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RECORD OF THE LATE DEVONIAN HANGENBERG GLOBAL POSITIVE CARBON-ISOTOPE EXCURSION IN AN EPEIRIC SEA SETTING: CARBONATE PRODUCTION, ORGANIC-CARBON BURIAL AND PALEOCEANOGRAPHY DURING THE LATE FAMENNIAN

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ABSTRACT

Latest Famennian marine carbonates from the mid-continent of North America were examined to investigate the Late Devonian (very late Famennian) Hangenberg positive carbon-isotope ($\delta^{13}C_{carb}$) excursion. This global shift in the $\delta^{13}C$ of marine waters began during the late Famennian Hangenberg Extinction Event that occurred during the Middle *Siphonodella praesulcata* conodont zone. The post-extinction recovery interval spans the Upper *S. praesulcata* Zone immediately below the Devonian–Carboniferous boundary. Positive excursions in $\delta^{13}C_{carb}$ are often attributed to the widespread deposition of organic-rich black shales in epeiric sea settings. The Hangenberg $\delta^{13}C_{carb}$ excursion documented in the Louisiana Limestone in this study shows the opposite trend, with peak $\delta^{13}C_{carb}$ values corresponding to carbonate production in the U.S. mid-continent during the highstand phase of the very late Famennian post-glacial sea level rise. Our data indicate that the interval of widespread black shale deposition (Hangenberg Black Shale) predates the peak isotope values of the Hangenberg $\delta^{13}C_{carb}$ excursion and that peak values of the Hangenberg excursion in Missouri are not coincident with and cannot be accounted for by high C_{org} burial in epeiric seas. We suggest instead that sequestration and burial of C_{org} in the deep oceans drove the peak interval of the $\delta^{13}C_{carb}$ excursion, as a result of a change in the site of deep water formation to low-latitude epeiric seas as the global climate shifted between cold and warm states.

RESUME

On a examiné des roches marines carbonatées du Famennien le plus tardif du mi-continent de l'Amérique du Nord pour étudier l'excursion positive de Hangenberg de l'isotope du carbone ($\delta^{13}C_{carb}$) du Devonien (Famennien le plus tardif). Ce déplacement global en $\delta^{13}C$ d'eaux marines a commencé pendant l'Evénement d'Extinction Hangenberg du Famennien supérieur, qui a eu lieu dans la Zone Moyenne de conodonts *Siphonodella praesulcata*. L'intervalle de rétablissement après l'extinction traverse la Zone Supérieure de *S. praesulcata*, directement au-dessous de la bordure du Devonien–Carbonifère. On attribue souvent des excursions positives de $\delta^{13}C_{carb}$ au grand dépôt de schistes noirs riches en organismes dans les mers épicontinentales. L'excursion de Hangenberg de $\delta^{13}C_{carb}$ qu'on voit dans le Calcaire de Louisiana au Missouri montre la tendance opposée, avec des valeurs maximales de $\delta^{13}C_{carb}$ correspondant à la production carbonatée dans le mi-continent des Etats-Unis pendant le haut niveau marin de la montée postglaciaire du Famennien le plus tardif. Nos données mettent en évidence que l'intervalle du dépôt étendu de schiste noir (Schiste Noir Hangenberg) s'est passée avant les plus hatues valeurs de l'excursion, qui, dans le Calcaire de Louisiana, ne sont pas coïncidentes avec et ne peuvent pas être expliquées par un grand enterrement de C_{org} dans des mers épicontinentales. Nous suggérons plûtot que la réduction et l'enterrement de C_{org} dans les océans profonds a poussé l'excursion de $\delta^{13}C_{carb}$, comme un résultat d'un changement du site de l'accumulation d'eau fonde à des mers épicontinentales de basse latitude, à mesure que le climat se changeait entre des états froids et des états chauds.

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INTRODUCTION

Models of transient positive carbon-isotope ($\delta^{13}C_{carb}$) excursions have centered on the importance of sequestration and burial of organic carbon (C_{org})as the driving mechanism (Arthur et al., 1987; Kump and Arthur, 1999). This common interpretation is based on the relatively large isotopic fractionation between dissolved inorganic carbon (DIC) in the oceans and organic matter produced during photosynthesis. This interpretation is also widely accepted due to the relatively fast response time of marine productivity and the "biological pump" (Hotinski et al., 2004) compared to changes in the riverine $\delta^{13}C$ input to the oceans (Kump et al., 1999). Increased C_{org} burial in the oceans (in shallow or deep waters) can be driven by oceanographic or tectonic factors that affect rates of primary productivity, sedimentation and microbial breakdown of organic matter (Sageman et al., 2003).

Several well known positive $\delta^{13}C_{carb}$ excursions in the Paleozoic have been found to occur during intervals of clean carbonate deposition rather than black shale deposition in epeiric sea environments (Bickert et al., 1997; Kump et al., 1999; Munnecke et al., 2003; Cramer and Saltzman, 2005). This is best demonstrated in the Silurian, where high-resolution biostratigraphic correlations demonstrate that the major positive $\delta^{13}C_{carb}$ excursions (Saltzman, 2001, 2002a; Calner et al., 2004) coincide with intervals of prolific reef development and expansion of carbonate platform environments in the low-mid latitudes (Brunton et al., 1998; Calner et al., 2004; Cramer and Saltzman, 2005; 2007).

Here, we present new carbon isotope data that permit a re-examination of the relationship of the latest Famennian Hangenberg $\delta^{13}C_{carb}$ excursion (Hangenberg Isotope Excursion, HIE) to epicontinental black-shale deposition as suggested by Brand et al. (2004). We conclude that the peak of the HIE post-dated widespread organic-rich black-shale deposition. We suggest that a shift in the site of deep-water formation to low latitudes drove an increase in global C_{org} burial in the deep oceans during the peak values of the HIE.

LATE FAMENNIAN HANGENBERG EXTINCTION VERSUS HANGENBERG CARBON-ISOTOPE EXCURSION

The Hangenberg Extinction Event (HE) and the Hangenberg $\delta^{13}C_{carb}$ Isotope Excursion (HIE) are distinct phenomena. Both the extinction interval and $\delta^{13}C_{carb}$ isotopic excursion are within the upper part of the upper Famennian (Fig. 1).

HANGENBERG EXTINCTION EVENT

The most extensive research on upper Famennian–Lower Carboniferous successions and the Hangenberg mass extinction event (HE) has been conducted on sections in Europe and North Africa in the context of the selection of the Devonian–Carboniferous boundary global stratotype section and point (GSSP) (Paproth and Streel, 1984; Walliser, 1984; 1996; Ziegler and Sandberg, 1984b; Flajs et al., 1988; Caplan and Bustin, 1996). The HE refers to the biotic crisis during the late Famennian as documented by major extinctions of ammonoid, conodont and trilobite faunas well below the Devonian–Carboniferous boundary. The HE is well-documented in Germany (and Europe and North Africa) by the near total extinction of ammonoid faunas of the *Wocklumeria sphaeroides* Zone (*Wocklumeria* genozone) at or just above the base of the overlying *Cymaclymenia nigra* Zone (*Cymaclymenia* genozone) within the Hangenberg Black Shale (Becker and House, 2000, p. 139, tables 3 and 4; Korn, 2000). The Hangenberg Black Shale (HBS) with *C. nigra* occurs entirely within the Middle *Siphonodella praesulcata* Zone (Fig. 1) and is overlain by grey silty Hangenberg Shale with nodular limestone (Stockum Limestone). The post-extinction interval of the Hangenberg Event is marked by the widespread appearance of survivors and recovery taxa in the silty Hangenberg Shale and Stockum Limestone that spans the Middle–Upper *S. praesulcata* zonal boundary and contains ammonoids of the lower part of the *Acutimitoceras* (*Stockumites*) *porsum* Zone (Becker and House, 2000).

As presently defined by Kaiser (2005), the "Hangenberg Event Interval" is recorded by deposits that span all of the latest Famennian Middle and Upper *S. praesulcata* conodont zones and extends into the earliest Carboniferous *S. sulcata* Zone (sensu Ziegler and Sandberg, 1984a). The most severe pulse of extinction took place during the Middle *S. praesulcata* Zone, coincident with the onset of deposition of the HBS in Germany and its equivalents in Austria, Italy, Spain and Morocco. The post-extinction recovery part of the HE extends well above the black shales (Kaiser, 2005).

