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Late Ordovician (Turinian–Chatfieldian) carbon isotope excursions and their stratigraphic and paleoceanographic significance

Greg A. Ludvigson[a,b,c,*], Brian J. Witzke[a,b], Luis A. González[e], Scott J. Carpenter[b,c], Chris L. Schneider[d], Franciszek Hasiuk[b]

[a] Iowa Geological Survey, Iowa City, IA 52242-1319, USA
[b] Department of Geoscience, University of Iowa, Iowa City, IA 52242-1379, USA
[c] Center for Global and Regional Environmental Research, University of Iowa, Iowa City, IA 52242-1297, USA
[d] Department of Geological Sciences, University of Texas at Austin, Austin, TX 78712-0254, USA
[e] Department of Geology, University of Kansas, Lawrence, KS 66045-7613, USA

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Abstract

Five positive carbon isotope excursions are reported from Platteville–Decorah strata in the Upper Mississippi Valley. All occur in subtidal carbonate strata, and are recognized in the Mifflin, Grand Detour, Quimbys Mill, Spechts Ferry, and Guttenberg intervals. The positive carbon isotope excursions are developed in a Platteville–Decorah succession in which background $\delta^{13}C$ values increase upward from about $-2‰$ at the base to about 0‰ Vienna Pee Dee belemnite (VPDB) at the top. A regional north–south $\delta^{13}C$ gradient, with lighter values to the north and heavier values to the south is also noted. Peak excursion $\delta^{13}C$ values of up to $+2.75$ are reported from the Quimbys Mill excursion, and up to $+2.6$ from the Guttenberg excursion, although there are considerable local changes in the magnitudes of these events. The Quimbys Mill, Spechts Ferry, and Guttenberg carbon isotope excursions occur in units that are bounded by submarine disconformities, and completely starve out in deeper, more offshore areas. Closely spaced chemostratigraphic profiles of these sculpted, pyrite-impregnated hardground surfaces show that they are associated with very abrupt centimeter-scale negative $\delta^{13}C$ shifts of up to several per mil, possibly resulting from the local diagenetic effects of incursions of euxinic bottom waters during marine flooding events.

Keywords: Ordovician; Carbon isotopes; Chemostratigraphy; Paleoceanography

1. Introduction

Carbon isotope excursions are stratigraphic intervals that are characterized by rapid systematic changes in carbon isotopic compositions in relation to underlying and overlying strata. Positive carbon isotope excursions in the marine chemostratigraphic record are intervals with increased $\delta^{13}C$ values ($^{13}C/^{12}C$ ratios), and are generally interpreted to record the influence of ^{12}C sequestration on the global carbon cycle through the burial of ^{12}C-enriched organic matter in sedimentary rocks (Kump and Arthur, 1999). A positive organic carbon isotope excursion in the Ordovician Guttenberg Limestone member of the Deco-

* Corresponding author. Iowa Geological Survey, 109 Trowbridge Hall, Iowa City, IA 52242-1319, USA.
E-mail address: gludvigson@igsb.uiowa.edu (G.A. Ludvigson).

