the Delle phosphorites of upper \(G. typicus\) Zone age. The Delle phosphatic event, which resulted in the demise of the shallow-water carbonate factory over a wide area, is marked by a heterogeneous succession of pelletal phosphatic crusts, phosphatic pisoliths, and winnowed and reworked grain aggregates.

The observed stratigraphic relationship between the positive \(\delta^{13}C\) excursion and Delle Phosphatic Member is consistent with a scenario in which high organic-carbon burial and seawater phosphate enrichment under anoxic conditions took place in deeper water masses of the Antler foreland system. This period of high \(\delta^{13}C\) in surface waters above the pycnocline was followed by an episode of persistent upwelling into a salinity-stratified water column and phosphogenesis that was triggered by regional uplift within the Antler foreland basin system in response to tectonic loading. Despite the high productivity associated with upwelling and the accumulation of organic matter on the seafloor, \(\delta^{13}C\) values remained low during phosphogenesis. This is attributed to the counterbalancing effects of organic-matter oxidation during low-stands of sea level, which ventilated the water mass and resulted in sediment winnowing and condensation of phosphatic particles and the incorporation of light carbon from the upwelling water mass. A low in \(\delta^{13}C\) coincident with phosphorite deposition suggests that upwelling, carbon oxidation efficiency, and phosphogenesis reached maxima at approximately the same time, a situation that may be analogous to several Precambrian–Cambrian intervals and the Middle Ordovician but is opposite to that observed for the Early Cretaceous.

Some measure of offset in the timing of peak burial periods of phosphorus and organic carbon is not unexpected because the formation of most major phosphorite deposits is thought to depend ultimately on the enrichment of phosphorus at or near the sediment–seawater interface through microbial breakdown of accumulated organic matter, which also liberates light (\(1^{2}C\)) carbon. A recent review of notable Phanerozoic examples by Shields and others (2000) underscored this spatial and temporal complexity, and it is clear that a major hurdle in such investigations involves the development of a reliable chronostatigraphic framework that allows for detailed correlations of carbonate sequences suitable for \(\delta^{13}C\) analysis and sections that preserve associated phosphorites. Here, the link between an enigmatic but well-dated Early Mississippian interval of phosphorite deposition (Delle Phosphatic Member; Sandberg and Gutschick 1984; Nichols and Silberling 1991) and a positive excursion in \(\delta^{13}C\) is examined in the Antler foreland basin and related strata of the western United States.

Lower Mississippian carbonates in the Great Basin region that occupy the position of the \(Siphonodella isosticha–Upper crenulata\) and lower part of the \(Gnathodus typicus\) conodont zones (late Kinderhookian and early Osagean stages) consistently record \(\delta^{13}C\) values \(\approx +6\%e\), which are among the heaviest known in the Phanerozoic (Saltzman et al. 2000a). This isotopic excursion has been documented in five stratigraphic sections in the distal Antler foreland of eastern Nevada and parts of southeast Idaho, western Wyoming, and northern Utah, using a range of limestone (Saltzman 2002) and dolomite (Budai et al. 1987) lithologies. In addition, brachiopod calcite data from the midcontinent U.S.A. (central Iowa), the southern Canadian Rockies, and western Europe record the excursion (locations provided in Fig. 1) and appear to signal a major paleoceanographic event that may be linked to high burial rates of organic carbon (Mii et al. 1999; Bruckschen et al. 1999; Buggisch and Haas 2000; see correlation of \(\delta^{13}C\) curves in Saltzman 2002). However, the task of establishing time equivalence for organic-rich sediments approaching that required for isotopic mass balance is problematic (Saltzman et al. 2000a; Silberling et al. 2001). The end of the \(\delta^{13}C\) excursion is recorded in the upper part of the Osagean \(G. typicus\) Zone and thus appears to immediately precede or overlap in time an important phosphogenic event in western North America (Delle phosphatic event; Silberling et al. 1997) that ended a long period of open-marine carbonate sedimentation over a wide region of the distal Antler foreland (Fig. 2).

The Delle Phosphatic Member consists of a heterogeneous succession of pelletal phosphatic crusts, pisolithic phosphates, and detrital aggregates of ooidal and other phosphatic grain aggregates (Nichols and Silberling 1990) which average 25% \(P_{2}O_{5}\) (Sandberg and Gutschick 1984). The Delle phosphorites are associated with black shale, fine-grained carbonate, and black chert and were considered a “condensed phosphite” by Jewell et al. (2000) in which multiple stages of phosphogenesis are interrupted by episodes of winnowing and reworking (Föllmi 1996). The Delle is characterized by the abrupt disappearance of normal shelf benthos and pervasive dissolution, and is anomalous with respect to the underlying thick sequence of normal subtidal to peritidal shelf carbonates and overlying peritidal carbonate and/or craton-derived siliciclastics (Nichols and Silberling 1990; Silberling et al. 1995; Silberling et al. 1997). The member extends over a region ~ 750 km long and 360 km wide and attains a maximum thickness of roughly 50 m (Sandberg and Gutschick 1984). The abrupt onset of the Delle phosphatic event in the upper part of the \(typicus\) Zone has been interpreted to reflect