HANGENBERG CARBON- ISOTOPE EXCURSION

Kaiser (2005) presented evidence of a positive $\delta^{13}C_{carb}$ excursion that began during the interval of the Hangenberg Extinction Event and HBS in the Middle *S. praesulcata* Zone and reached peak values approaching +4.0‰ during the Upper *S. praesulcata* Zone (Fig. 1). By contrast, Brand et al. (2004) indicated that peak $\delta^{13}C_{carb}$ values from brachiopod calcites (+4‰ to +7‰) are recorded during the Middle *S. praesulcata* Zone, then return to lower values of +1‰ in the Upper *S. praesulcata* Zone. Their data for the Middle *S. praesulcata* Zone are based on analyses of brachiopod calcites from the Louisiana Limestone of Missouri. The Brand et al. (2004, fig. 7) curve is therefore problematic in that the Louisiana Limestone is Upper (not Middle) *S. praesulcata* Zone in age (Figs. 1, 2), as demonstrated by conodont, trilobite and ammonoid faunas of the Louisiana Limestone (see below). Our data collected from the subsurface of southeastern Iowa

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and the type area of the Louisiana Limestone in northeastern Missouri are consistent with that of Kaiser et al. (2004) and Kaiser (2005) derived from studies of $\delta^{13}C_{carb}$ data from Austria, Italy, Germany, France, Spain and Morocco, which show peak $\delta^{13}C_{carb}$ values in the Upper *S. praesulcata* Zone.

GEOLOGICAL SETTING

Four Famennian sections were examined from the mid-continent of North America for $\delta^{13}C_{carb}$ stratigraphy (Figs. 2, 3). Deposition of the Louisiana Limestone took place in a cratonic basin setting (Iowa Basin) on the western flank of the Illinois Basin (Witzke, 1990; Day, 1996; Day et al., 1996). The Louisiana sections of this region provide one of the only known successions in the mid-continent of North America to study the latest Devonian in carbonate strata.

PALEOGEOGRAPHY

Paleogeographic reconstructions for the latest Devonian place the mid-continent of North America near 30° S latitude (Witzke, 1990; Scotese and McKerrow, 1990). The sections investigated in this study would likely have been within the southern sub-tropical high-pressure zone during the Famennian (Parrish, 1982; Parrish et al., 1983; Caplan and Bustin, 1999). The Devonian epeiric sea in the North American mid-continent (Fig. 3) occupied the deeper Illinois Basin while shallower water developed in the adjacent Iowa Basin in southeastern Iowa and northeastern Missouri (Bunker and Witzke, 1992; Day, 1996). The three outcrop sections in Missouri were deposited along the crest of a structural high, the Lincoln Fold. The only Devonian strata to be deposited on the crest of the Lincoln fold are Famennian in age.

REGIONAL STRATIGRAPHY AND BIOSTRATIGRAPHY

Middle and Late Famennian deposits exposed in surface sections in the study area are included in three stratigraphic units that overlay a major regional unconformity developed on Silurian, Givetian (middle Devonian) or younger middle Famennian (Late Devonian) deposits (Fig. 2). These are in ascending order the Grassy Creek Shale (fissile black shale), the Saverton Shale (grey calcareous siltstone) and

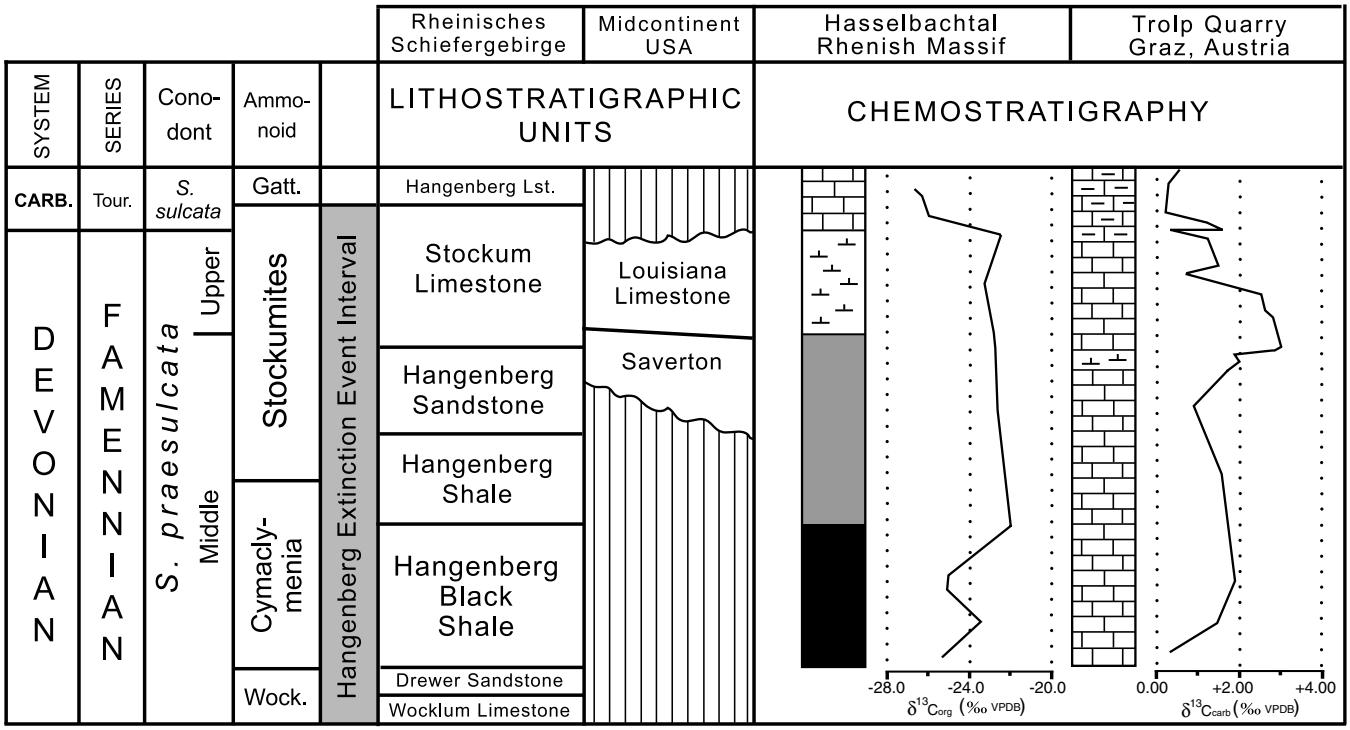

Figure 1. Correlation chart showing conodont (sensu Zeigler, 1984a) and ammonoid (sensu Becker and House, 2000) biostratigraphy of the upper Famennian shown with the lithostratigraphic units discussed herein. The grey bar at left depicts the entirety of the Hangenberg Extinction Event as defined by Kaiser (2005). $\delta^{13}C$ data are from Kaiser (2005). Abbreviations are: Carb-Carboniferous; Tour=Tournaisian; Gatt=*Gattendorfia*; Wock=*Wocklumeria*.

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the Louisiana Limestone comprised of sub-lithographic carbonate mudstone, with thin shale interbeds and one or two very thin skeletal packstones in the lower one-to-two metres.

In our surface sections, the Grassy Creek Shale and Saverton shales are separated from the overlying Louisiana Limestone by a pronounced disconformity (Fig. 2). The Grassy Creek consists of organic-rich black shales, with common carbonized plant material, in northeastern Missouri (Ralls and Pike counties) that are up to 4 m thick and usually overlie Silurian dolomites or Middle Devonian carbonates of the Cedar Valley Group. Woodruff (1990) sampled the Grassy Creek (3.72 m thick) and Saverton Shale (17 cm thick) in the New Jersey Zinc DDH-04 core in Ralls County, approximately 10 km west of our outcrop sample localities. Woodruff (1990, p. 48) observed an erosional disconformity at the contact between the Grassy Creek and the overlying Saverton and recovered conodonts that indicate an age no younger than the Upper *Palmatolepis marginifera* Zone from his highest sample in the Grassy Creek (Woodruff, 1990, p. 41). Therefore the middle Famennian black shales of the Grassy Creek (Lower *P. marginifera* Zone) in the outcrop area in eastern Missouri are significantly older (eight conodont zones older) than the HBS (Figs. 1, 2).