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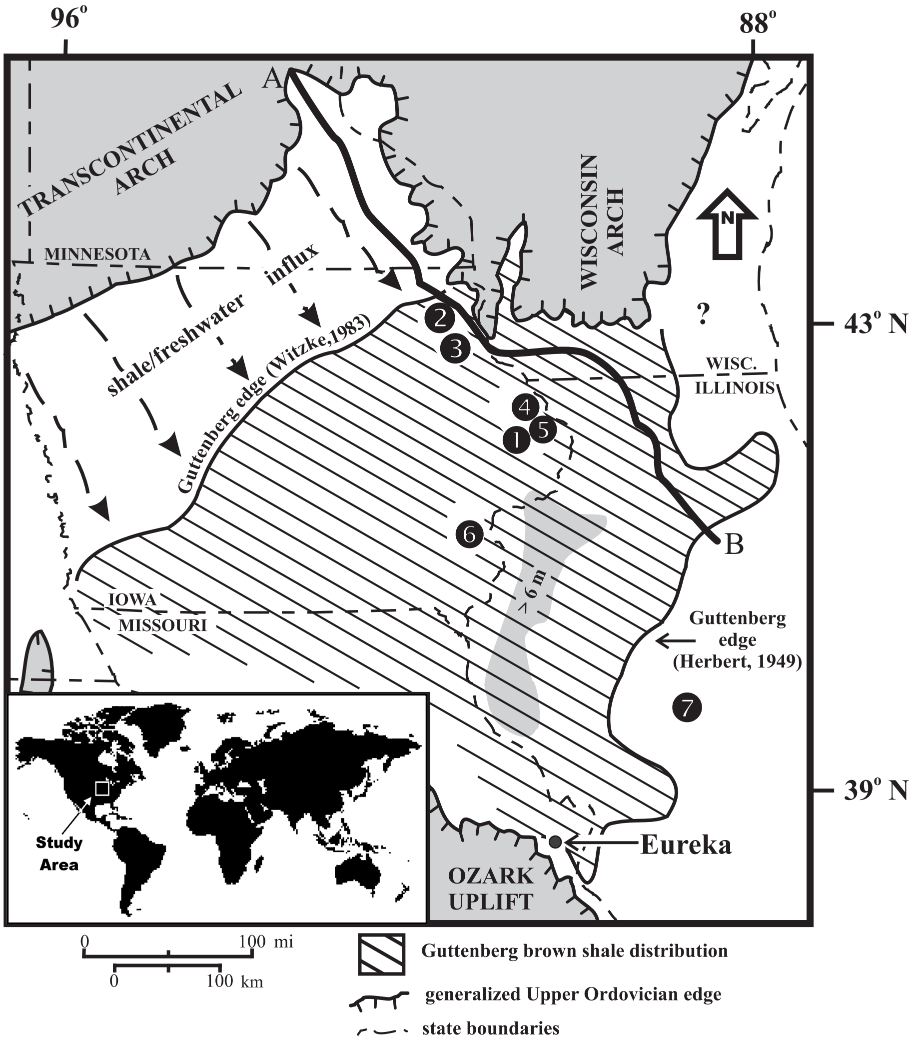

Fig. 1. Location and lithofacies map of the Decorah Formation in the Upper Mississippi Valley region, North American interior. Position of the study area is shown in the inset map to lower left. The A–B line of section is shown in Fig. 3. Numbered localities refer to drillcores used for chemostratigraphic profiles in this report. A chemostratigraphic profile of exposed Plattin–Kimmswick strata at the Eureka section in east-central Missouri was published by Ludvigson et al. (2000). Drawing modified from Ludvigson et al. (1996).

rah Formation in Iowa (Figs. 1 and 2) was first reported by Hatch et al. (1987). Ludvigson et al. (1996) reported a positive carbonate carbon isotope excursion from the same stratigraphic position in the Cominco Millbrook Farms SS-9 drillcore in eastern Iowa (locality 1 in Figs. 1 and 3), and similar carbonate carbon isotope records of this same excursion event have since been reported from Pennsylvania (Patzkowsky et al., 1997), Kentucky, Tennessee, New York, and Sweden (Saltzman et al., 2001; Bergström et al., 2001), and the Baltic states (Ainsaar et al., 1999). This chemostratigraphic event occurs above the position of the Millbrig K-bentonite bed (Fig. 2; dated at 453.7 ± 1.3 Ma), which was defined as the Turinian–Chatfieldian Stage boundary by Leslie and Bergström (1995). Additional studies of the succession of organic biomarkers in the same Cominco Millbrook Farms SS-9 core in Iowa were published by Pancost et al. (1998, 1999), further characterizing the paleoenvironmental record from this important reference section.