INTRODUCTION

The link between the burial of phosphorus and organic carbon is a key component of the Earth’s evolving climate system because phosphorus likely limits oceanic productivity on geological time scales and thus affects ocean–atmosphere oxygen and carbon dioxide levels (Arthur and Jenkyns 1981; Föllmi 1996; Van Cappellen and Ingall 1996; Compton et al. 2000). The cycling of phosphorus and carbon has therefore been central to discussions of greenhouse–icehouse transitions (e.g., Vincent and Berger 1985; Compton et al. 1990; Filippelli and Delaney 1994), glacial–interglacial cycles (Broecker, 1982; Filippelli and Delaney 1994), and episodes of faunal turnover (Cook and Shergold 1984; Hotinski et al. 2001). However, the nature of the various feedbacks involved is still a matter of controversy, which in part reflects the complex temporal relationship between significant phosphorite deposits (e.g., Precambrian–Cambrian Meishucun, Permian Phosphoria, and Miocene Hawthorn formations) and positive changes in the carbon isotope (\(\delta^{13}C\)) ratios of marine carbonates, which may be a proxy for the burial of organic matter (Compton et al. 1993; Föllmi et al. 1994; Mallinson and Compton 1997).

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organics burial and phosphogenesis in the Antler foreland basin

Fig. 1.—Early Carboniferous paleogeography for the Kinderhookian and early Osagean Stages (Tournaisian) after Witzke (1990). Filled circles represent ten localities in North America (Nevada, Utah, Idaho, Wyoming, Iowa, and Alberta) and one in western Europe where the late Kinderhookian–early Osagean δ¹³C excursion is recorded (Budai et al. 1987; Mii et al. 1999; Bruckschen et al. 1999; Buggisch and Haas 2000; Saltzman 2002). Land areas are shaded, and mountains shown by inverted V symbol.

Fig. 2.—Paleogeographic map of the Antler foreland basin and adjacent shelf showing the distribution of facies during the upper part of the typicus conodont zone, middle Osagean (modified from Sando 1976; Gutschick et al. 1980; Sandberg and Gutschick 1984; Jewell et al. 2000). This time interval represents the main period of phosphatic deposition in the distal Antler foreland above the δ¹³C excursion recorded during the isosticha and lower typicus zones. Sections labeled and discussed in the text are CF = Clark Fork Canyon, SC = Strawberry Creek, SA = Samak, FR = Fitchville Ridge, GC = Gardiner Canyon, CM = Crawford Mountains, PR = Pahranagat Range, AC = Arrow Canyon Range.

Fig. 3.—Locality map of the western United States showing the positions of eight Lower Mississippian (Kinderhookian and Osagean) sections in Wyoming, Idaho, Utah, and Nevada that record a positive (≥ +6‰) δ¹³C excursion. See Figure 2 for section names.

Regional setting: Tectonics and sequence stratigraphy

The Antler orogeny and development of the Antler foreland basin system during the late Devonian through at least mid-Mississippian time profoundly affected sediment accommodation space and facies patterns in western North America (Poole and Sandberg 1991; Dorobek et al. 1991; Chen and Webster 1994; Giles and Dickinson 1995; Silberling et al. 1995). The dimensions of the flexurally induced topography, including the positive forebulge element and downwarped backbulge basin, and the migration of these features through time, have been discussed in terms of both theoretical modeling and outcrop-based sequence stratigraphic analysis (e.g., Giles 1996; Silberling et al. 1997). Local variability in subsidence rates in the Antler foreland basin would have had a dynamic influence on water-mass characteristics during the Early Mississippian, affecting vertical stratification.
tion and horizontal exchange between different parts of the foreland system that likely influenced the burial of carbon and phosphorus on a regional scale (Saltzman et al. 2000a; Jewell et al. 2000). Global changes in sea level and climate were also important (Ross and Ross 1988) in the facies evolution of the Antler foreland and adjacent shelf, and determination of the relative roles of such factors continues to challenge investigators.

Near the beginning of the earliest Mississippian Kinderhookian Stage (Lower crenulata Zone of Sandberg, 1979), a major flooding event re-established the shallow-marine carbonate facies over wide regions of the Antler foreland and adjacent shelf, and resulted in generally aggradational to progradational successions assigned to the lower parts of the Joana and Lodgepole limestones and equivalents (Sando 1976; Poole and Sandberg 1991; Elrick and Read 1991; Chen and Webster 1994; Morris Sequence of Silberling et al. 1995; Sequence 1 of Giles 1996). The overlying, dominantly retrogradational sequence in the distal foreland (Sequence 2 of Giles 1996; lower part of the Sadlick Sequence of Silberling et al. 1995) and adjacent shelf spans the Kinderhookian–Osagean boundary, including most of the S. isosticha and lower part of the typicus zones, and records the ≃ +6‰ δ13C excursion in units assigned to the Dawn, upper Joana Lime-
stone, and equivalents (Saltzman 2002). The overlying sequence includes the Delle Phosphatic Member and marks the demise of the carbonate facies over most of the distal foreland (Fig. 2), with the notable exception of the Arrow Canyon Range in southern Nevada, where normal marine faunas and carbonate environments (Anchor Limestone) continued uninterrupted throughout the Osagean. In the adjacent shelf regions of Wy-
oming and Montana, shallowing during the Osagean led to semirestricted carbonate (mainly dolomite) and evaporite deposition (Fig. 2; Mission Can-
yon Formation and equivalents; Sando 1974, 1976; Gutschick et al. 1980; Reid and Dorobek 1993; Smith and Dorobek 1993).