The thin grey calcareous siltstone that lies between the Grassy Creek and Louisiana Limestone in the study area has been considered to be the highest strata of the Saverton Formation (Fig. 2), a lithostratigraphic unit with an age range spanning much of the late Famennian. Saverton Shale here refers to the grey calcareous siltstones between the Grassy Creek Shale and Louisiana Limestone in our surface localities in northeastern Missouri. At our surface localities, the contact between the Saverton and the Louisiana Limestone is gradational suggesting reworking of the upper Saverton Shale during the very late Famennian Louisiana Limestone transgression and onlap of the Lincoln Fold. Conodonts listed from the Louisiana Limestone in Branson (1944, p. 173) were considered by Chauffe and Nichols (1995) to have been collected from the Saverton immediately below the Louisiana. These conodonts were likely reworked based on correlations of the upper Grassy Creek with the Upper *P. marginifera* Zone based on Grassy Creek conodonts recovered in the nearby core studied by Woodruff (1990, p. 31, table 6, sample 23).

The H-28 core from the subsurface of Lee County in southeastern Iowa (Figs. 2, 3) features a relatively complete Famennian section (Witzke and Bunker, 2002, fig. 1). The late Famennian succession in the H-28 core consists of approximately six metres of siltstones of English River Formation, overlain by 20 m of the Louisiana Limestone. In Lee County of southeastern Iowa Pavlicek (1986) recovered shallow water conodonts from the English River Formation assigned to the informal *Polygnathus delicatulus* Zone in the H-29 core section (close to the H-28 core). Pavlicek (1986, fig. 4) provisionally aligned the *P. delicatulus* Zone within the late Famennian *Palmatolepis expansa* Zone below the Lower *Siphonodella praesulcata* Zone of the standard Famennian Zonation of Ziegler and Sandberg (1984a).

The Louisiana Limestone is latest Famennian (Upper *S. praesulcata* Zone) based on its conodont, ammonoid and trilobite faunas known from surface exposures in northeastern Missouri (Fig. 2). The first comprehensive description of the shelly faunas of the Louisiana Limestone was by Williams (1943). Conodont-based correlations of the Louisiana Limestone in the outcrop area of northeastern Missouri and western Illinois are discussed in Scott (1961), Scott and Collinson (1961), Klapper and Philip (1971), Klapper et al. (1971), Sandberg et al. (1972), Chauffe and Nichols (1995) and Feist and Petersen (1995). Scott (1961) and Scott and Collinson (1961) illustrated the bulk of the Louisiana conodont fauna and suggested a correlation of the Louisiana with the upper Famennian *Wocklumeria* Stufe of Germany based on the occurrence of species of form taxa assigned at that time to *Siphonodella*. Klapper et al. (1971) and Sandberg et al. (1972) indicated a latest Devonian age based on the occurrence of the conodont *Protognathodus kockeli* (Bischoff, 1957) illustrated by Scott and Collinson (1961) and later re-illustrated by Chauffe and Nichols (1995). The first occurrence of the aforementioned species defines the base of the latest Devonian Upper *S. praesulcata* Zone of Ziegler and Sandberg (1984a).

The trilobite *Pudoproetus missouriensis* (Shumard, 1855) is associated with the brachiopod, ammonoid and conodont faunas in the lower few metres of the Louisiana and its range is restricted to the Upper *S. praesulcata* Zone (Feist and Petersen 1995, fig. 3). Feist and Petersen (1995) further demonstrated that latest Famennian trilobites of the genus *Pudoproetus* survived the HE. House (1978) illustrated and reported the occurrence of *Acutimitoceras* (*Stockumites*) *louisianensis* (Rowley, 1895) in the Louisiana Limestone and this occurrence is correlated with the lower part of the global *Acutimitoceras* (*Stockumites*) genozone and the *Acutimitoceras* (*Stockumites*) *porsum* Zone of Germany, spanning the Upper *S. praesulcata* conodont Zone (Becker and House, 2000).

METHODS

Non-luminescent brachiopods have been traditionally considered to be the most reliable recorder of primary marine isotopic signatures for chemostratigraphic investigation of Paleozoic strata (e.g., Mii et al., 1999). Brand et al. (2004, fig. 7) published limited $\delta^{13}C$ data from brachiopod calcites collected from the Louisiana Limestone in our study area ranging from + 4‰ to + 7‰. Brachiopods suitable for such analyses in the Louisiana Limestone are limited to the lower 2–5 m of surface sections in eastern Missouri and western Illinois. Unfortunately, use of brachiopod calcites has limited applicability to sections or intervals where brachiopods are not

available for analysis. Continuous high resolution (<50,000 years) sampling for Paleozoic carbon isotope analysis can be accomplished using micrite as the primary carbonate source for $\delta^{13}C_{carb}$ analysis (e.g., Saltzman, 2005). Primary marine carbonates containing admixtures of micrite and select skeletal grains (i.e. crinoids and brachiopods) have been shown to faithfully record primary marine carbon isotopic values throughout the Paleozoic (Cambrian: Ripperdan et al., 1992; Saltzman et al., 1998; 2000; Ordovician: Finney et al., 1999; Kump et al., 1999; Silurian: Saltzman, 2001; Cramer and Saltzman, 2005; Devonian: Joachimski and Buggisch, 1993; Wang et al., 1996; and Mississippian: Saltzman, 2002b). Dolomitization has also been shown to have a negligible effect on overall $\delta^{13}C_{carb}$ trends (Glumac and Walker, 1998). Our $\delta^{13}C$ micrite data from the Louisiana (Figs. 4–7, Tables 1–4) are consistent with the brachiopod calcite data reported by Brand et al. (2004, fig. 7) from their site located between our Hotel Bluff and Bowling Green section localities (Fig. 3).

Carbonate samples were cut and polished before the powders were drilled from the pure micrites of the Louisiana Limestone and analyzed at the Saskatchewan Stable Isotope Laboratory, University of Saskatchewan. Carbonate samples were roasted in a vacuum oven at 200°C for 1 hour to remove water and volatile organic contaminants that may confound stable-isotope values of carbonate. Stable-isotope values were obtained using a Finnigan Kiel-III carbonate preparation device directly coupled to the dual inlet of a Finnigan MAT 253 isotope ratio mass spectrometer. 10–50 μg of carbonate were reacted at 70°C with 3–5 drops of anhydrous phosphoric acid for 180–300 seconds. Isotope ratios were corrected for acid fractionation and ^{17}O contribution and reported in per mille (‰) notation relative to the V-PDB standard. Precision and calibration of data were monitored through routine analysis of the IAEA NBS-19 standard. Standard deviations for $\delta^{13}C$ and $\delta^{18}O$ are 0.05‰ and 0.10‰, respectively (one sigma).

