Carbon and oxygen isotope stratigraphy of the Lower Mississippian (Kinderhookian–lower Osagean), western United States: Implications for seawater chemistry and glaciation

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ABSTRACT

A positive carbon isotope ($\delta^{13}C$) excursion has been recognized in upper Kinderhookian and early Osagean carbonates in three sections in southeast Idaho and Nevada. The oldest $\delta^{13}C$ peak (+7‰) is dated to the *isosticha* conodont zone, and a younger peak occurs in the *typicus* Zone. The shifts are recorded in a range of carbonate lithofacies representing various water depths along the shelf. Lithofacies sampled for $\delta^{13}C$ and $\delta^{18}O$ at the Samaria Mountain section in southeast Idaho record the shallowest-water conditions, indicated by cross-bedded skeletal and peloidal grainstones. The deepest water conditions are present in the Pahranagat Range section in eastern Nevada, which consists mainly of bioturbated lime mudstone and skeletal wackestone. The $\delta^{13}C$ values from these widely separated sedimentary basins show a consistent trend that correlates with Early Mississippian curves generated from brachiopod calcite in western Europe and the Midcontinent of North America, as well as dolomites in Utah and Wyoming. $\delta^{18}O$ values become more positive up section, generally paralleling the positive trend in $\delta^{13}C$ during the late Kinderhookian. No subaerial exposure surfaces are recognized in the sections examined in southeast Idaho and Nevada, and at least the $\delta^{13}C$ trends are interpreted as primary seawater fluctuations. Sea-level changes occurred near the beginning of the late Kinderhookian $\delta^{13}C$ shift (early to middle parts of the *isosticha* Zone) and within the peak of the $\delta^{13}C$ excursion (Kinderhookian-Osagean boundary), although tectonic changes associated with the Antler orogeny have likely modified the eustatic signature.

Keywords: carbon-13, conodont, glaciation, Kinderhookian, Mississippian, oxygen-18.

INTRODUCTION

The Early Mississippian marked a transitional period in Earth history between the greenhouse conditions of the early Paleozoic and the late Paleozoic ice ages. The middle Paleozoic greenhouse-icehouse transition has traditionally been viewed in terms of progressive cooling and ice buildup throughout the Carboniferous, linked ultimately to changes in carbon cycling associated with the rise of vascular land plants (Berner, 1990) and to changes in the positions of the continents with respect to the poles (Crowell, 1995). Indeed, the Early Mississippian was characterized by small-scale buildup of ice in South America (Hunicken et al., 1986; Garzanti and Sciunnach, 1997) that preceded widespread ice-sheet development on Gondwana and cyclothemic deposition in Euramerica by tens of millions of years (Veevers and Powell, 1987). However, an emerging $\delta^{13}C$ and $\delta^{18}O$ record hints at a relatively abrupt oceanographic event in earliest Carboniferous time (Mii et al., 1999; Bruckschen et al., 1999; Saltzman et al., 2000b). These studies represent a further refinement of the Devonian-Carboniferous transition that has been recognized by previous investigators (Veizer et al., 1986; Popp et al., 1986; Lohmann and Walker, 1989; Carpenter and Lohmann, 1997) and that may have had a profound impact on the overall pace and severity of the middle Paleozoic greenhouse-icehouse transition.

A globally significant oceanographic event during the Kinderhookian Provincial Series (middle Tournaisian) is signaled by a large, positive $\delta^{13}C$ shift that reaches a maximum value of >+7‰, which is among the highest peaks known in the Phanerozoic (Veizer et al., 1999). The late Kinderhookian $\delta^{13}C$ shift has been observed by four independent research groups working with a range of carbonate components (brachiopod calcite, micrite, replacive dolomite) in both European and North American sedimentary basins (Fig. 1) (Budai et al., 1987; Bruckschen and Veizer, 1997; Mii et al., 1999, 2001; Saltzman et al., 2000b). The possibility that this positive $\delta^{13}C$ shift marks the onset of the Carboniferous glaciation was suggested by Mii et al. (1999) on the basis of a positive shift in $\delta^{18}O$ values in brachiopod calcite that paralleled the $\delta^{13}C$ shift in North America and Europe. The Kinderhookian $\delta^{18}O$ shift (up to +3‰ in the Midcontinent region of North America) has been interpreted to reflect a combination of temperature and ice-volume effects that occurred in response to a period of enhanced organic matter burial (high $\delta^{13}C$) and decreased atmospheric carbon dioxide levels (Bruckschen and Veizer, 1997; Bruckschen et al., 1999; Mii et al., 1999, 2001). However, the precise magnitude and relative synchroneity of the $\delta^{13}C$ and $\delta^{18}O$ shifts in different parts of the world are known in only limited detail, and thus a causal link to the full-blown icehouse state that was to follow remains uncertain. In fact, one of the major hurdles in the acceptance of parallel $\delta^{13}C$ and $\delta^{18}O$ trends as representative of global changes during any time period is the independent evidence of their correlation using biostratigraphy. The purpose of this paper is to provide evidence for substantial shifts in $\delta^{13}C$ and $\delta^{18}O$ values during the late Kinderhookian in three sections in North America that can be well dated by using the established standard conodont zonation (Sandberg et al., 1978; Lane et al., 1980) and to discuss their primary versus diagenetic nature.

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GEOLOGIC BACKGROUND

Study Area and Sample Collection

Carbonate samples for $\delta^{13}C$ and $\delta^{18}O$ come from three localities spanning the (Lower Mississippian) Kinderhookian Provincial Series and lower part of the Osagean Provincial Series in the western United States (Figs. 1, 2). The limestone successions sampled include the Joana Limestone and Limestone X in the Pahranagat Range, east-central Nevada (Alamo section of Singler, 1987); the Crystal Pass, Dawn, and Anchor Limestones in the Arrow Canyon Range, southeast Nevada (Hidden Valley section of Brenckle, 1973); and the Henderson Canyon Formation at Samaria Mountain in southeast Idaho (Gardner Canyon section of Chen and Webster, 1994) (Fig. 3). These limestone units were deposited in roughly north-trending facies belts that correspond generally to a distal foreland basin bordering the Antler orogenic highlands (Pahranagat Range), a forebulge setting east of the foreland (Samaria Mountain), and a shelf-margin facies (Arrow Canyon Range) (Fig. 4; Poole and Sandberg, 1991; Chen and Webster, 1994; Giles, 1996). The foreland basin and forebulge were bordered on the west by a flysch trough and adjacent highlands (Fig. 4), all of that formed in response to thrust loading and flexural subsidence during the contractional Late Devonian to Early Mississippian Antler orogeny (Giles, 1996).

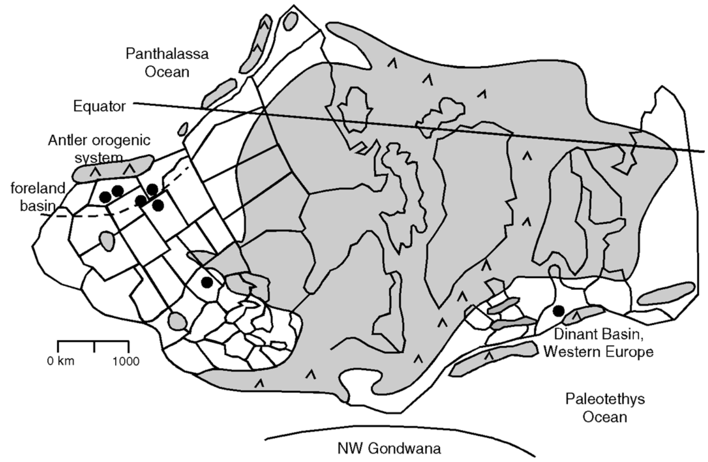

Figure 1. Mississippian paleogeography for the Kinderhookian and lower Osagean Provincial Series (Tournaisian Stage) after Witzke (1990). Filled circles represent localities in North America (Nevada, Utah, Idaho, Wyoming, and Iowa) and western Europe where a late Kinderhookian $\delta^{13}C$ excursion has been detected (Budai et al., 1987; Mii et al., 1999; Bruckschen et al., 1999). Land areas are shaded.