The four sections investigated in this study (Fig. 3) provide additional control points spanning the Kinderhookian and Osagean stages in the distal Antler foreland and new sections in the adjacent carbonate shelf region (Fig. 2). Sections at Fitchville Ridge in the East Tintic Range of central Utah and at the town of Samak in the western Uinta Mountains include the anomalous Delle phosphorites in their upper parts, while the sections above Strawberry Creek in the Overthrust Belt of western Wyoming and along the walls of Clark Fork Canyon in the Beartooth Mountains record laterally equivalent evaporitic facies. Together, the four sections allow for documentation of secular trends in δ13C in a detailed regional stratigraphic framework and thus provide an important tool for correlation and paleoceanographic interpretation of depositional sequences, which may ultimately be traced to other Euramerican basins in an effort to evaluate their global significance (Fig. 1).

METHODS AND RESULTS

Sample Selection and Rationale

Although brachiopod shells are considered the most reliable component for δ13C analysis because they are originally made up of low-magnesium calcite, the thick stratigraphic sequences examined in this study contained relatively few horizons with well-preserved brachiopods. As an alternative, the generation of high-resolution curves was carried out using fine-grained, micritic components (Gao and Land 1991; Saltzman et al. 1998; Kump et al. 1999; Montañez et al. 2000; Joachimski et al. 2002; among others). Confidence in this methodology is based on: (1) comparisons of δ13C curves generated with brachiopod calcite and micrites for the same time periods, which yield similar trends in the Mississippian (Mii et al. 1999; Saltzman 2002) and other time periods, including the Ordovician (e.g., Marshall et al. 1997; Finney et al. 1999) and the Silurian (e.g., Azmy et al. 1998; Saltzman 2001); (2) the good reproducibility of high-resolution micrite-based δ13C curves, which in many cases have been correlated intercontinentally using biostratigraphy (e.g., Middle Ordovician in Ainsa-
ar et al. 1999; Late Cambrian in Saltzman et al. 2000b; Late Devonian in Joachimski et al. 2002); and (3) the results of quantitative modeling studies that show δ13C values are likely to be rock-buffered over a wide range of diagenetic settings commonly encountered in ancient carbonate successions (Banner and Hanson 1990; Gao and Land 1991).

Nonetheless, despite the good potential for reliable results, diagenetic alteration of primary δ13C values is a concern in the interpretation of matrix micrite data, which represent an average of variable proportions of both original lime mud and early marine or late diagenetic products. The proportion of diagenetic carbonate is likely to be particularly high in successions displaying shallowing-upward cycles capped by subaerial exposure surfaces, which have been shown to be marked by abrupt, negative δ13C deflections (generally recorded within a meter or less of the exposure ho-
rizon) resulting from incorporation of soil-derived CO2 (Allan and Mat-
thews 1982; Goldberg 1991). For example, in thick sections characterized by relatively high-amplitude and high-frequency stratigraphic cyclicity such as the intracratonic basins of middle to late Pennsylvanian age in the south-
western U.S. (e.g., Orogrande and Pedregosa basins), highly variable δ13C trends with strongly negative excursions marking cycle tops have been observed (e.g., Algeo et al. 1992). In addition to minimizing the percentage of late diagenetic products analyzed, an aim of micrite-based chemostra-
tigraphy is to target those carbonates that formed in relatively open-marine environments representing maximal exchange rates with the open ocean (Immenhauser et al. 2002). There is good evidence that the interiors of carbonate platforms, such as those associated with steep-sided reef or build-
up margins studied by Immenhauser and others (2002), become increas-
ingly depleted in δ13C in proportion to the local residence time of seawater and the rate of organic-matter remineralization (Holmden et al. 1998).

To minimize the degree of overprinting of the global seawater δ13C record, the depositional environments preferred for selection of micritic samples in this study represent dominantly subtidal, ramp successions that lack obvious or frequent exposure features. This was not possible at all times, and thus we must in part rely on the extent to which the sections display relatively steady δ13C trends that can be correlated interbasinally (i.e., between sections likely to have experienced contrasting diagenetic pathways) in order to assess their usefulness in approximating seawater trends. Carbonate powders drilled from fresh rock surfaces in this study were roasted under vacuum at 380°C for one hour to remove volatile contaminants and reacted with 100% phosphoric acid at 75°C in an online carbonate preparation line (Carbo-Kiel—single sample acid bath) connected to a Finnigan Mat 252 or 251 mass spectrometer. The analytical precision based on duplicate analyses and on multiple analyses of NBS19 was ≤ 0.04‰. All results are tabulated in the JSR data repository (see Acknowledgments).