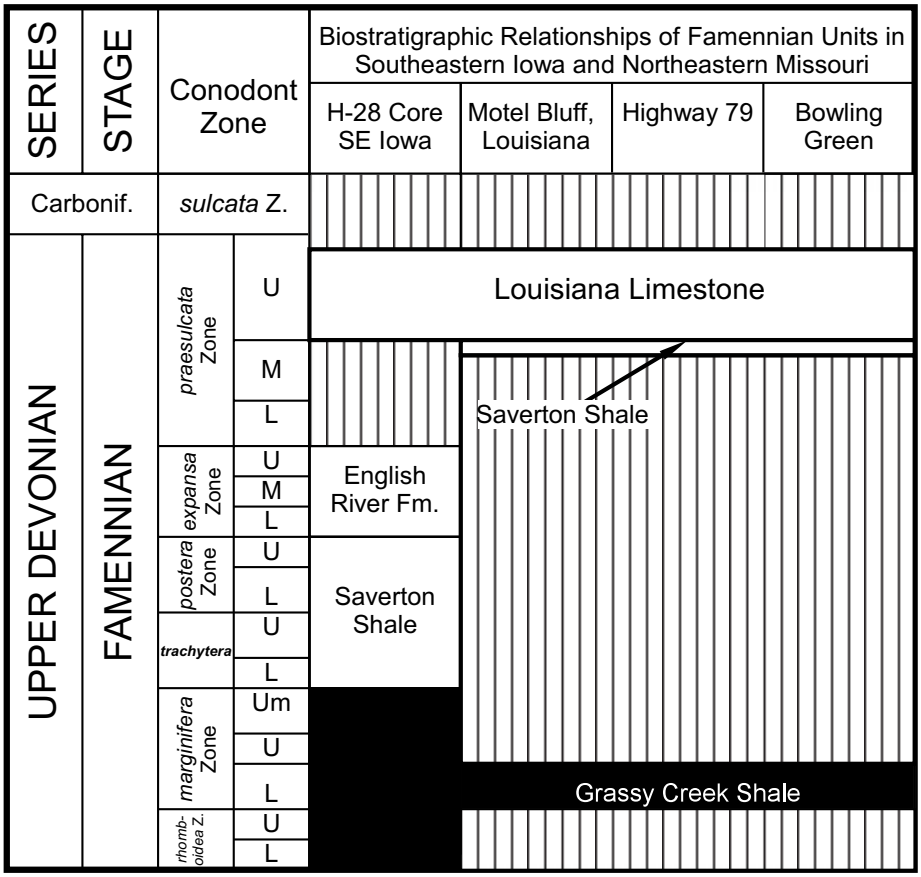

Figure 2. Chart showing biostratigraphic relationships of middle-upper Famennian lithostratigraphic units in the subsurface of Lee County of southeastern Iowa (H-28 core) and surface exposures in Ralls and Pike counties of northeastern Missouri. Conodont data from Scott (1961), Scott and Collinson (1961), Pavlicek (1986), Woodruff (1990), Chauffe and Nichols (1995). Famennian conodont zonation after Ziegler and Sandberg (1984a).

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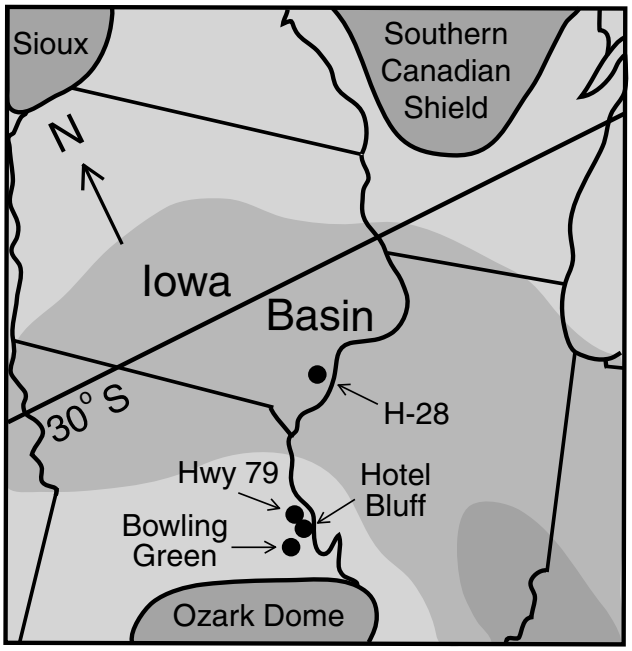

Figure 3. Paleogeographic and paleobathymetric reconstruction for the mid-continent of North America. Modified from Witzke (1990). Black dots indicate locations of sampled sections in southeast Iowa and northeast Missouri. The absolute size and location of emergent landmasses shown are speculative.

RESULTS

Of the four sections sampled from the Iowa Basin (Figs. 3–7; H-28 core from southeastern Iowa, three outcrops in northeastern Missouri) for carbon isotope analysis, the H-28 core represents the most complete section of the Louisiana Limestone studied. The three surface sections in Missouri (Figs. 3, 5–7) were targeted because of the following attributes: the Bowling Green section (Fig. 5) contains the "Louisiana Shell Bed" in the lower metre of the Louisiana as noted in older biostratigraphic literature; the Highway 79 section (Fig. 6) displays the contact with the underlying Saverton Shale; and the Hotel Bluff section (Fig. 7) is the main reference section of the Louisiana in its type area and is the thickest outcrop exposure of the Louisiana in eastern Missouri. The Bowling Green section (Fig. 5) is one of the only known sections where hummocky cross-stratification is observed (upper two-thirds of the outcrop) in the Louisiana in its type area.

H-28 CORE, LEE COUNTY, IOWA

Stable isotope data from the H-28 core in Lee County of southeastern Iowa (Fig. 4; Table 1) is the most complete section of the Louisiana Limestone sampled. Carbon isotope values of ~+4.0‰ are recorded at the base of the Louisiana in the H-28 core and immediately begin to rise, reaching a peak of +6.4‰ at 6.10 m above the base of the Louisiana (305 ft downcore) and $\delta^{13}C_{carb}$ values return to ~+4.0‰ at the top of the Louisiana (20.72 m). $\delta^{13}C_{carb}$ values remain relatively high (above +2.0‰) for several tens of metres above the end of the excursion (see Table 1). Consistently elevated $\delta^{13}C_{carb}$ baseline values (2–3‰) are a well known feature of both the late Famennian (Lower *P. expansa*–Middle *S. praesulcata* Zones; Kaiser, 2005) and the early Mississippian (e.g., Mii et al., 1999; Saltzman, 2002b; 2005).

BOWLING GREEN (HWY 61/HWY 54 INTERCHANGE), MISSOURI

The Bowling Green section (Fig. 5; see Thompson, 1993, p. 181) is located at the intersection of U.S. Highway 61 and U.S. Highway 54 in Bowling Green, Pike County, Missouri. It was sampled for conodont biostratigraphy for this investigation (J.D.) and yielded a low diversity conodont fauna with Pa and Pb elements of *Cryptotaxis culminidirecta* (Klapper and Philip, 1971) and Pa and S elements of *Polygnathus communis* (Branson and Mehl, 1934) from the thin (2–5cm) brachiopod-echinoderm skeletal grain/packstone bed 0.32 m above the base of the Louisiana. These two species also occur low in the Louisiana Limestone in western Illinois, just east and south of the type area in association with *P. kockeli*, whose first appearance defines the base of the Upper *S. praesulcata* zone. This fauna clearly indicates a latest Famennian age for the Louisiana consistent with earlier reports by Klapper et al. (1971) and Feist and Petersen (1995). Above the thin irregularly bedded carbonate skeletal mudstones and lower shell bed, the Louisiana at this outcrop is characterized by hummocky cross-stratification and increased clastic input at 0.62 m above the base of the outcrop, indicating shallowing from a deep sub-wavebase ramp to within storm wavebase.

$\delta^{13}C_{carb}$ data (Fig. 5; Table 2) record values of +3.4‰ at the base of the outcrop and increase to an initial high of +3.8‰ by 0.20 m above the base before falling to an intermediate low of +1.9‰ at 0.40 m. $\delta^{13}C_{carb}$ values begin to rise immediately and return to another peak of +4.3‰ at 1.10 m above the base of the section before returning to +0.8‰ at the top of the section (2.80 m).