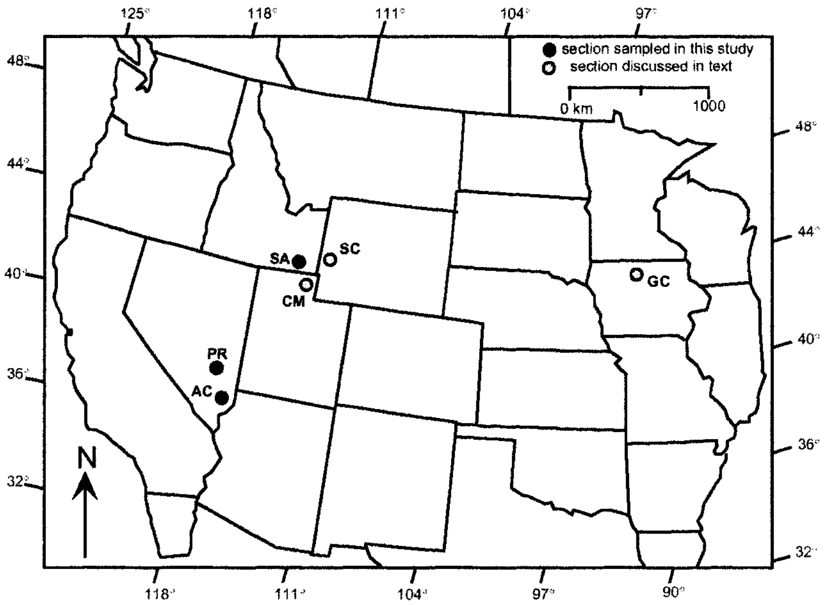

Figure 2. Locality map showing the six North American localities discussed in text. Sampling for $\delta^{13}C$ at each locality has revealed a large, positive excursion during the late Kinderhookian. Sections sampled for this study include PR—Pahranagat Range, AC—Arrow Canyon Range, SA—Samaria Mountain. Sections sampled by previous workers include SR—Salt River Range, GC—Gilmore City, CM—Crawford Mountains (Budai et al., 1987; Mii et al., 1999).

Biostratigraphic Framework

The $\delta^{13}C$ curves in this study have been correlated by using the standard *Siphonodella* (Sandberg et al., 1978) and post-*Siphonodella* conodont zonations (Lane et al., 1980) for the (Lower Mississippian) Kinderhookian and Osagean Provincial Series (Fig. 3). Most of the study interval falls within the uppermost Kinderhookian *Siphonodella isosticha*–late *crenulata* Zone (hereafter referred to as the *isosticha* Zone) and earliest Osagean *Gnathodus typicus* Zone (this zone was divided into early and late parts by Lane et al., 1980, but is hereafter referred to collectively as the *typicus* Zone). The base of the *isosticha* Zone is defined by the first occurrence of the earliest gnathodiid species *Gnathodus delicatus* (Sandberg et al., 1978). The base of the *typicus* Zone, and the boundary between the Kinderhookian and Osagean Provincial Series (Fig. 3), has been placed at the first occurrence of *Gnathodus typicus* morphotype 2, which evolved from *G. delicatus* (Lane et al., 1980). In practice, the Kinderhookian-Osagean boundary has also been placed just above the last occurrence of *Siphonodella* or at the first occurrence of *Polygnathus communis carina* (Sandberg et al., 1978; Thompson and Fellows, 1970; Lane, 1974, 1978; Carman, 1987; Chen et al., 1994).

FACIES AND DEPOSITIONAL ENVIRONMENTS

The three stratigraphic successions examined in southeast Idaho and Nevada are made up of limestone lithofacies that are grouped

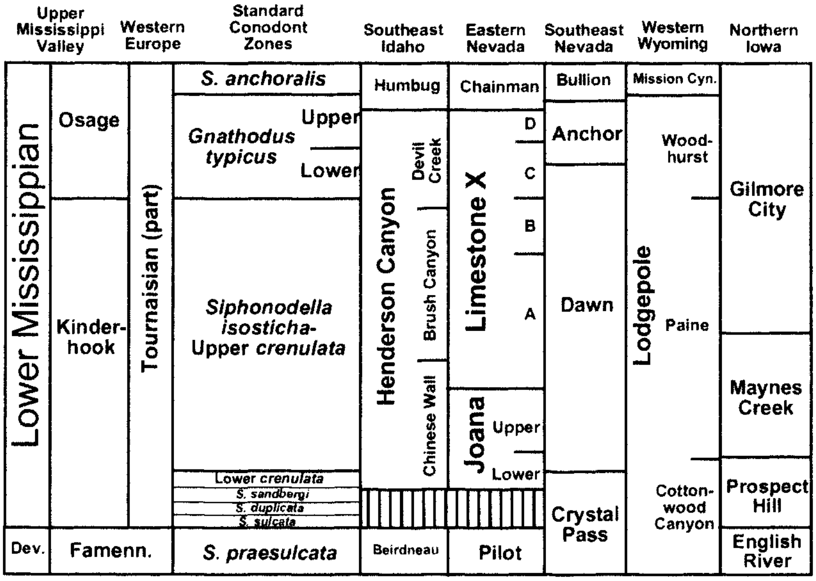

Figure 3. Chart showing stratigraphic nomenclature used in text based on the following sources: Wickwire et al. (1985) and Chen et al. (1994), southeast Idaho and western Wyoming; Singler (1987), eastern Nevada; Poole and Sandberg (1991) and Pierce and Langenheim (1974), southeastern Nevada; and Witzke and Bunker (1996), northern Iowa. Standard conodont zonation after Sandberg et al. (1978) and Lane et al. (1980). The study interval corresponds to the *Siphonodella isosticha* and *Gnathodus typicus* zones. Zonal boundaries are approximate, and not all zones are found in all areas. The *S. sulcata* through *S. sandbergi* Zones may be present in western Wyoming, southeastern Nevada, and northern Iowa, but this interpretation remains conjectural because of unfossiliferous intervals.

generally into shoal-water and deep-ramp facies associations, indicative of water depths above and below normal wave base, respectively. In general, the Pahranagat Range section contains the largest proportion of deeper-water limestone facies, and the shallowest water facies are most abundant in the Samaria Mountain section (Figs. 5–7). Both the deep- and shallow-water lithofacies consist of nearly pure limestone; dolomite makes up <5% of the sections, and clastic materials are restricted to thin shaly partings that make up a trivial amount of exposed section. Lithofacies are arranged generally in meter-scale carbonate cycles, with the exception of the encrinitic (Waulsortian-like) packstones and grainstones of the upper Joana Limestone in the Pahranagat Range (Fig. 6). All three sections contain the full spectrum of carbonate lithofacies represented on the lithologic key in Figure 5, the general features of which are described next.

Shoal-Water Facies

The shoal-water facies association includes skeletal and peloidal packstone and grainstone, with locally abundant intraclasts and ooids. Skeletal grains include fragments of crinoids and brachiopods with lesser amounts of bryozoans, foraminifera, corals, and mollusks. In the Samaria Mountain section, well-sorted skeletal grainstones exhibit low-angle cross-stratification, with less common high-angle cross-bedding indicative of the highest-energy conditions on the shelf. Poorly to moderately sorted packstone and grainstone facies in the Samaria, Pahranagat, and Arrow Canyon sections are planar to massively bedded and likely represent in situ skeletal banks (Chen and Webster, 1994). The observed features of the coarse-grained shoal-water facies association are consistent with open-marine deposition above normal wave base in a mound-and-channel topographic setting.

Deep-Ramp Facies

The deep-ramp facies association includes bioturbated and laminated lime mudstone and skeletal wackestone. Horizontal burrows are most common, with vertical burrows only locally abundant. Bedding-plane occurrences of *Zoophycus* are abundant in parts of Limestone X in the Pahranagat Range and indicate relatively deep-water conditions near the lower limits of storm influence (Singler, 1987). Thin (20–30 cm) beds of moderately sorted packstone occur as the basal units of meter-scale, fining-upward sequences in the Pahranagat Range and are interpreted as storm-generated, allochthonous deposits. Bedded and nodular chert are locally abundant, particularly in the lower part of the Samaria Mountain section and the upper part of the Arrow Canyon Range section. Sponge spicules are very abundant in the wackestones and lime mudstones of the deep-ramp facies association, with lesser amounts of crinoids, brachiopods, and bryozoans. Corals are locally abundant and appear to be in growth position at several stratigraphic levels in the Pahranagat Range section. Fine pyrite is found throughout this facies, particularly in association with the laminated mudstone facies in the Pahranagat Range that may reflect intermittent deposition in poorly oxygenated waters between major storm events. The observed features of the fine-grained limestones that make up the deep-ramp facies association point to deposition in quiet water below normal wave base.