δ13C and Stratigraphic Trends in Individual Sections

Fitchville Ridge Section.—An exceptionally well-exposed and well-dat-
ed Lower Mississippian carbonate sequence is present at Fitchville Ridge in the East Tintic Range of central Utah (Fig. 4). Detailed conodont collec-
tions reveal the presence of the isosticha and three earlier Siphonodellid zones (sulcata, sandbergi, and crenulata) in the middle and upper parts of the Fitchville Formation and the typicus Zone in the upper part of the Gardison Limestone (Poole and Sandberg 1991), indicating nearly contin-
uous deposition beginning in the earliest Mississippian. The sampled por-
tion of the Fitchville Formation consists of a heterogeneous mixture of argillaceous lime mudstone, skeletal wackestone, and skeletal packstone facies, which contain sparse to abundant macrofossils (brachiopods and syringoporid corals). Fossil abundance generally decreases up-section as dolomite content increases. The topmost beds of the Fitchville include bird-
sseye textures capped by an ~ 1-m-thick stromatolite unit (Fig. 4) that is know-
t to form a widespread marker bed in the region (Silberling et al. 1997). A prominent flooding surface above the stromatolite bed (Morris–Sadlick sequence boundary of Silberling et al. 1995) marks the base of the
Gardison Limestone, which consists of a thick and relatively uniform lithofacies association of skeletal wackestone and laminated peloidal packstone lithologies with interbeds of graded skeletal lags containing well-preserved crinoids, corals, and gastropods. Towards the top of the Gardison, skeletal wackestone and lime mudstone units increase in abundance, and chert nodules are common. The contact between the Gardison Limestone and the Delle Phosphatic Member of the Deseret Limestone is placed at an abrupt transition to a poorly exposed succession of phosphatic siltstones and shales.

The $\delta^{13}C$ values rise from a low of $\sim 0‰$ in the middle part of the Fitchville Formation and hover around $+3‰$ in the lower part of the isosticha Zone in the upper Fitchville (Fig. 4; see also data repository). Values rise again in the lowermost Gardison Limestone to reach peaks of $\approx +6‰$ in the middle parts of the succession. The observed trend with two distinct peaks separated by a local minimum of $\sim +4‰$ near the Kinderhookian–Osagean boundary is strikingly similar to that recognized elsewhere in the Great Basin (e.g., Pahranagat Range and Samaria Mountain; Saltzman 2002). The $\delta^{13}C$ values then decrease again to pre-excursion levels near $0‰$ in samples of the Lower typicus Zone collected just below the base of the Delle, where a lack of favorable exposures and lithologies prevented further sampling.

Clark Fork Canyon Section.—Lower Mississippian platform carbonates exposed above Clark Fork Canyon on the east flank of the Beartooth Mountains in northwestern Wyoming (Fig. 5) have been examined in detail by Sandberg and Klapper (1967), Sando (1975), and Elrick and Read (1991). The Cottonwood Canyon and the lowermost few meters of the Little Big Horn members of the Lodgepole Formation yield faunas diagnostic of the sulcata, sandbergi, crenulata zones, but higher up in the section only coral zones can be used to subdivide the Kinderhookian and Osagean (Sando 1976). The Cottonwood Canyon Member consists of shaly, dolomitic siltstones, which are abruptly overlain by crinoidal dolowackestone facies of the Little Big Horn Member. The Woodhurst Member consists of cyclical packages of ooid shoal and skeletal–pellet wackestone lithologies that are periodically capped by laminated wackestone and packstone. The overlying Mission Canyon Formation (Big Goose and Little Tongue members) consists of predominantly shattered and brecciated cherty dolomicrite and interbedded crinoidal wackestone and packstone. The $\delta^{18}O$ values rise from near $0‰$ in the lower part of the Lodgepole succession to reach two $+6‰$ peaks in the Woodhurst Member (Fig. 5). Following the two $\delta^{13}C$ peaks, commonly observed at coeval sections to the west (Fig. 4), values fall steadily back to near $0‰$ into the overlying Mission Canyon Formation.
Samak Section.—Lower Mississippian carbonates exposed at the west end of the Uinta Mountains (Fig. 6) near Samak, Utah, have been examined by Spreng (1979), Lane et al. (1980), Dockal (1980), and Nichols and Silberling (1991). The biostratigraphic succession is known to contain the *isosticha* and *typicus* zones, although there has been controversy regarding the age of the lowermost units (and applicable stratigraphic nomenclature). Dockal (1980) suggested that the lowermost unit, a partially dolomitized oolitic grainstone, is Mississippian in age, forming the basal transgressive unit of the Redwall Limestone. However, Spreng (1979) argued on the basis of macrofossils and regional lithologic correlations that this dolomitized unit is part of the Devonian Fitchville Formation, with an unconformity of unknown duration marking the Devonian–Mississippian boundary. Above this basal unit (Unit 1 of Nichols and Silberling 1991), a thick sequence of predominantly skeletal wackestone, laminated pelletal pack...
stone, and crinoidal grainstone was deposited (Units 2–4 of Nichols and Silberling 1991; upper part of Member A, all of Member B and Lower Clifty Member of Dockal 1980), which is very similar to the partly coeval Gardison Limestone succession described at Fitchville Ridge (Fig. 4; see also Nichols and Silberling 1991; Silberling et al. 1997). The equivalent of the Delle Phosphatic Member is represented by a poorly exposed sequence of phosphatic shales and ostracod lime mudstones at the base of the Cherty Member of Dockal (1980)—or Unit 5 of Nichols and Silberling (1990). The Cherty Member shallows into the overlying Upper Clifty Member, made up of pelletoidal packstone and crinoidal grainstone that contain shattered and brecciated horizons similar to those observed in the partly coeval shelf limestones of the Mission Canyon Formation in Wyoming.