HIGHWAY 79 ROADCUT, MISSOURI

The Highway 79 roadcut (see Thompson, 1993, p. 168) was chosen for this investigation due to the exposure of the contact of the Louisiana and underlying Saverton Shale near the base of the section (Fig. 6; Table 3). $\delta^{13}C_{carb}$ values of ~+4.0‰ characterize the Saverton–Louisiana contact, much like the values shown in the H-28 core. $\delta^{13}C_{carb}$ values are consistently elevated throughout the section with an initial peak of +5.6‰ at 3.25 m above the Saverton–Louisiana contact. The highest values are recorded in the upper part of the section, reaching

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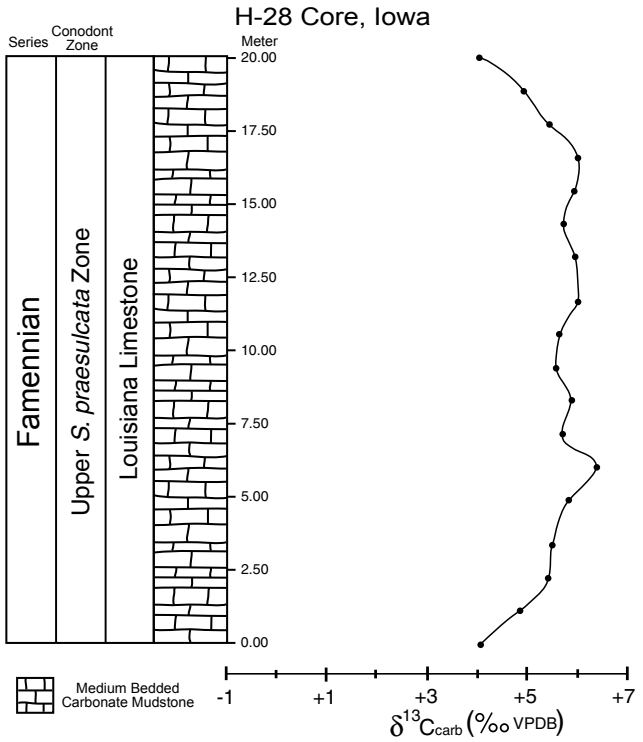

Figure 4. Carbon-isotope stratigraphy of the H-28 core from Lee County, southeast Iowa. The whole Louisiana Limesone was sampled as shown in Figure 2. The Hangenberg Excursion begins with high values. Numbers to the right of the column indicate metres above the sampling datum (base of the Louisiana Limestone).

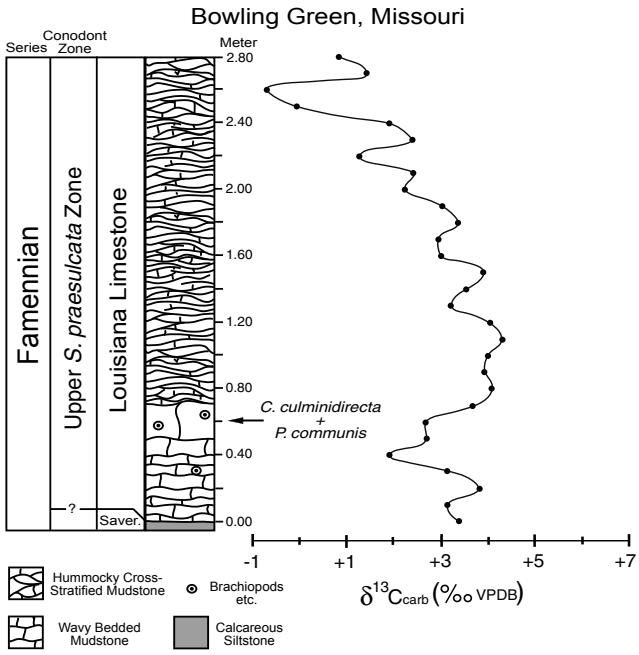

Figure 5. Carbon-isotope stratigraphy of the Bowling Green section, Bowling Green, Pike County, Missouri. Hummocky cross-stratification characterizes the upper Louisiana Limestone here. The echinoderm–brachiopod skeletal packstone in the lower Louisiana yielded conodonts diagnostic of the Upper *Siphonodella praesulcata* Zone. Numbers to the right of the column indicate metres above the sampling datum (lowest exposed Louisiana Limestone bed).

a high of +6.8‰ at 6.50 m. Values remain high through to the top of the outcrop (+6.7‰ at 8.00 m).

CHAMP CLARK BRIDGE BLUFF (HOTEL BLUFF), MISSOURI

The Hotel Bluff section is located just north of the Champ Clark Bridge over the Mississippi River in the town of Louisiana and is the type section of the Grassy Creek and Saverton Shales as re-designated by Thompson (1993, p. 166). This was designated as the principle reference section of the Louisiana Limestone in its type area (by Thompson, 1993) because the original type section is now almost entirely covered. Although this outcrop is one of the thickest sections of Louisiana exposed in the area, the outcrop is also overgrown and extremely difficult to sample in the upper portions without climbing equipment. The Louisiana section (Fig. 7; Table 4) is most similar to the Highway 79 section (Fig. 6) where the shell bed seen at Bowling Green is absent. Although the Saverton–Louisiana contact was not exposed in this section, the top of the Saverton is visible a few hundred metres down the road and falls at a position where our lowermost sample is within 50 cm of the base of the Louisiana. $\delta^{13}C_{carb}$ values are variable near the base of the Louisiana with values ranging between -0.7‰ and +4.0‰ over the first 2.5 m. Values stabilize upsection and a peak of +5.3‰ occurs at 5.50 m with elevated values continuing throughout the section. The uppermost sample in this section was immediately below a tree root in outcrop and highly altered in polished section calling into question the reliability of the $\delta^{13}C_{carb}$ value of -0.4‰ at the top of the section.

DISCUSSION

The Hangenberg $\delta^{13}C_{carb}$ excursion (HIE) shows a close correlation to changes in carbonate sedimentology throughout the mid-continent and elsewhere. We first discuss the series of events demonstrated by the stratigraphic sequence of the study area and their implications for the timing of Devonian global oceanographic events. We then discuss the HIE in the context of a paleoceanographic model developed for Silurian $\delta^{13}C_{carb}$ excursions.

CORRELATION AND TIMING OF LATE FAMENNIAN EVENTS

The type area of the Hangenberg Black Shale (HBS) in the Rhenish Massif (Rheinische Schiefergebirge, Germany;

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Table 1
Stable Isotope Data, H-28 Core, SE Iowa

ft. down core	meter*	$\delta^{13}C$	$\delta^{18}O$	Formation
199	37.34	2.97	-4.14	Dolbee Creek
201	36.73	3.14	-3.03	Dolbee Creek
203	36.12	3.13	-3.82	Dolbee Creek
205	35.51	3.05	-4.50	Dolbee Creek
207	34.90	3.26	-3.07	Dolbee Creek
209	34.29	3.11	-4.83	Dolbee Creek
210	33.99	3.00	-4.75	Dolbee Creek
210.5	33.68	3.52	-4.78	Wassonville
211	33.53	3.53	-4.82	Wassonville
215	32.31	3.22	-4.95	Wassonville
219	31.09	2.82	-4.72	Wassonville
223	29.87	3.01	-4.29	Starrs Cave
253	21.95			Prospect Hill
257	20.73	4.03	-5.07	Louisiana
261	19.51	4.89	-4.96	Louisiana
265	18.29	5.41	-5.05	Louisiana
269	17.07	5.96	-4.76	Louisiana
273	15.85	5.90	-4.82	Louisiana
277	14.63	5.71	-5.01	Louisiana
281	13.41	5.93	-5.04	Louisiana
285	12.19	5.99	-4.99	Louisiana
289	10.97	5.60	-5.39	Louisiana
293	9.75	5.55	-4.44	Louisiana
297	8.53	5.88	-4.58	Louisiana
301	7.32	5.67	-4.45	Louisiana
305	6.10	6.37	-4.59	Louisiana
309	4.88	5.79	-4.27	Louisiana
313	3.66	5.47	-4.80	Louisiana
317	2.44	5.38	-4.40	Louisiana
321	1.22	4.82	-4.51	Louisiana
325	0.00	4.05	-3.46	Louisiana