STABLE ISOTOPE STRATIGRAPHY

Methods

In order to generate relatively high-resolution (meter-scale), continuous stable isotope curves, the $\delta^{13}C$ and $\delta^{18}O$ values in this study were derived from the full range of fine-grained to coarse-grained lithologies previously described and illustrated in Figures 5–7. Micrites were preferentially drilled from fresh rock surfaces (generating 0.5–1.0 mg of powder), although nearly a third of the samples included coarser-grained facies cemented with sparry calcite. All samples were roasted under vacuum at 380 °C for 1 h to remove volatile contaminants. Samples from the Arrow Canyon and Samaria Mountain localities were analyzed at the University of Iowa and University of Michigan stable isotope laboratories, where carbonate powders were 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 251 or 252 mass spectrometer. All isotope ratios were corrected for ^{17}O contribution and are reported in per mil relative to the Peedee belemnite (PDB) isotope standard. Analytical precision for $\delta^{13}C$ and $\delta^{18}O$ based on duplicate analyses and on multiple analyses of NBS19 was $\leq$0.04‰.

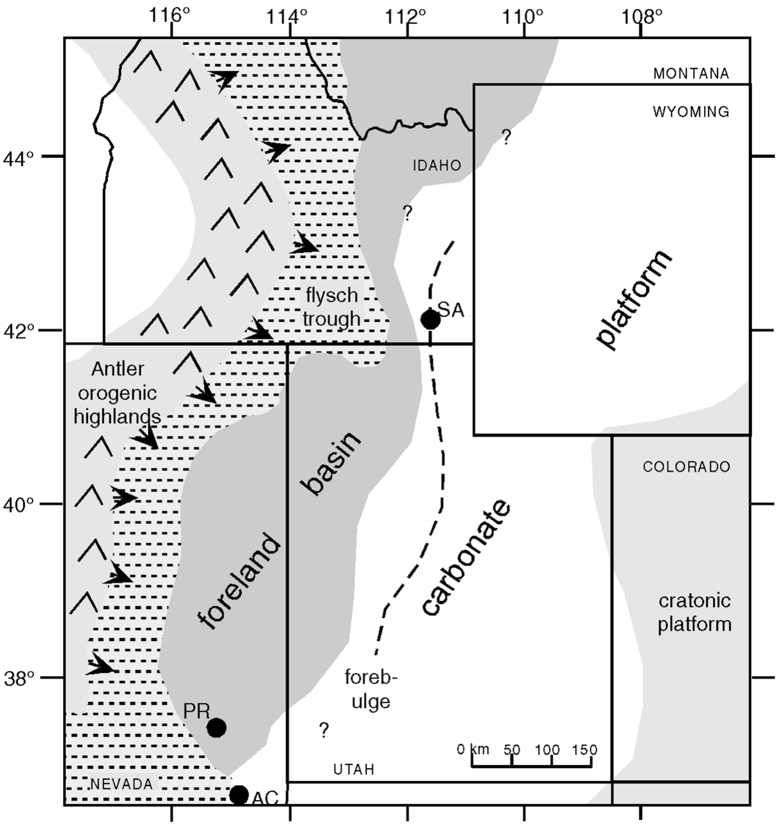

Figure 4. Major paleogeographic features and facies belts of the western United States during the Kinderhookian–early Osagean, simplified after Poole and Sandberg (1991), Chen and Webster (1994) and Giles (1996). See text for discussion. PR—Pahranagat Range, AC—Arrow Canyon Range, SA—Samaria Mountain.

Arrow Canyon Range, Southeastern Nevada

The Early Mississippian $\delta^{13}C$ and $\delta^{18}O$ values from the Arrow Canyon Range are presented in stratigraphic profile in Figure 5 (also see Data Repository Table DR1[1]). The section begins with $\delta^{13}C$ values of ~0‰ near the base of the Mississippian section and peak at +7‰ in the Dawn Limestone. The monotonic rise and fall is interrupted near the peak of the excursion, where values show a brief negative shift to near +5‰ before rising again above +6‰ (Fig. 5). After a return to near preexcursion values below +2‰ near the base of the Anchor Limestone, values begin to rise again. Key fossil collections that set age limits on shifts in $\delta^{13}C$ in the Arrow Canyon section include specimens of *P. communis carina* at ~20 m above the base of the Anchor Limestone (Pierce and Langenheim, 1974), as well as those collections in the upper Dawn and lower Anchor that contain conodonts diagnostic of the *typicus* Zone shown in the biostratigraphic column of Poole and Sandberg (1991).

The $\delta^{18}O$ values from the Crystal Pass Limestone in the basal part of the Arrow Canyon section are relatively low at <–8‰ (Fig. 5). The $\delta^{18}O$ values of remainder of the samples are more positive than −7‰ and show a general trend toward higher values up section through the Dawn Limestone, with a total shift of ~+3‰ generally paralleling the positive change in $\delta^{13}C$. Values are largely invariant through most of the upper Dawn and lower Anchor Formations, although the top four samples in the Anchor form a notable positive spike above −3‰.

[1] GSA Data Repository item 2002015, Lower Mississippian stable isotope data from Nevada and Idaho, is available on the Web at http://www.geosociety.org/pubs/ft2002.htm. Requests may also be sent to editing@geosociety.org.

Pahranagat Range, Eastern Nevada

The Early Mississippian $\delta^{13}C$ and $\delta^{18}O$ curves from the Pahranagat Range are presented in Figure 6 (and Table DR2 [see footnote 1]). The $\delta^{13}C$ values are near 0‰ at the base of the Mississippian section and rise to a peak of >+7‰ near the base of Member B of Limestone X. The $\delta^{13}C$ values then fall back below +4‰ before rising again to a second distinct peak above +6‰ within Member C. The ages of inflections in the $\delta^{13}C$ curve in the Pahranagat Range are defined by collections containing *S. isosticha* throughout Member A of Limestone X and collections containing *G. typicus* M2 in the lower third of Member C (Singler, 1987) (Fig. 6).

The lowest $\delta^{18}O$ values occur in the basal part of the Pahranagat section and show a brief shift to values more negative than −6‰ before a gradual increase from −5‰ to near −2‰ in the lower part of Member B of Limestone X at about the level of the initial $\delta^{13}C$ peak above +7 (Fig. 6). Values then fall briefly back below −4‰ in the upper part of Member B before rising again and hovering generally between −4‰ and −2‰ for the remainder of the sampled section.

Samaria Mountain, Southeastern Idaho

The Early Mississippian $\delta^{13}C$ and $\delta^{18}O$ curves from the Samaria Mountain section are presented in Figure 7 (and Table DR3 [see footnote 1]). Values of $\delta^{13}C$ are near +1‰ at the base of the Mississippian section and rise to a peak of >+6‰ in the lower third of the Brush Canyon Member of the Henderson Canyon Formation. This rise is interrupted by a brief negative shift back below +2‰ toward the top of the Chinese Wall Member. Following peak values in the middle of the Brush Canyon Member, $\delta^{13}C$ values fall back to +4‰ before rising up above +5‰ to form a secondary peak near the top of the member. A fall back to preexcursion values below 0‰ occurs in the Devil Creek Member of the Henderson Canyon Formation (Fig. 7). The $\delta^{13}C$ shifts at Samaria Mountain are dated by conodont collections containing *G. delicatus* and *G. typicus* M2, at 1 m and 45 m above the base of the Chinese Wall and Brush Canyon Members, respectively (Wickwire et al., 1985; Chen et al., 1994). In addition, abundant specimens of *P. communis carina* are found in the upper part of the Devil Creek Member (Chen et al., 1994).

The $\delta^{18}O$ values in the Samaria Mountain section become generally more positive up section, shifting from near −8‰ to −3‰ (Fig. 7). The $\delta^{18}O$ values within the upper Brush Canyon and Devil Creek Members show brief shifts back below −4‰, defined by only a few points. The $\delta^{18}O$ curve at Samaria Mountain