The δ13C values shift abruptly from a low of < 0‰ to +6‰ in the basal few meters of section (Fig. 6), showing evidence for a major hiatus consistent with the unconformity at the Devonian–Mississippian boundary described by Spreng (1979). The rest of the thick upper Kinderhookian–Osagean succession is marked by two δ13C peaks of ≥ +6‰ in the lower 50 meters of the sequence followed by a long-term decline to near 0‰ at the level of the Delle, which is well dated to the base of the Upper typicus Zone (Lané et al. 1980). This fall is interrupted by a brief return to values above +4‰ not seen in other localities, which likely reflects a thicker post-excursion sequence at Samak. The δ13C values begin rising again above the Delle to reach a baseline of +2–3‰ in the anchoralis Zone.

**Strawberry Creek Section.**—Steeply dipping Lower Mississippian carbonates assigned to the Madison Group are exposed in the Overthrust Belt of western Wyoming (Fig. 7). This section has been examined by Chen and Webster (1994) and Chen et al. (1994), and the same sequence a few kilometers away at Haystack Peak has been studied by Sando (1976, 1977) and Budai et al. (1987). Dolomitic silstones of the Devonian Darby Formation are abruptly overlain by the Lodgepole Limestone, consisting of dark-colored, faintly laminated lime mudstones and interbedded skeletal wackestone–packstone, with increasing packstone and grainstone interbeds towards the top of the sequence. The overlying Mission Canyon is coarser grained and partially dolomitized, with shattered and brecciated beds similar to those at Clark Fork Canyon and elsewhere in the Wyoming–Montana region above the top of the Lodgepole. The δ13C values begin at +5‰ in the lowermost carbonates above the Devonian Darby Formation (Fig. 7). Values are steady at this level in the lower 75 meters of section before increasing to a recorded high for the region of +7.5‰ in the upper quarter of the Lodgepole succession. δ18O then falls rapidly to below +2‰ in the overlying Mission Canyon Limestone.

**DISCUSSION**

**Primary or Secondary Signals?**

Each of the four Lower Mississippian sections examined in the Antler foreland basin and adjacent carbonate shelf of Utah and Wyoming records a positive δ13C anomaly that postdates peak excursion levels (Fig. 8). On the basis of biostratigraphic correlation of δ13C profiles among sections representing a wide range of depositional and diagenetic settings, it is evident that values have been interpreted to represent a late Kinderhookian–early Osagean seawater “isotopic excursion.” In fossiliferous successions, the excursion interval (dated to the *isosticha* and the lower part of the *typicus* zones) is followed by a return in the upper part of the *typicus* Zone to lower δ13C values (~ +3 to +4‰), which lie within the range of values commonly considered representative of Mississippian seawater (e.g., Meyers and Lohmann 1985). A more contentious issue is the interpretation of the minimum in δ13C values (~ +2‰) that postdates peak excursion levels (Fig. 8). In the profiles examined for this study, the post-excursion δ13C minimum is recorded immediately below or within facies inferred to have been deposited under episodically anoxic (Delle Phosphatic Member) or evaporative (Mission Canyon Formation) conditions. Carbonates in these environments may be expected to be particularly susceptible to resetting of primary marine values as a result of interaction with light carbon derived from organic-matter oxidation or meteoric waters (Jewell et al. 2000; Immennhauser et al. 2002). However, this interval of low δ13C (~ +2‰) dated to the upper part of the *typicus* Zone is also recorded above the excursion in carbonates at Arrow Canyon, Nevada (Fig. 8), which were deposited in normal, open-marine conditions and show no clear petrographic or δ18O
evidence of strong diagenetic alteration (Saltzman 2002). If we view the Arrow Canyon curve as a best approximation to seawater $\delta^{13}C$ because of its mid- to outer-ramp setting, nearly monofacial limestone succession and uniform, relatively heavy $\delta^{18}O$ values ($\sim$3‰ to 4‰), a comparison with the sections examined in the present study reveals an overall similarity of trends in the Kinderhookian and Osagean stages.

The issue of whether or not the low $\delta^{13}C$ carbonates ($\leq +2\%e$) in the upper part of the typicus Zone have undergone diagenetic resetting of primary marine values is a difficult one to resolve conclusively (see also discussion in Jewell et al. 2000). For example, arguments based on $\delta^{18}O$ covariation are somewhat equivocal because both the anomalously heavy $\delta^{13}C$ carbonates, which define the excursion, and the post-excision low $\delta^{13}C$ carbonates show strong negative $\delta^{18}O$ values at some levels (see data repository, and Fig. 9). Whether or not these anomalously low $\delta^{13}C$ values are viewed as primary has important implications for the diagenetic history of the basin and the magnitude of organic-carbon oxidation in the context of relative sea level. Here, the paleoceanographic implications of the stratigraphic relations outlined in this study (Figs. 8, 10) are discussed and a model is presented to explain the fundamental shift in the Antler foreland system from a late Kinderhookian period characterized by a healthy shallow-water carbonate factory and anomalously high $\delta^{13}C$ to an early Osagean phosphogenic event (Delle Phosphatic Member) that is marked by low $\delta^{13}C$ values.