*Sampling datum is the base of the Louisiana Limestone

Table 2
Stable Isotope Data, Bowling Green, Missouri

meter*	$\delta^{13}C$	$\delta^{18}O$	Formation
2.80	0.84	-5.44	Louisiana
2.70	1.42	-5.61	Louisiana
2.60	-0.69	-5.33	Louisiana
2.50	-0.07	-5.29	Louisiana
2.40	1.91	-4.81	Louisiana
2.30	2.41	-4.38	Louisiana
2.20	1.28	-4.43	Louisiana
2.10	2.43	-4.54	Louisiana
2.00	2.25	-4.41	Louisiana
1.90	3.05	-4.32	Louisiana
1.80	3.38	-4.21	Louisiana
1.70	2.97	-4.49	Louisiana
1.60	3.02	-4.30	Louisiana
1.50	3.90	-3.86	Louisiana
1.40	3.55	-4.30	Louisiana
1.30	3.22	-4.22	Louisiana
1.20	4.05	-4.15	Louisiana
1.10	4.31	-3.97	Louisiana
1.00	4.00	-4.07	Louisiana
0.90	3.93	-4.11	Louisiana
0.80	4.08	-3.68	Louisiana
0.70	3.67	-4.09	Louisiana
0.60	2.68	-3.86	Louisiana
0.50	2.70	-3.95	Louisiana
0.40	1.92	-4.75	Louisiana
0.30	3.13	-4.04	Louisiana
0.20	3.82	-4.00	Louisiana
0.10	3.14	-3.69	Louisiana
0.00	3.38	-4.01	Louisiana

*Sampling datum is the base of the Louisiana

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Table 3
Stable Isotope Data, Highway 79, Missouri

meter*	$\delta^{13}C$	$\delta^{18}O$	Formation
8.00	6.65	-5.77	Louisiana
7.75	6.67	-5.62	Louisiana
7.50	3.93	-5.49	Louisiana
7.25	4.91	-5.57	Louisiana
7.00	6.81	-5.56	Louisiana
6.75	4.85	-5.79	Louisiana
6.50	6.84	-5.42	Louisiana
6.25	6.17	-5.30	Louisiana
6.00	3.48	-5.41	Louisiana
5.75	4.06	-5.29	Louisiana
5.50	4.29	-5.51	Louisiana
5.25	4.17	-5.24	Louisiana
5.00	4.62	-5.41	Louisiana
4.75	4.82	-5.47	Louisiana
4.50	4.48	-5.27	Louisiana
4.25	5.15	-5.58	Louisiana
4.00	5.18	-5.50	Louisiana
3.75	4.65	-5.41	Louisiana
3.50	4.98	-5.30	Louisiana
3.25	5.55	-5.23	Louisiana
3.00	5.34	-5.03	Louisiana
2.75	5.01	-5.08	Louisiana
2.50	5.22	-5.11	Louisiana
2.25	5.14	-5.42	Louisiana
2.00	4.90	-4.97	Louisiana
1.75	4.62	-4.98	Louisiana
1.50	5.49	-4.36	Louisiana
1.25	5.09	-4.95	Louisiana
1.00	4.77	-4.69	Louisiana
0.75	4.55	-4.53	Louisiana
0.50	4.69	-4.81	Louisiana
0.25	4.72	-4.65	Louisiana
0.00	3.62	-3.15	Louisiana
-0.08	3.90	-1.25	Saverton
-0.25	4.11	-0.82	Saverton
-0.55	3.93	-1.49	Saverton

*Sampling datum is the base of the Louisiana

Table 4
Stable Isotope Data, Hotel Bluff, Missouri

meter*	$\delta^{13}C$	$\delta^{18}O$	Formation
11.50	-0.42	-4.66	Louisiana
11.25	4.62	-4.49	Louisiana
11.00	4.76	-4.57	Louisiana
10.75	4.92	-4.58	Louisiana
10.50	4.74	-5.44	Louisiana
10.25	5.09	-4.74	Louisiana
9.25	4.95	-4.94	Louisiana
9.00	4.83	-4.81	Louisiana
8.75	4.66	-5.11	Louisiana
8.50	4.99	-4.83	Louisiana
8.00	3.59	-4.94	Louisiana
7.50	4.95	-4.91	Louisiana
7.00	3.23	-5.06	Louisiana
6.50	4.62	-5.74	Louisiana
6.00	4.98	-5.60	Louisiana
5.50	5.34	-5.83	Louisiana
5.00	5.22	-5.42	Louisiana
4.50	4.26	-5.91	Louisiana
4.00	4.04	-5.44	Louisiana
3.50	3.46	-5.33	Louisiana
3.00	4.23	-5.21	Louisiana
2.50	-0.62	-5.11	Louisiana
2.00	0.16	-5.08	Louisiana
1.50	2.64	-5.30	Louisiana
1.00	4.00	-5.40	Louisiana
0.75	-0.71	-5.31	Louisiana
0.50	1.66	-5.02	Louisiana
0.25	2.74	-5.07	Louisiana
0.00	2.47	-5.56	Louisiana

*Sampling datum is the lowest exposed Louisiana

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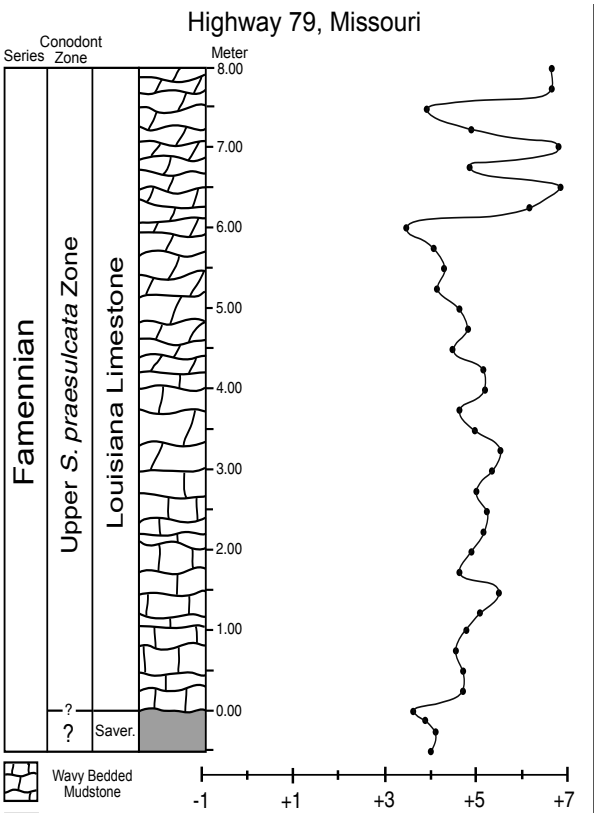

Figure 6. $\delta^{13}C_{carb}$ stratigraphy of the Highway 79 section, Ralls County, Missouri. This was the only section included in this investigation where the contact between the Saverton and Louisiana was well exposed. Sampling datum is the contact between these two units.

Walliser, 1984; 1996; Becker et al., 1993) contains organic-rich black shales only immediately above the Wocklum limestone (Fig. 1). The top of the Wocklum, which yields ammonoids of the *Wocklumeria sphaeroides* Zone, is no younger than the middle of the Middle *Siphonodella praesulcata* conodont zone (Ziegler and Sandberg, 1984a; Becker and House, 2000) and the organic-rich interval of the HBS ended prior to the first appearance of the *P. kockeli*, which delineates the base of the Upper *S. praesulcata* biozone. The base of the overlying grey silty Hangenberg Shale with nodules of the Stockum Limestone in the upper part, yields ammonoids of the lower part of the *Acutimitoceras* (*Stockumites*) *porsum* Zone (Becker and House, 2000).

The occurrence of *A.* (*S.*) *louisianensis* (Rowley, 1895) with the trilobite *Pudoproetus missouriensis* (Shumard, 1855) in the Louisiana Limestone (Williams, 1943, pl. 9) permit correlation of the rocks yielding these forms in central and eastern North America with the lower part of the *A.* (*S.*) *porsum* Zone in Germany (House, 1978, Becker and House, 2000). The conodont, trilobite and ammonoid occurrences discussed above indicate that the base of the Louisiana Limestone is no older than the Upper *S. praesulcata* conodont zone. Therefore, the organic rich black shale interval (HBS) found in Germany (Middle *S. praesulcata* Zone) is older than the Louisiana Limestone in the study area (Figs. 1, 2). The HBS of the Middle *S. praesulcata* Zone marks the onset of the latest Famennian interglacial sea level rise (Dreesen et al., 1988; Isaacson et al., 1999; Feist et al., 2000; Streel, 2003) and associated epeiric seaway eutrophication (Fig. 8).