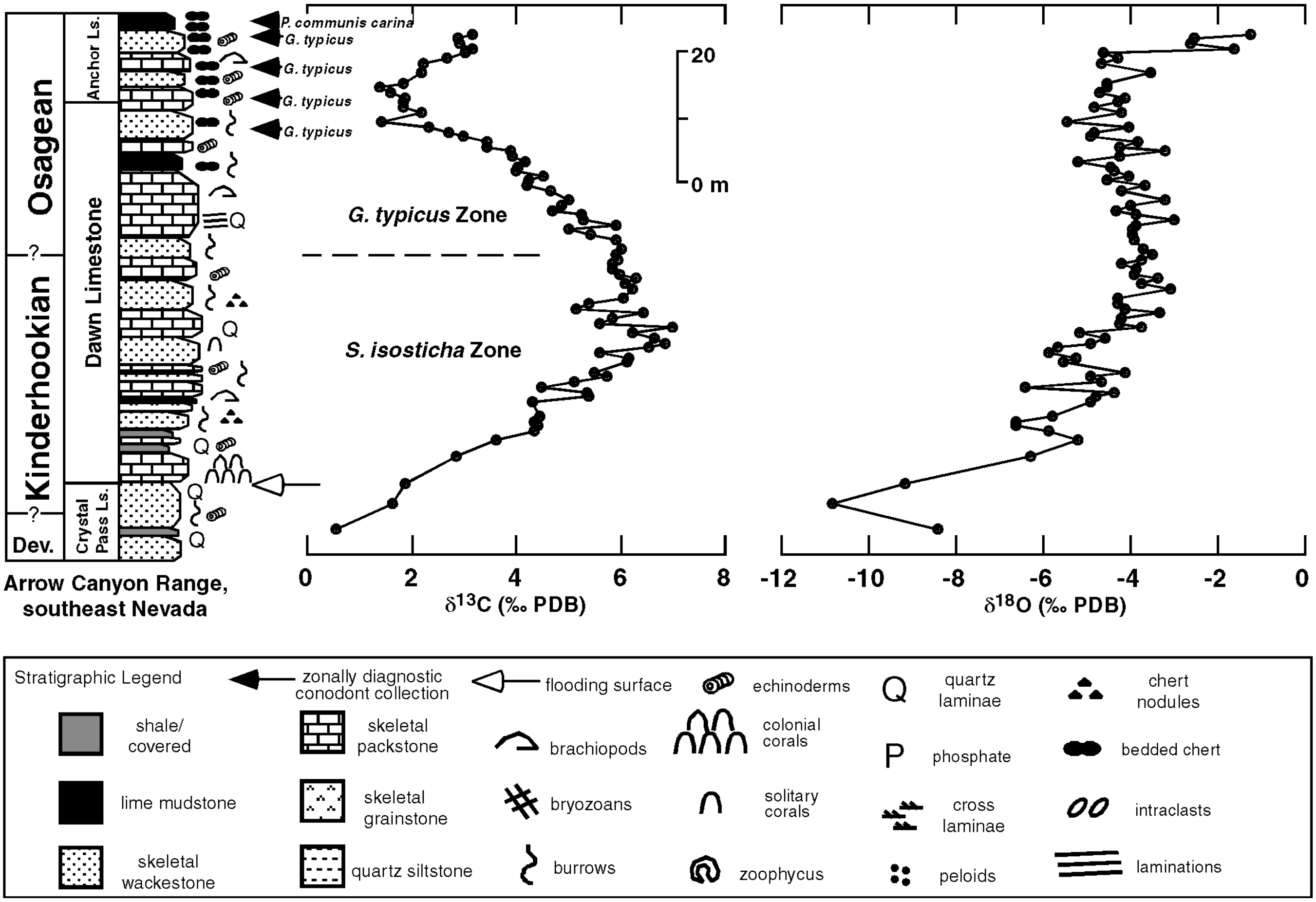

Figure 5. Lithologic column and δ¹³C and δ¹⁸O results from the Arrow Canyon Range, southeastern Nevada (Fig. 2). Boundary between *isosticha* and *typicus* Zones based on diagnostic conodont collections in Pierce and Langenheim (1974) from the Anchor Limestone and on the biostratigraphic column in Poole and Sandberg (1991).

is generally noisier than the Pahranagat and Arrow Canyon sections (Figs. 5, 6).

DISCUSSION

The discussion is divided into two parts. The first addresses the issue of diagenesis for both the δ^{13}C and δ^{18}O curves presented in Figures 5–7. The second assesses the relative synchroneity of important δ^{13}C and δ^{18}O shifts and interprets them in the context of Lower Mississippian biostratigraphy and sequence stratigraphy.

Primary Versus Diagenetic Signatures

Carbon Isotopes

Determining the primary versus secondary nature of observed trends of stable isotopes in ancient carbonate sequences is a longstanding debate. The nature of the problem with respect to carbon isotopes was pointed out early on by Hudson (1975), who noted that Keith and Weber's (1964) comprehensive survey revealed that most ancient limestones have δ^{13}C values similar to unlithified carbonate sediment in modern marine settings (0 to +2‰ relative to PDB), whereas recent limestones lithified by meteoric diagenesis (e.g., Bermudan limestones) are often highly depleted in ^{13}C (their δ^{13}C values go as low as −8‰). Hudson (1975) concluded that these ancient limestones could not have been cemented by the same processes that occur in modern, near-surface freshwater diagenetic settings, such as Bermuda, which involve the addition of extraneous CO_2 to the system, and suggested alternatively that lithification may have taken place during burial diagenesis and was effectively a closed system with respect to carbon. In the 1980s and 1990s, quantitative studies of carbonate diagenesis and water-rock interaction added to the debate by demonstrating that δ^{13}C values are likely to be preserved over a wide range of water:rock ratios and degrees of diagenetic alteration, including some involving near-surface diagenesis, because diagenetic fluids acquire most of their carbon directly from the dissolution of metastable carbonates (Magaritz, 1983; Lohmann, 1988; Banner and Hanson, 1990). Nonetheless, there are documented cases in which the δ^{13}C values of ancient limestones have been shifted toward very low values in close proximity (usually within <10 m) to known exposure surfaces, likely reflecting the addition of oxidized organic carbon during meteoric diagenesis (Allan and Matthews, 1982; Algeo et al., 1992. Thus, it is important to place the δ^{13}C shifts in this paper in a sequence stratigraphic framework that can be used to evaluate the presence or absence of exposure surfaces.

The limestone successions sampled for stable isotopes (Figs. 5–7) consist of shoal-water and deep-ramp lithofacies that are interpreted to reflect deposition in entirely subtidal (permanently submerged) environments. Even the shallowest water facies in the Samaria Mountain section (e.g., cross-bedded skeletal and

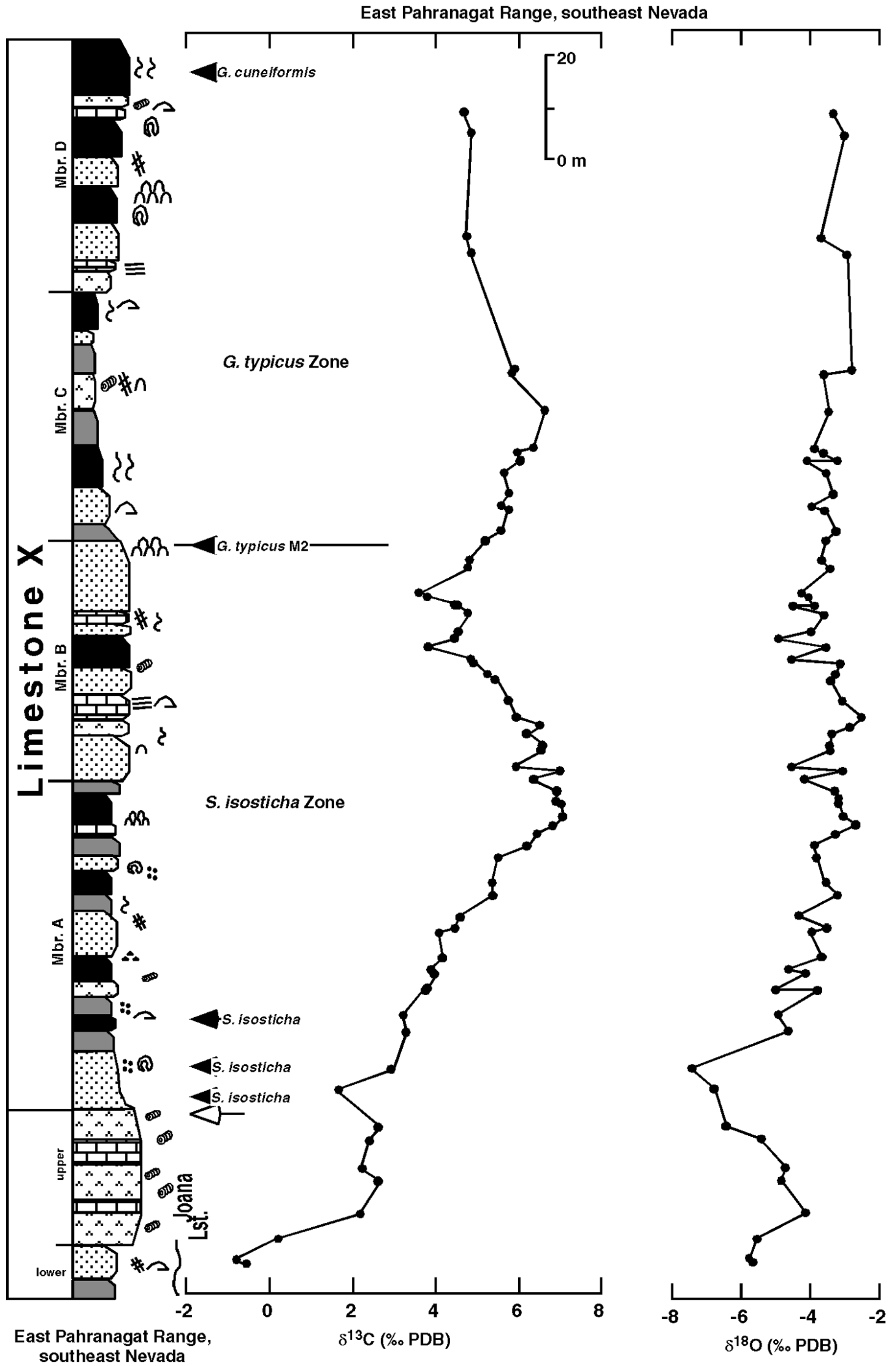

Figure 6. Lithologic column and δ^{13}C and δ^{18}O results from the Pahranagat Range, southeastern Nevada (Fig. 2). Boundary between *isosticha* and *typicus* Zones based on diagnostic conodont collections from Limestone X documented in Singler (1987). See Figure 5 for stratigraphic legend.