**Phosphogenesis and $\delta^{13}C$: A Proposed Paleoceanographic Link**

The late Kinderhookian to early Osagean positive $\delta^{13}C$ excursion has been interpreted to reflect a period of high burial rates of isotopically light organic carbon (Mii et al. 1999; Bruckschen et al. 1999), due either to increased phosphate delivery to the surface oceans (from the continents or the deep ocean) or enhanced preservation. Alternatively, the addition of heavy carbon ($^{13}C$) due to enhanced carbonate weathering may produce an excursion in $\delta^{13}C$ (Kump and Arthur 1999; Kump et al. 1999). The global record of sea-level change and the distribution of sedimentary organic matter during the early Mississippian are too poorly known at this time to confidently rule out any of the above hypotheses. A well-known Late Devonian through earliest Mississippian period of organic-rich deposition (Klemme and Ulmishek 1991) includes units such as the Exshaw Formation in western Canada (Savoy 1992) and the “Liegende Alaunschiefer” in central Germany (Trappe 1998), but these and correlative black-shale units appear to be entirely older (early to middle Kinderhookian; no younger than the S. crenulata conodont Zone) than the onset of the $\delta^{13}C$ excursion in the late Kinderhookian isosticta conodont Zone. Locally, in the Antler foreland basin and adjacent shelf of the western United States, changes in relative sea level and facies distributions are known in greater detail and raise the expectation of both enhanced carbonate weathering and organic burial during the late Kinderhookian and early Osagean (Frye and Giles 1997; Saltzman et al. 2000a).

Although quantitative evidence for elevated rates of organic-carbon burial that can be tied to $\delta^{13}C$ curves are generally lacking, there are indications that tectonically driven bathymetric deepening (Giles 1996; Silberling et al. 1997) produced a stratified water column with locally enhanced preservation. For example, dark, laminated lime mudstones of late Kinderhookian age are conspicuous in distal foreland (or backbulge) sections in the Pahranagat Range of Nevada (Limestone X of Singler 1992; Saltzman 2002) and Strawberry Creek in Wyoming (Fig. 7; Chen and Webster 1994). However, such rocks are not necessarily organic-rich (Sandberg and Gut- schick 1984). In more proximal foreland settings in central Nevada, potential source-rock deposits are less well dated but include thick, laminated black shale (Homestead Canyon Shale of Giles and Dickinson 1995; possibly also lower parts of the Dale Canyon Formation) and spiculitic–radiolarian lime mudstones (Island Mountain Formation of Silberling et al. 1997). Although storage of organic matter in the Antler foreland basin...
system in Nevada and Utah cannot account for a global δ13C excursion to values ≈ +7‰ (Saltzman et al. 2000a; Silberling et al. 2001), it provides a starting point for investigation of causal factors. Furthermore, because the magnitude of the δ13C peak is roughly +1‰ larger in the Antler foreland than it is in the midcontinent, U.S.A. (Mii et al. 1999) and western Europe (Bruckschen et al. 1999), this could be taken as an indication of the importance of local contributions and reservoir effects in producing the overall carbon isotope shift in this region of the epicontinental sea (e.g., Patzkowsky et al. 1997; Holmden et al. 1998; Murphy et al. 2000).

The presence of phosphorite as part of the Delle Phosphatic Member may provide the most convincing evidence that high rates of organic-carbon burial occurred at some stage in the Antler foreland system. The Delle appears to be a regional phenomenon, with no concomitant phosphatic events described in the literature or included in compilations (Cook and McElhinny 1979; Shields et al. 2000). The phosphorus in the Delle is likely to have been derived from microbial release of organic phosphorus rather than iron-bound inorganic phosphate because an iron-rich terrigenous sediment source should result in a lateral or overlapping association with glauconitic (or other Fe-rich) units, as is observed in Upper Cretaceous phosphorite–greensand deposits in Egypt and on the eastern shelf of Australia today (Glenn et al. 1994). While most models for phosphorite deposition begin with the liberation of large quantities of organic phosphorus (e.g., Compton et al. 1993; Föllmi et al. 1994), important questions surround the timing and nature of the steps by which this phosphate becomes incorporated into mineral apatite (authigenic carbonate fluorapatite).

Assuming that organic-carbon accumulated at a relatively high rate in oxygen-depleted parts of the Antler foredeep during the late Kinderhookian, remobilization of organic phosphorus during bacterial degradation should have significantly increased phosphate ion concentrations within meters of the sediment–water interface (Fig. 10). The dissolved phosphate in interstitial waters may have been adsorbed to iron oxyhydroxide minerals (generally considered a short-term sink; Filippelli 2001), precipitated as authigenic carbonate fluorapatite or released back to the overlying water column (Compton et al. 2000). Carbonate fluorapatite particles have a relatively high specific gravity and are particularly prone to being concentrated to form conspicuous laminae or lenses in sedimentary deposits (Föllmi 1996). Thus the apparent absence of such particles in upper Kinderhookian sediments that can be reasonably well dated to the time of the positive δ13C excursion in western North America may reflect preferential diffusion of phosphate from interstitial waters into the overlying water column. This lack of a sedimentary sink for released phosphorus is consistent with global compilations that suggest that the late Kinderhookian (early Mississippian) was not a time of significant phosphorite deposition (e.g., Cook and McElhinny 1979). However, because of the relatively long duration of the δ13C excursion compared to the residence time of phosphate in the oceans (~ 104 yr; Föllmi 1996), some measure of phosphatic deposition would be predicted in certain late Kinderhookian environments that have yet to be identified. The capacity of sediments to withhold phosphate from diffusive escape seems to be oxygen dependent, although other factors such as sedimentation rate, microbial influences, and the thermodynamics or kinetics of apatite mineral formation can act independently (Föllmi 1996).