Detailed $\delta^{13}C_{carb}$ stratigraphy has recently been returned for some of these classic European sections and indeed the onset of the excursion does occur within the HBS (Kaiser, 2005). However, only the very beginning of the rising limb of the HIE is recorded within the HBS, while the majority of the excursion is recorded in the overlying Hangenberg Shale and Stockum Limestone effectively ending at the base of the Carboniferous. A similar observation can be made for the stratigraphic sequence of the mid-continent where the expansion of carbonate deposition in the study area (Upper *S. praesulcata* Zone) is coincident with the peak values of the HIE.

The Devonian–Carboniferous boundary eustatic sea-level fall is recorded by the well documented erosional unconformity developed on top of the Louisiana Limestone (see Williams, 1943; Thompson, 1993), separating it from the overlying Lower Mississippian (Tournaisian) Hannibal Shale

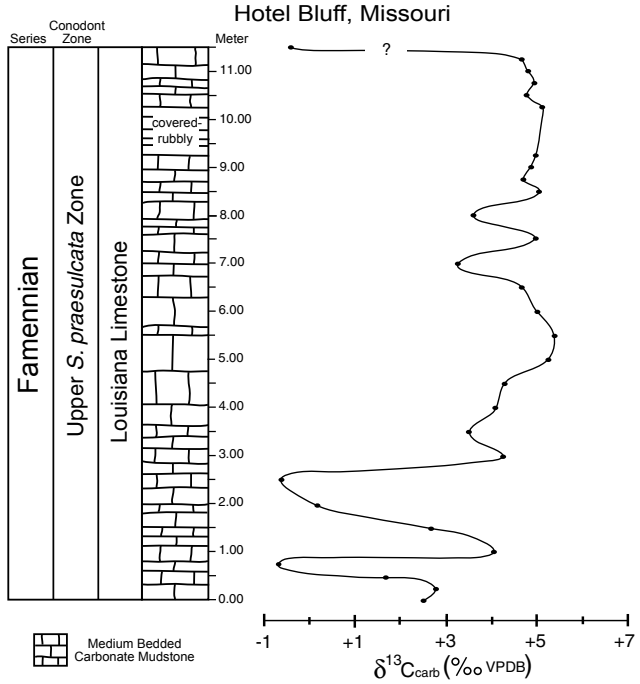

Figure 7. $\delta^{13}C_{carb}$ stratigraphy of the Hotel Bluff section, Louisiana, Pike County, Missouri. This represents the most expanded outcrop section included in this study. The sampling datum is the lowest exposed Louisiana bed, which should be within 50 cm of the Saverton–Louisiana contact. The uppermost sample was immediately beneath a tree root in outcrop and was highly altered in polished section. Therefore a question mark has been placed near this data point to remind the reader that this may not be a reliable data-point.

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in the study area. There are currently no known sections where the Louisiana is conformable with overlying strata.

Precise correlations of the sections investigated in this study with each other or with European sections based solely on $\delta^{13}C_{carb}$ stratigraphy still need refinement afforded by additional biostratigraphic data and additional isotopic sampling. The disconformities above and below the Louisiana (Figs. 1, 2) make it difficult to clearly define where the HIE begins and ends in the region. As a result, we cannot definitively say where we are within the excursion in outcrops with a limited thickness of Louisiana Limestone. What is clear however, is that the Louisiana Limestone is Upper *S. praesulcata* Zone in age and contains the maximum values of the HIE. Likewise, isotopically correlating the Louisiana to the classical European sections is complicated by the large difference in sedimentation rates. According to Kaiser (2005), the entire Upper *S. praesulcata* Zone is often only a few cm thick throughout Europe while the Louisiana is over 20m thick in places. In order to resolve this issue high-resolution sampling for $\delta^{13}C_{carb}$ must be done on the European sections and a stratigraphically more complete reference section must be sampled in the mid-continent.

LATE FAMENNIAN PALEOCEANOGRAPHY AND CARBONATE PRODUCTION

Over the past decade, the importance of nutrient availability on carbonate production has been increasingly emphasized (Hallock, 1988; 2001; and Schlager, 1986; Föllmi et al., 1994; Caplan et al., 1996; Peterhänsel and Pratt, 2001; Mutti and Hallock, 2003; Rankey, 2004; Halfar et al., 2004). The control of nutrient availability and consequent primary productivity on carbonate sedimentation is primarily the result of the competing influences of bioeroders of carbonate grains versus bioproducers of carbonate grains (Hallock, 1988). Bioeroders of carbonate grains have a competitive advantage over carbonate producers in high-nutrient waters and vice-versa. As a result, carbonate sequences can be interpreted as also responding to changes in nutrient availability as opposed to changes in sea level alone. Several authors have previously attributed Late Devonian epicontinental black shale deposition and the demise of western North American carbonate platforms to eutrophication (Caplan et al., 1996; Peterhänsel and Pratt, 2001), asserting that nutrient availability and primary production were a major control over Late Devonian carbonate deposition. This assessment of Late Devonian carbonate sedimentology agrees well with our interpretation of the Late Famennian sequence of the North American mid-continent and is a central tenet of our discussion of the HIE.

We suggest that the interval of increased carbonate production, which records the peak values of the Hangenberg Excursion in the North American mid-continent, was associated with a decrease in nutrient availability and consequently primary productivity. The low abundance of the post-extinction recovery fauna indicative of the Upper *S. praesulcata* Zone likely reflects the lack of available nutrients during this time (see Jeppsson, 1990; Stricanne et al., 2006).

EPEIRIC SEA PALEOCEANOGRAPHY AND $\delta^{13}C_{carb}$

Based on the above discussion, the HIE appears to be related to a decrease in organic carbon burial and nutrient availability

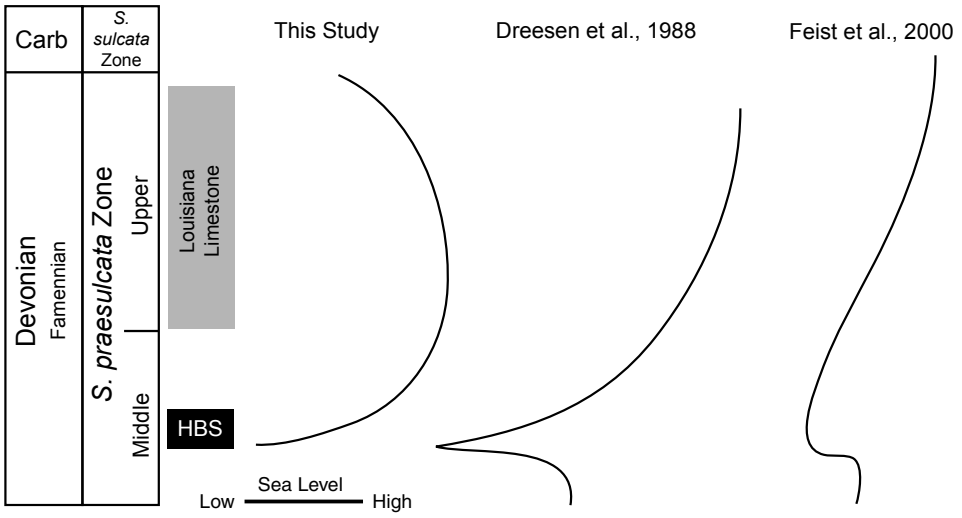

Figure 8. Correlation of the Hangenberg Black Shale (HBS) and the Louisiana Limestone with comparison to several eustatic sea level curves. Note that the HBS is associated with the very onset of transgression and that the Louisiana Limestone is associated with the highstand interval.