oolitic grainstones) do not preserve evidence of subaerial exposure, such as pedogenic features (sandy, oxidization crusts), karstic weathering (solution-enlarged joints and pits), fenestrae, mud cracks, or evaporite deposition (Allan and Matthews, 1982; Tucker and Wright, 1990; Algeo et al., 1992). The most prominent stratigraphic surfaces in the sections sampled, at the tops of the Joana Limestone in the Pahranagat Range and Crystal Pass Formation in the Arrow Canyon Range, are best described as marine flooding surfaces and locally show evidence for submarine hardground formation and condensation (conodont-rich marker horizon of Giles, 1996). These surfaces coincide with minor δ^{13}C shifts (<0.5‰) or no shift at all, inconsistent with prolonged exposure. The most distinct stratigraphic interval of lowered δ^{13}C values occurs near the top of Member B of Limestone X in the Pahranagat Range (Fig. 6) within rocks of the deep-ramp facies associations that are found throughout the section and are indicative of deposition below normal wave base. Similarly, the relatively low δ^{13}C values near the top of the Dawn Limestone in the Arrow Canyon Range occur within wackestone and packstone lithologies that show no evidence of exposure. More generally, the relatively smooth anatomy of the trends of decreasing δ^{13}C values over tens of meters of section, as shown in Figures 5–7, do not appear consistent with episodes of subaerial exposure, which are typically marked by short-lived δ^{13}C shifts (on the order of meters leading up to exposure surfaces) that produce abrupt breaks in the δ^{13}C trend (Allan and Matthews, 1982; Algeo et al., 1992).

An additional line of evidence that would seem to argue for the primary nature of δ^{13}C shifts seen in this study is based on estimates of the δ^{13}C value of normal Early Mississippian seawater. In order for the large δ^{13}C shifts in southeast Idaho and Nevada (Figs. 5–7) to be attributed entirely to the effects of meteoric diagenesis, one would need to argue that normal Mississippian seawater was near +7‰. This conclusion appears to be inconsistent with published δ^{13}C values for Mississippian seawater of ≤+4‰ (Brand, 1982; Meyers and Lohmann, 1985; Popp et al., 1986; Mii et al., 1999). Values of δ^{13}C as high as +7‰ are very rarely encountered in Phanerozoic limestones and occur exclusively at the peaks of similar positive δ^{13}C excursions during the Late Ordovician (Kump et al., 1999; Finney et al., 1999) and Late Silurian (Azmy et al., 1998), reminiscent of the large δ^{13}C shifts in the Neoproterozoic (Knoll et al., 1986; Derry et al., 1992; Kaufman and Knoll, 1995; Grotzinger et al., 1995; Hoffman et al., 1998; Kennedy et al., 1998).

The interpretation of δ^{13}C trends in this paper as primary is also consistent with the increasing number of published studies in the Paleozoic and Precambrian that have reported similar δ^{13}C trends from widely separated stratigraphic sequences by using a range of carbonate components (Gao and Land, 1991; Ripperdan et al., 1992; Joachimski and Bug-

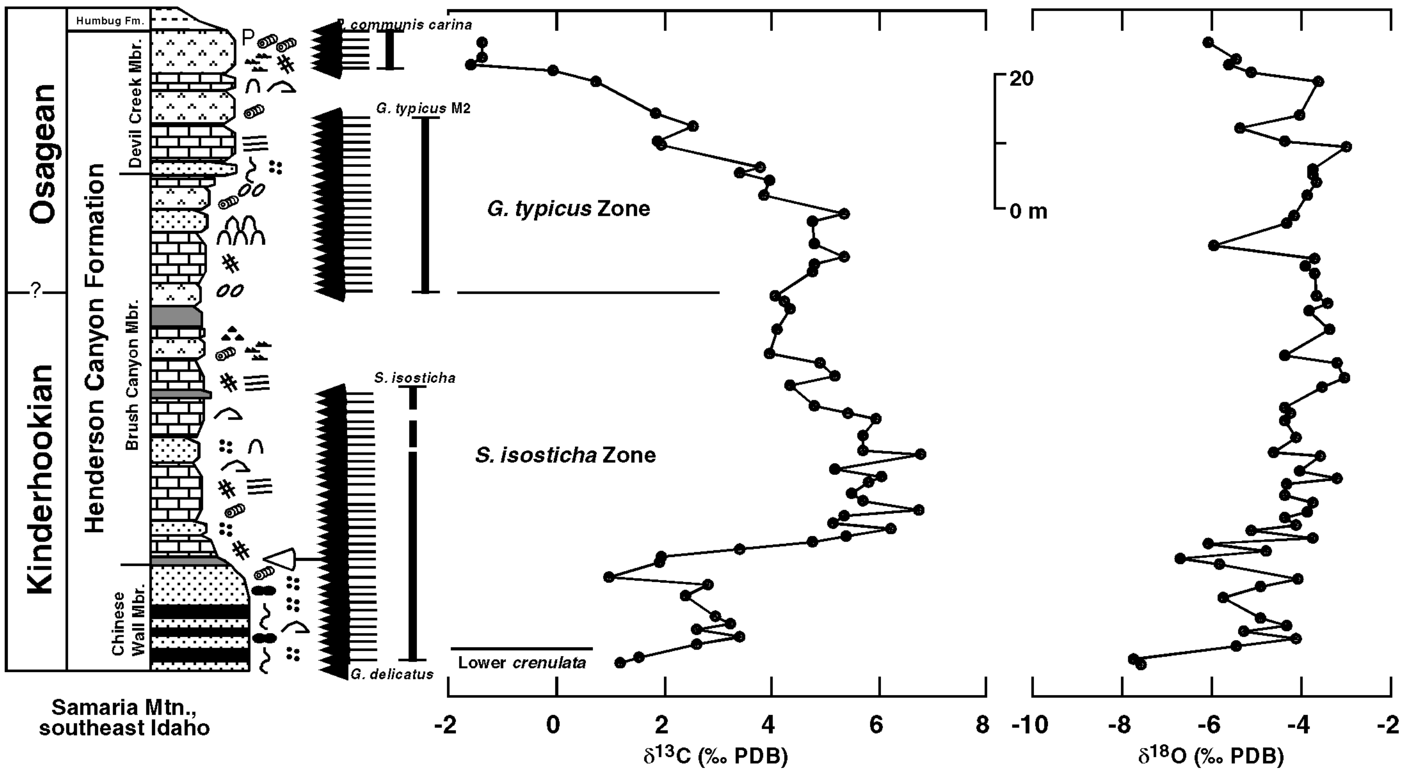

Figure 7. Lithologic column and $\delta^{13}C$ and $\delta^{18}O$ results from Samaria Mountain, southeastern Idaho (Fig. 2). Boundary between *isosticha* and *typicus* Zones based on diagnostic conodont collections from the Henderson Canyon Formation in Wickwire et al. (1985) and Chen et al. (1994). See Figure 5 for stratigraphic legend.

gisch, 1993; Saltzman et al., 1995, 1998, 2000a; Pelechaty et al., 1996; Wang et al., 1996; Kaljo et al., 1997; Patzkowsky et al., 1997; Glumac and Walker, 1998; Saylor et al., 1998; Kump et al., 1999), including marine cements (Carpenter and Lohmann, 1997) and brachiopod calcite (Marshall et al., 1997; Azmy et al., 1998). It is particularly encouraging that comparisons of $\delta^{13}C$ curves generated from brachiopod calcite and micrites yield similar trends not only for the Mississippian, but for the Ordovician and Silurian as well. For example, in the Ordovician of North America (Finney et al., 1999; Kump et al., 1999) and the Silurian of Europe (Kaljo et al., 1997; Wigforss-Lange, 1999) and North America (Saltzman, 2001), essentially bulk-rock analyses of micritic limestones faithfully record several of the major positive $\delta^{13}C$ excursions that have been recognized in brachiopod calcite worldwide (Wenzel and Joachimski, 1996; Marshall et al., 1997; Bickert et al., 1997; Azmy et al., 1998).