As excess phosphate began to build up in water masses in the Antler foredeep and was recirculated into the photic zone to maintain primary production, a positive feedback cycle dependent on preferential regeneration of phosphorus compared to carbon in organic matter underlying oxygen-poor waters may have developed (Van Cappellen and Ingall 1994; Murphy et al. 2000; see also Anderson et al. 2001 for a contrasting viewpoint). Continued productivity and biological pumping of 12C out of the surface waters from which carbonates precipitated likely sustained elevated δ13C values during the late Kinderhookian and early Osagean, but maintenance of a healthy shallow-water carbonate factory in the region suggests that eutrophic conditions did not develop (Caplan et al. 1996). Nutrient loading from rivers draining subaerially exposed Antler orogenic highlands to the west may provide an additional mechanism for stimulation of productivity during this time interval. The subsequent decline of δ13C to pre-excursion values in shallow-water carbonate-producing environments could

![FIG. 8.—Continued.](image)
signal a progressive lowering of productivity that reversed net export of $^{12}$C from the surface waters, perhaps linked to more efficient trapping of phosphate in the deepening water masses of the foreland system. Alternatively, the post-excursion decline in $\delta^{13}$C could mark enhanced delivery of $^{12}$C to surface waters from beneath a weakening pycnocline.

Following this period in which $\delta^{13}$C values gradually dropped towards a post-excursion steady state (Fig. 10), bathymetric and oceanographic conditions changed abruptly in the foreland basin and resulted in the disappearance of normal shelf benthos and deposition of the anomalous phosphate–black shale–chert association of the Delle Phosphatic Member. Phosphogenesis and the demise of a healthy carbonate platform in the upper part of the typicus Zone is ultimately attributed to ventilation and vigorous upwelling of the P-enriched water masses (Fig. 11). An earlier, analogous carbonate platform drowning event during the late Famennian and earliest Kinderhookian has also been attributed to upwelling and progressive eutrophication (Caplan et al. 1996). Vigorous upwelling in the upper part of the typicus Zone (Osagean) was likely topographically induced, as argued by Silberling et al. (1997), and related to uplift of the accretionary wedge (Roberts Mountains allochthon) or the associated forebulge (see also Giles and Dickinson 1995), although global cooling, strengthening of the trade winds, and sea-level fall may have further promoted ventilation of parts of the Antler seaway (Osagean cooling step of Mii et al. 1999). Development of a shore-parallel wind regime favorable for coastal upwelling, similar to that which existed later in the region during formation of the Permian Phosphoria rock complex (Sheldon 1986), is consistent with atmospheric circulation models (Parrish 1982) and the association of Delle phosphorites with angular, well-sorted and laminated phosphatic quartz siltstones containing little or no clay, here interpreted as eolian-derived (cf. Carroll et al. 1998).

Widespread accumulation of organic matter in a zone of upwelling during the upper part of the typicus Zone (Fig. 11) may have been enhanced by salinity stratification in the distal Antler foreland and adjacent carbonate platform set up by brackish water derived from the peripheral-bulge region (Jewell et al. 2000). Perhaps of equal importance was the influx of hypersaline water from the adjacent carbonate platform of Wyoming and Montana (Fig. 11), which is marked by evaporite deposition (Mission Canyon Formation; Sando 1974, 1976; Budai et al. 1987; Reid and Dorobek 1993). Upwelling proximal to a warm, shallow evaporative sea has been suggested.

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**Fig. 9.** Crossplot of $\delta^{13}$C and $\delta^{18}$O for individual sections (see JSR data repository).

**Fig. 10.** Generalized lithologic columns from the carbonate platform and distal Antler foreland, showing correlation of phosphatic and evaporite facies associations during the upper part of the typicus Zone. Stratigraphic columns are plotted against a generalized $\delta^{13}$C curve, history of relative sea level, and paleoeceanographic interpretations. Organic-carbon burial and seawater phosphate enrichment peak at the Kinderhookian–Osagean boundary (see text for discussion). Water depths in the distal foreland during the upper typicus Zone are still a matter of debate (Sandberg and Gutschick 1984; Jewell et al. 2000).
as a model for the Permian Phosphoria Formation (Dahl et al. 1993; Carroll et al. 1998; Stephens and Carroll 1999; Hiatt and Budd 2001).