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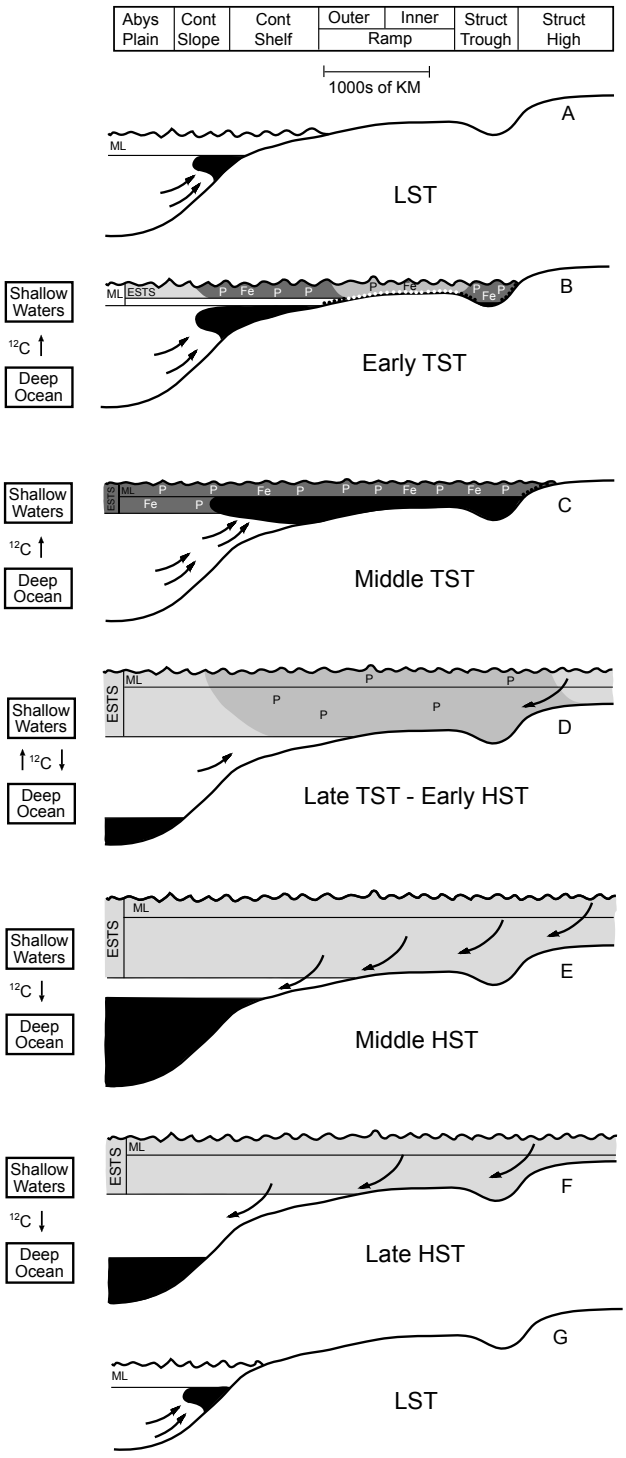

in epeiric sea settings, particularly in the U.S. mid-continent. This conflicts with the notion that the HIE was the direct result of intense black shale deposition in epeiric seas (Brand et al., 2004). Kaiser (2005) showed that the excursion began within the interval of black shale deposition, but peaked during the post-extinction recovery interval within organic-poor grey shales and limestones (Fig. 1). Based on the data of Kaiser (2005) and our data from this investigation (Figs. 4–7), we suggest that peak $\delta^{13}C_{carb}$ values significantly post-date the HBS and here interpret the HIE to reflect changing paleoceanographic conditions during the late Famennian that sequestered organic carbon away from epeiric seas.

Because organic-rich black shale deposition in epeiric sea settings ended during the initial onset of the increasing limb of the HIE (Fig. 1), the increased organic carbon burial in epeiric sea settings represented by the HBS is not likely to be responsible for the peak values of the bulk of the HIE. We suggest that the HBS reflects intense deep ocean upwelling that delivered nutrients to shallow epeiric sea waters, but also introduced isotopically light carbon ($^{12}CO_2$[aq]) into these water masses. This upwelling water mass signature helped attenuate the burial of isotopically light organic matter in epeiric seas, which can help explain why the interval of increased C_{org} burial during transgression (HBS) did not correspond to peak values of the HIE.

The correlation of peak values of the HIE with the re-establishment of carbonate production in epeiric seas of the U.S. mid-continent and elsewhere (Fig. 9) is interpreted to reflect a change in epeiric sea circulation to an anti-estuarine mode (Witzke, 1987; Jeppsson, 1990; Bickert et al., 1997; Cramer and Saltzman, 2005; Cramer et al., 2006). This change in circulation produced downwelling saline waters in continental interiors and progressively disconnected epeiric sea-water masses from their deep-ocean sources of nutrients

Figure 9. Application of the Silurian oceanographic model to the latest Devonian across a hypothetical craton. Boxes to the left of the diagram represent the net transfer of ^{12}C between shallow and deep water. ESTS=Epeiric Sea Trophic State. The base of this zone is a constant horizon with respect to the craton. The shading represents trophic state: dark grey=eutrophic, grey=mesotrophic, light-grey= oligotrophic, ML=mixed layer. Note the impingement of the mid-water oxygen minimum zone onto the craton during transgression. The HBS is a product of this event. The net flux of ^{12}C into shallow water during transgression is nearly isotopically balanced by the increased sequestration and burial of C_{org} in epeiric seas. The transition to anti-estuarine circulation during highstand promotes warm saline bottom water production promoting deep ocean anoxia. The sequestration and burial of C_{org} in the deep ocean during highstand drove the HIE. Note the difference in timing and location of the two periods of anoxia and consequent black shale deposition: Transgressive black shales in epeiric seas resulting from primary productivity induced anoxia versus highstand black shales in the deep ocean resulting from sluggish poorly oxygenated bottom water production (oceanographically induced anoxia).

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and light carbon. As a result, carbonate production (e.g., Louisiana Limestone) could be re-established in epeiric sea settings. Nutrients and isotopically light carbon (^{12}C) were sequestered in deep-ocean environments that progressively became anoxic (or euxinic, Kump et al., 2005) as a result of warm saline bottom-water production (Bralower and Thierstein, 1984; Herbert and Sarmiento, 1991). Due to the fact that deep-ocean upwelling was not the only source of nutrients available for primary production (Ekman upwelling, oceanic divergences, terrestrial runoff, etc.), global primary productivity continued under these conditions albeit at a reduced level. This allowed ^{12}C, in the form of organic matter, to continue to be pumped down from surface waters globally while the return of light carbon to shallow epeiric waters from depth was compromised, which resulted in a positive $\delta^{13}C_{carb}$ excursion.

High organic carbon burial in the deep ocean, which drove the positive $\delta^{13}C_{carb}$ excursion, eventually began to lower global atmospheric CO_2 levels (Berner and Kothavala, 2003). The consequent decrease in global temperatures and increased latitudinal temperature gradient responsible for vigorous thermohaline circulation helped to re-establish polar downwelling. This progressively oxygenated the deep ocean and ended the HIE.

CONCLUSIONS

Our data indicate that organic-rich deposition in epeiric seas appears to have preceded the Hangenberg $\delta^{13}C_{carb}$ excursion, which was coincident with an increase in carbonate production throughout the mid-continent and elsewhere world-wide. Although this may seem to contradict current models for carbon-isotope excursions, the only real difference between this interpretation and the one presented by Brand et al. (2004) is the location of the C_{org} burial that drove the excursion. We conclude that the increased C_{org} burial, responsible for the Hangenberg Excursion occurred in deep-marine settings rather than in epeiric seas. The C_{org} burial in epeiric seas represented by the Hangenberg Black Shale and other correlative deposits are a record of eutrophication of the craton during the onset of the very late Famennian post-glacial sea-level rise, which immediately preceded the carbon-isotope excursion.

This proposed connection between deep-ocean anoxia, anti-estuarine circulation, expansion of carbonate platform environments and positive carbon-isotope excursions has been well documented in the Silurian (see Munnecke et al., 2003; Calner et al., 2004; Cramer and Saltzman, 2005, 2007; Cramer et al., 2006). The onset of the Hangenberg $\delta^{13}C_{carb}$ Interval appears to be an icehouse–greenhouse transition (P–S transition in Silurian terminology). This interpretation indicates that the interval of latest Devonian time considered herein represents a brief interval of warmth between two successive glaciations. The effects of the rapid icehouse–greenhouse transition on global oceanography produced the Hangenberg Extinction Event and Excursion, as well the eventual return to icehouse conditions near the Devonian–Carboniferous boundary.

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