Oxygen Isotopes

In contrast to $\delta^{13}C$, $\delta^{18}O$ values are commonly not presented in chemostratigraphic studies of ancient limestones (e.g., Ripperdan et al., 1992; Kennedy et al., 1998), in part because water-rock modeling and empirical studies have shown that the $\delta^{18}O$ signature can be overprinted by even small pore volumes of meteoric diagenetic fluids even where the $\delta^{13}C$ signature is preserved (Banner and Hanson, 1990; Carpenter and Lohmann, 1997). Values of $\delta^{18}O$ that have been presented for Paleozoic micritic or bulk-rock limestones often show no trend when plotted against major $\delta^{13}C$ excursions (Saltzman et al., 1998; Kump et al., 1999), consistent with modeling predictions. However, recent work on Paleozoic brachiopods has consistently provided evidence for substantial positive shifts in $\delta^{18}O$ values associated with large positive $\delta^{13}C$ excursions in the Ordovician (Brenchley et al., 1994; Marshall et al., 1997), Silurian (Wenzel and Joachimski, 1996; Bickert et al., 1997; Azmy et al., 1998), and Mississippian (Bruckschen et al., 1999; Mii et al., 1999). Although the presence of covariant $\delta^{18}O$ and $\delta^{13}C$ trends has been traditionally associated with meteoric diagenesis in that the more negative values represent samples stabilized in meteoric waters that had less ^{18}O and contained ^{12}C from respiration of subaerial vegetation (Hudson, 1977; Allan and Matthews, 1982; Lohmann, 1988), Paleozoic brachiopod workers have viewed these same trends as indicators of global shifts in biogeochemical cycling. Specifically, when considered in a geologic framework that includes evidence of glaciation, positive covariance is taken to indicate episodes of enhanced burial of ^{12}C-enriched organic matter; such episodes result in drawdown of atmospheric CO_2 and global cooling (see also discussion of covariant stable isotope trends in Marshall, 1992; Veizer et al., 1999).

The $\delta^{18}O$ profiles in all three Lower Mississippian sections in Figures 5–7 show trends toward more positive values up section in the upper Kinderhookian, paralleling positive trends in $\delta^{13}C$ and showing a covariant relationship (Tables DR1–DR3 [see footnote 1]) as already discussed. The positive shift in $\delta^{18}O$ is best displayed in the Arrow Canyon Range section where values change from −6‰ in the lower part of the Dawn Limestone to −3‰ in the middle part of the Dawn, whereas over the same interval, the carbon changes from +4 to +7‰. The $\delta^{18}O$ values begin to decline again in the upper part of the Dawn Limestone, again in step with $\delta^{13}C$ (Fig. 5). The trends in $\delta^{18}O$ show important similarities with trends derived from studies of time-equivalent brachiopod calcite. The $\delta^{18}O$ results in Bruckschen et al.'s (1999) brachiopod calcite study show a transition from values of <–6‰ to more positive values in the late Kinderhookian (Tournaisian CI to CII transition in their Fig. 9), and Mii et al.'s (1999) $\delta^{18}O$ values change from near −5‰ (although these low values from the Glen Park Formation did not meet strict preservation criteria) to −1‰ over the same time interval (D-CI transition in their Figs. 6 and 8). Differences in the magnitude of the $\delta^{18}O$ shifts during the late Kinderhookian in these different studies could be due to biostratigraphic uncertainty, local seawater variability, or species or diagenetic effects. On the basis of the available data, it seems likely that at least the most negative $\delta^{18}O$ values in the lowermost parts of the three sampled sections represent signatures of burial (high-temperature) diagenesis. An entirely diagenetic interpretation of the remainder of the $\delta^{18}O$ trends presented in this paper must remain an open question pending (1) further study of the diagenetic pathways of the lithologies sampled and (2) comparison with published trends generated from well-preserved brachiopods or calcite cements.

In summary, it is viewed as encouraging that the changes in $\delta^{13}C$ and $\delta^{18}O$ values recorded in this study (Figs. 5–7) show important similarities with published curves generated by using distinctly different sampling strategies, including (1) microsampling of replacive dolomite, crinoidal calcite, calcite cement, and dolomite cement from the shelf-margin facies of the Madison Group in Wyoming and Utah by Budai et al. (1987) and (2) the isolation of petrographically well-preserved brachiopod calcite in the U.S. Midcontinent (Mii et al., 1999) and western Europe (Bruckschen and Veizer, 1997; Bruckschen et al., 1999). The remaining section focuses on the correlation of $\delta^{13}C$ shifts (Fig. 8) with important biostratigraphic and sequence stratigraphic boundaries.

Mississippian Biostratigraphy and $\delta^{13}C$

Making the assumption that the large shifts in $\delta^{13}C$ identified in this and other studies in North America and Europe (Fig. 9) are reflective of primary seawater values, an important question arises as to the relative synchroneity of the shifts in the different oceanic basins. Conodont biostratigraphy has been used widely in the correlation of Lower Mississippian depositional successions: the global standard *Siphonodella* (Sandberg et al., 1978) and post-*Siphonodella* zonations (Lane et al., 1980) subdivide the Kinderhookian and Osagean Provincial Series, respectively. The conodont biostratigraphy at Samaria Mountain (Fig. 7) is the most intensively studied, and the boundaries of the *isosticha* and *typicus* zones have been documented by Wickwire et al. (1985) and Chen et al. (1994). The initial $\delta^{13}C$ peak (>+6‰) at Samaria Mountain occurs within the boundaries of the *isosticha* Zone, marked by collections containing *G. delicatus* and *G. typicus* M2, at 1 m and 60 m above the base of the Henderson Canyon Formation, respectively; and the second peak (>+5‰) is within the *typicus* Zone. The minimum in $\delta^{13}C$ between the peaks is poorly dated owing to a sparsely fossiliferous nondiagnostic interval that characterizes the 15 m of section below the first occurrence of *G. typicus* M2, precluding a precise location of the Kinderhookian-Osagean boundary within the Brush Canyon Member of the Henderson Canyon Formation (Fig. 7). The ages of the inflections in the $\delta^{13}C$ curves for the Pahranagat and Arrow Canyon sections are also consistent with peaks in the *isosticha* and *typicus* Zones (Fig. 8), as argued subsequently.

In the Pahranagat Range, evidence for which part of the $\delta^{13}C$ curve occupies the *isosticha* Zone is based on (1) six collections containing specimens of *S. isosticha* in the lower 55 m of Limestone X and (2) two collections containing specimens of *G. typicus* M2 from horizons at 100 and 126 m above the base of Limestone X (Singler, 1987). The initial $\delta^{13}C$ peak (+7‰) lies at 55–60 m above the base of Limestone X (Fig. 6) and cannot be older than the *isosticha* Zone. Although specimens of *G. delicatus*, the defining species for the *S. isosticha* Zone (*S. isosticha* itself ranges into the early *crenulata* Zone), were not recovered, an early *crenulata* Zone age for the initial $\delta^{13}C$ peak is precluded by two factors: (1) the general lack of conodont diversity (Sandberg et al., 1978; Ziegler and Lane, 1987) and (2) the recognition that the early *crenulata* Zone is everywhere represented by a very thin interval (averaging ~3 m in thickness), which has been recovered only from the basal beds of the Paine Member of the Lodgepole Limestone and from lag deposits in the underlying Cottonwood Canyon Member (Klapper, 1966; Sandberg, 1979). The younger $\delta^{13}C$ peak (>+6‰) in the Member C of Limestone X is above specimens containing *G. typicus* M2 and thus lies within the *typicus* Zone (Fig. 6), as seen at Samaria Mountain (Fig. 7). In both the Pahranagat and Samaria Mountain sections, the minimum in the $\delta^{13}C$ curve between the two peaks is poorly dated because of an interval yielding only long-ranging, undiagnostic conodont taxa.

Although conodont collections containing specimens of *Siphonodella* are not known from the Arrow Canyon Range, similar arguments based on zonal thickness and the recovery of important collections containing *P. communis carina* from the lower part of the Anchor Limestone (Pierce and Langenheim, 1974) place the +7% $\delta^{13}C$ peak within the *isosticha* Zone (Fig. 5). This age is further supported by a sample containing *G. delicatus* near the top of the Dawn Limestone (Goebel, 1991) and is consistent with the conodont zonation presented in Poole and Sandberg (1991). Further study will be necessary to better locate the position of the Kinderhookian-Osagean boundary in the Arrow Canyon Range, and the zonal boundary drawn in Figure 5 must be considered tentative.