Despite high productivity and the accumulation of organic matter at this stage, δ13C did not increase in association with phosphogenesis and deposition of the Delle Phosphatic Member (Figs. 8, 10). This paradox is attributed to the counterbalancing effects of the incorporation of light carbon from the upwelling water mass and organic-matter oxidation during lowstands of sea level that ventilated the water mass (Fig. 10). Evidence for coeval lowstands, which may have provided an additional source of phosphorus to the surface ocean in the upper part of the typicus Zone, includes winnowing and reworking of Delle oolitic and pisolithic phosphorites to form detrital aggregates. In addition, well-developed endolithic algal borings in both oolitic and pisolithic phosphorites provide evidence for a phoscrete origin that formed on semi-emergent tidal flats (Nichols and Silberling 1990). Geochemical data directly from the Delle Phosphatic Member published by Jewell et al. (2000) are also consistent with periodic lowstands of sea level that ventilated the water mass (Fig. 10). Evidence for coeval lowstands, which may have provided an additional source of phosphorus to the surface ocean in the upper part of the typicus Zone, includes winnowing and reworking of Delle oolitic and pisolithic phosphorites to form detrital aggregates. In addition, well-developed endolithic algal borings in both oolitic and pisolithic phosphorites provide evidence for a phoscrete origin that formed on semi-emergent tidal flats (Nichols and Silberling 1990). Geochemical data directly from the Delle Phosphatic Member published by Jewell et al. (2000) are also consistent with periodic lowstands of sea level that ventilated the water mass (Fig. 10).

Comparison with Other Periods of δ13C Shifts and Phosphogenic Events

In the proposed scenario, the Delle phosphorites are the end product of a period of high organic-carbon burial and seawater phosphate enrichment in deep water masses of the subsiding Antler foredeep during the late Kinderhookian–early Osagean (represented by a positive δ13C excursion in shallow-water carbonates) followed by upwelling into a water mass that fluctuated between anoxic and oxic conditions (Figs. 10, 11). The fact that a low in δ13C is associated with phosphatic deposition suggests that water mass ventilation, organic-carbon oxidation efficiency, and phosphogenesis reached maxima at the same time, a situation analogous to several Precambrian–Cambrian P-giant episodes (Shields et al. 2000). For example, Early Cambrian phosphorite deposition on the Yangtze Platform in southwest China is focused in a stratigraphic interval (Zhongyicun Member of the Meishucun Formation) marked by strongly negative δ13C values, which generally follow a period of heavier values in the late Neoproterozoic (Shen and Schidlowski 2000). The opposite scenario has also been presented in which δ13C excursions and organic-matter burial coincide with or even postdate phosphogenesis (e.g., Early Cretaceous; Föllmi et al. 1994). More complex, smeared-out patterns have been established in association with younger P-giant episodes such as the Miocene, where high-resolution dating is possible (Compton et al. 1993). The phosphatic deposits of the Permian phosphoria Formation, which occur in a paleogeographic setting similar to the Delle Phosphatic Member, are more difficult to place in the context of δ13C stratigraphy but may follow a period of anomalously high values recorded in the Lower Guadalupian (Grossman 1994).

In most of the above examples from the literature, the processes of reactive P enrichment are ultimately linked to global changes in climate and weathering (i.e., glacially induced oceanic overturn or an accelerated water cycle during intensified greenhouse conditions; Föllmi 1996). In this context, reworked phosphorite deposits may represent a sink for a reactive phosphorus flux that ultimately cannot be accommodated by burial of organic matter (Compton et al. 2000). However, in the case of the Early Mississippian events discussed here, global changes are poorly known, and there is little evidence for increased reactive P flux to the ocean reservoir (in fact it appears that 87Sr/86Sr decreases over this interval; Bruckschen et al. 1999), leaving open the possibility that the Delle Phosphatic Member represents a focused output of phosphorus in response to local oceanographic events. Perhaps a comparable situation occurred during the Middle Ordovician (Mohawkian), where a positive δ13C excursion (≈+3‰) interpreted to reflect enhanced organic-carbon burial in the Appalachian foreland basin (Taconic orogeny; Patzkowsky et al. 1997) also appears to precede a significant period of phosphogenesis (e.g., Bigby–Cannon Limestone in central Tennessee of Cathcart 1989; Holland and Patzkowsky 1997). The recommendation by Shields et al. (2000) that proposed "links between phosphogenesis and global changes in δ13C or P-input continue to be re-examined on a case-by-case basis" is certainly echoed here.

Conclusions

The results of this study demonstrate that a large positive δ13C excursion spanning the late Kinderhookian and early Osagean was followed closely by the Delle phosphogenic event in the Antler foreland system and coeval evaporite deposition on the adjacent carbonate shelf. A paleoceanographic explanation consistent with the relative timing of these events begins with flexural subsidence in the Antler foreland during the late Kinderhookian and the creation a stratified water column in which significant quantities of organic carbon accumulated. Microbial degradation of this organic matter led to the enrichment of phosphate in the water mass, and as the basin deepened this P gradually accumulated beneath a pycnocline. In the upper part of the typicus Zone (early Osagean), topographic upwelling associated with uplift of the thrust load (allochthon) or forebulge, possibly enhanced by climatic cooling and circulation changes, resulted in deposition of the Delle Phosphatic Member. Accumulation of organic matter in the foreland region may have been promoted by a flux of hypersaline bottom waters from the adjacent platform region where evaporites were forming. However, this period of high productivity and organic burial in the Antler foreland system did not increase δ13C. The removal of light carbon in organic matter was apparently balanced by its oxidation during lowstands of sea level and/or continued upwelling, which ventilated the water mass and also resulted in winnowing and condensation of phosphatic particles. This pat-
tern of low $\delta^{13}C$ coincident with phosphate deposition may be analogous to several Precambrian-Cambrian intervals, the middle Ordovician and possibly the Miocene, and suggests that phosphogenesis was related to high organic matter oxidation efficiency.

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