Mississippian Sequence Stratigraphy and $\delta^{13}C$

The correlation between the late Kinderhookian $\delta^{13}C$ excursion (Fig. 8) and sea-level change is important in gaining a better understanding of potential controls on Early Mississippian carbon cycling, particularly in regards to the possible causal connection between decreased atmospheric carbon dioxide contents (and concomitant high $\delta^{13}C$), and the onset of ice buildup in Gondwana (Mii et al., 1999). Comparison of relative sea-level curves between sections in the western and Midcontinent regions of North America may provide one of the more reliable tests of Early Mississippian eustasy available because the regions have been reasonably well correlated with each other through the use of conodont biostratigraphy but occur in distinctly different paleotectonic settings. In the Pahranagat Range in Nevada, a significant sequence boundary occurs at the top of the Joana Limestone (Fig. 6) and marks a regional shift from progradational to retrogradational parasequence sets (sequence 1–sequence 2 boundary of Giles, 1996; equivalent to the Morris-Sadlick sequence boundary of Silberling et al., 1997). This sequence boundary occurs within the *isosticha* Zone, near the beginning of the rising limb of the $\delta^{13}C$ peak, and has been interpreted by Giles (1996) as a tectonically forced retrogradation resulting from flexural subsidence in the distal Antler foreland basin. The possibility that this boundary was enhanced by a eustatic rise is supported by correlation with a significant cycle boundary in the Midcontinent (the base of the Chouteau Limestone in Illinois, equivalent to the base of cycle 3, Witzke and Bunker, 1996), as well as sections in western Europe and Russia

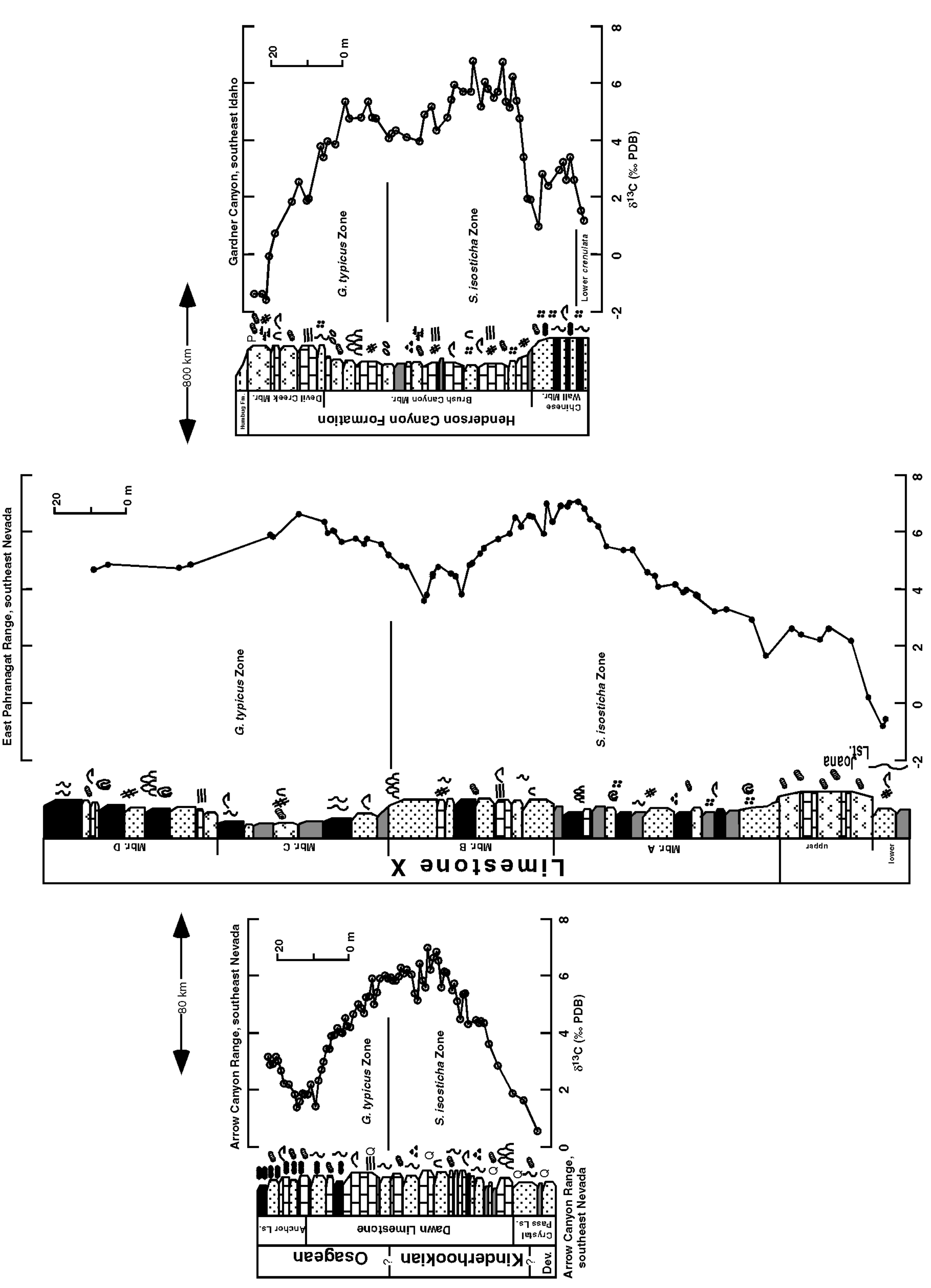

Figure 8. $\delta^{13}C$ **stratigraphy for the three sections examined in southeast Idaho and Nevada. Curves are aligned by peaks within individual conodont zones.**

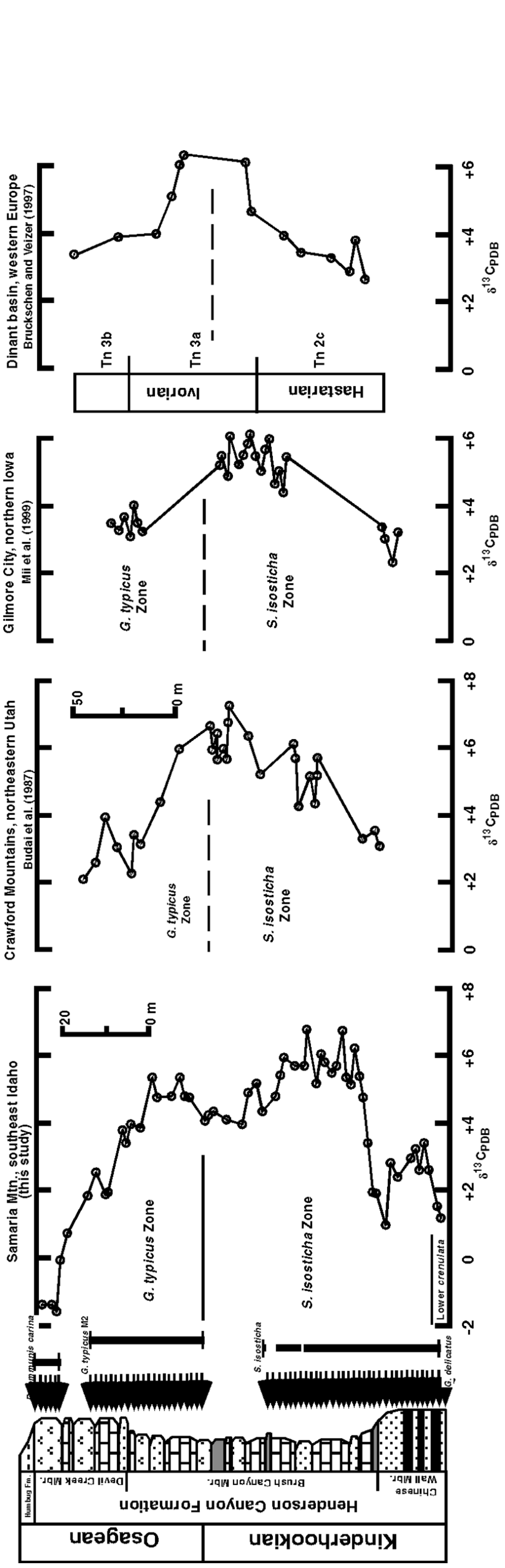

Figure 9. $\delta^{13}C$ results from Samaria Mountain, southeastern Idaho, plotted against time-equivalent data sets from Iowa (Gilmore City Formation; Mii et al., 1999), Utah (Lodgepole Limestone; Budai et al., 1987), and the Dinant basin of Belgium (Bruckschen and Veizer, 1997) (locations shown in Fig. 1). Line of correlation is the top of the *S. isosticha* Zone. Nevada and Utah data sets are essentially bulk-rock analyses, whereas Iowa and Belgium data sets represent brachiopod calcite. No scale is given for Iowa and Belgium data sets, and a measured section can only be approximated from composite-section information in Mii et al. (1999) and Bruckschen and Veizer (1997).

(Ross and Ross, 1988). This eustatic rise may have contributed to the onset of the $\delta^{13}C$ excursion through enhanced burial of organic carbon in deep, stratified foreland basins (Saltzman et al., 2000b).

The most prominent sequence boundary in the Lower Mississippian occurs at the Kinderhookian-Osagean boundary in the Midcontinent region (the top of the Chouteau and Wassonville Limestones in southeast Iowa and the base of cycle 4, Witzke and Bunker, 1996); this sequence boundary coincides with the $\delta^{13}C$ peak in the western United States. This sequence boundary has also been recognized by Lane (1978) and Ross and Ross (1988) (see Fig. 10) in time-equivalent sections in New Mexico, western Europe (Tn2-Tn3 boundary) and Russia (top Cherepetian), although it is not consistently expressed in southeast Idaho or Nevada (Giles, 1996). A shallowing event at the Kinderhookian-Osagean boundary is recognized in the Pahranagat Range by a coral-rich zone in Limestone X (Fig. 6); however, this relative fall is not apparent at equivalent levels in the Arrow Canyon Range or at Samaria Mountain. The degree of tectonic overprinting of the eustatic signature in these western sections, related to changes in the rates of subsidence of the foreland basin or uplift at the forebulge (Chen et al., 1994; Giles, 1996; Link et al., 1996), is difficult to assess. The Sr isotope curve of Bruckschen et al. (1995) indicates a shift to more radiogenic ratios near the Kinderhookian-Osagean boundary (superimposed on a longer term decline) that could reflect increased continental weathering during sea-level fall (Fig. 10); however, as Bruckschen et al. (1995) have pointed out, tighter biostratigraphic controls will be necessary in attempts to evaluate the significance of Sr isotope ratios in the context of Tournaisian paleoceanography. Future sequence stratigraphic studies that integrate chemostratigraphy and biostratigraphic means of correlation will be needed to shed light on the significance of the major sequence boundary (glacio-eustatic?) at the boundary between the Kinderhookian Provincial Series and the Osagean Provincial Series in the Midcontinent region of the United States and its relationship to the large positive shift in $\delta^{13}C$ at time-equivalent levels in the western United States.

CONCLUSIONS

Three Lower Mississippian (Kinderhookian and lower Osagean) stratigraphic sections representative of different paleotectonic and paleogeographic settings in the western United States show similar trends in both $\delta^{13}C$ and

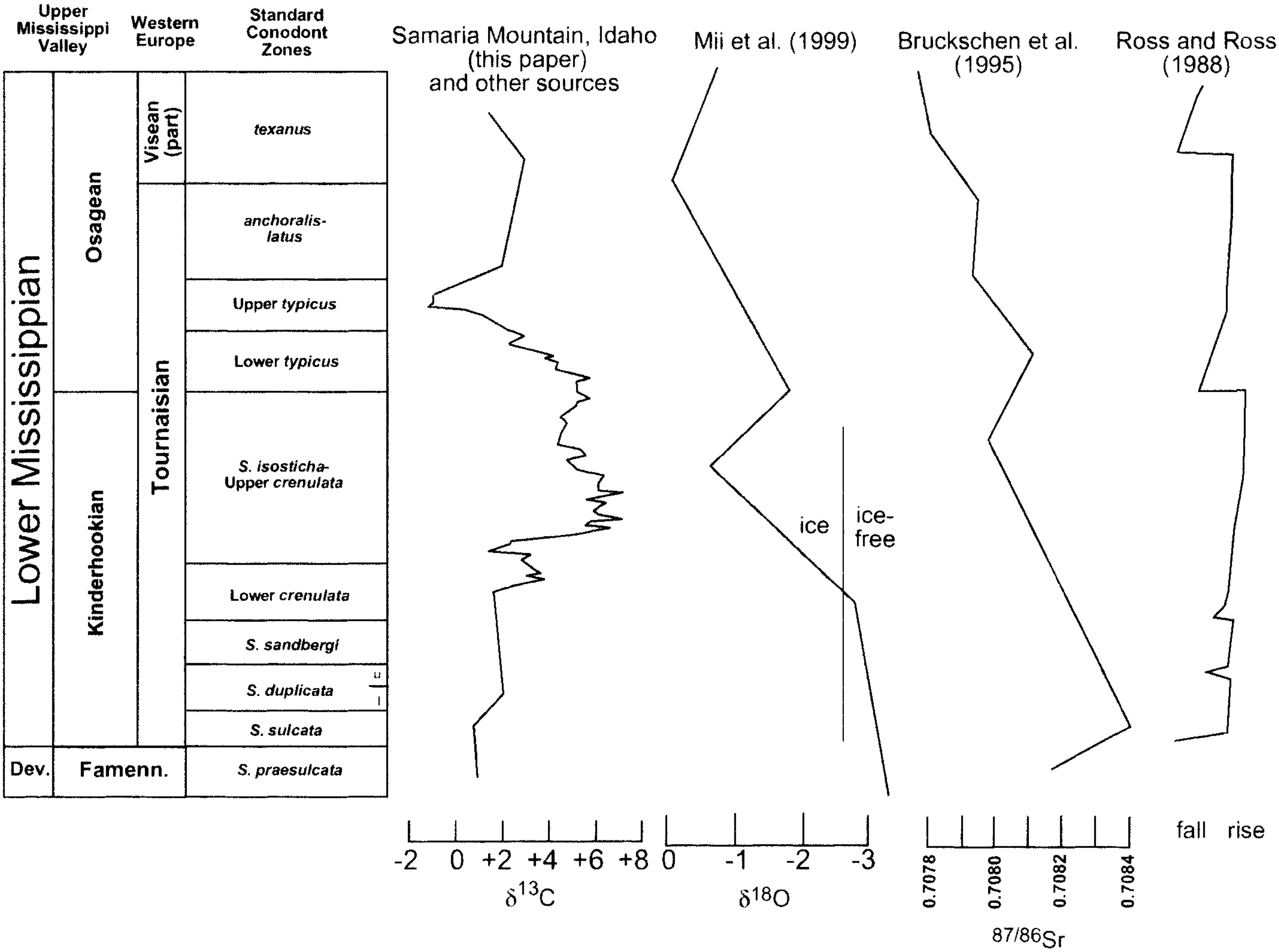

Figure 10. Stratigraphic nomenclature for North America and Europe plotted against trends in $\delta^{13}C$, $\delta^{18}O$, Sr isotopes, and sea level. $\delta^{13}C$ curve is a composite from this study and the work of Budai et al. (1987) and Mii et al. (1999). Note $\delta^{13}C$ and $\delta^{18}O$ covariation as well as the sea-level change near the $\delta^{13}C$ peak at the Kinderhookian-Osagean boundary. Also, note Sr shift to more radiogenic ratios near the Kinderhookian-Osagean boundary (superimposed on a longer term decline), which could reflect enhanced continental weathering during sea-level fall.

$\delta^{18}O$ values. Biostratigraphic correlation using the standard North American conodont zonation indicates synchroneity of two closely spaced $\delta^{13}C$ peaks $>+7‰$ in the late Kinderhookian *isosticha* conodont zone and the early Osagean *typicus* Zone. The $\delta^{13}C$ shifts could reflect meteoric diagenesis; however, the sections examined in southeast Idaho and Nevada lack evidence of exposure surfaces (or alteration by ground water in phreatic zones). Furthermore, the shifts have also been recognized in well-preserved brachiopods from western Europe and the Midcontinent region of North America. The cause of the $\delta^{13}C$ shift is uncertain, but may involve a significant amount of organic carbon burial in deep-marine basins associated with subsidence during the Antler orogeny and eustatic rise. A significant fall in sea level occurred in the Midcontinent of North America, near the peak of the $\delta^{13}C$ excursion in the western United States (Kinderhookian-Osagean boundary) and could reflect glaciation. However, this sea-level event is not recognized in western United States because tectonic changes associated with the Antler orogeny have likely modified the eustatic signature. The primary versus secondary nature of the positive $\delta^{18}O$ shifts associated with the $\delta^{13}C$ excursion is unclear at this time and requires further evaluation.

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