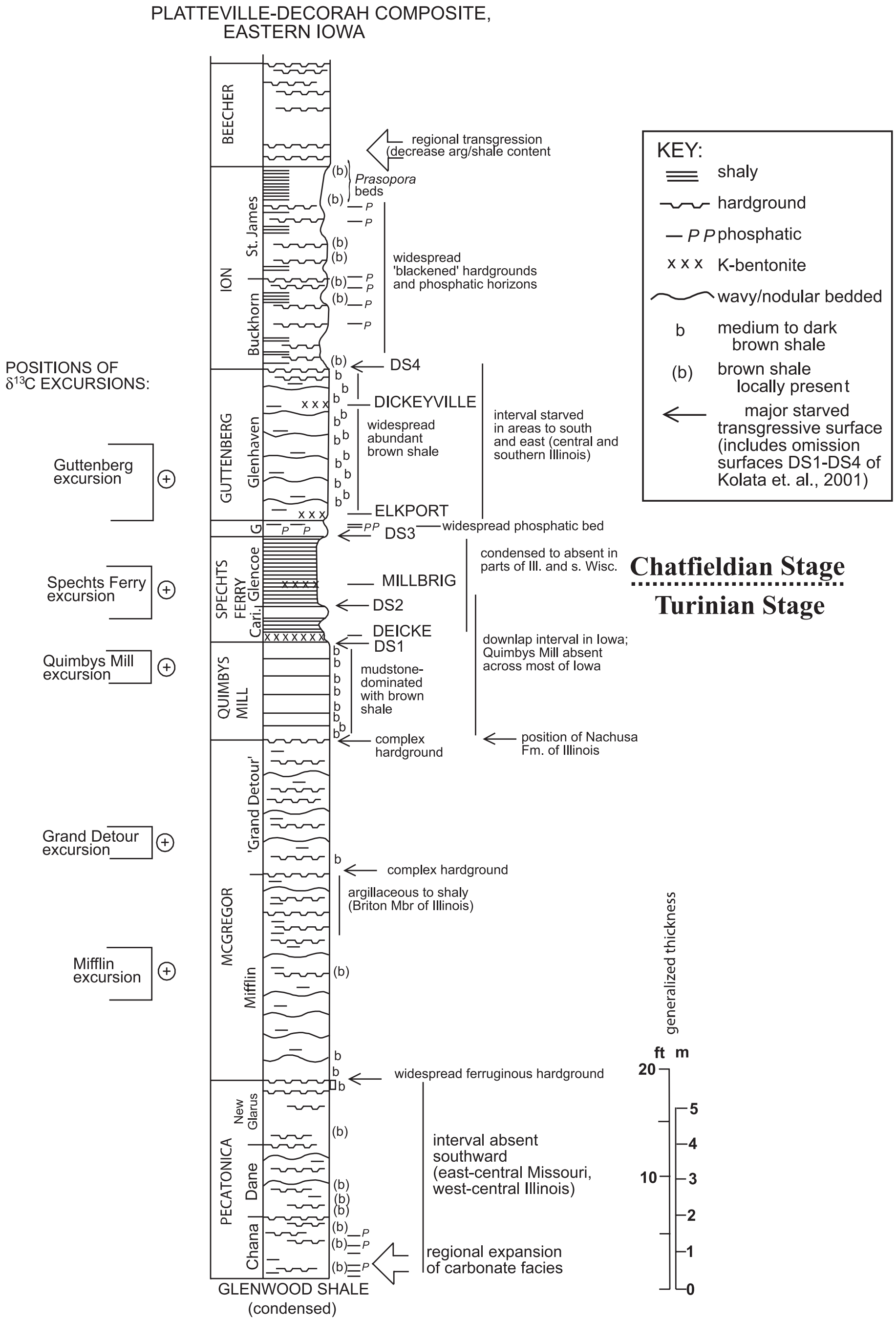

Fig. 2. Composite stratigraphic section of the Platteville and Decorah Formations in eastern Iowa. Abbreviations: G = Garnavillo; Cari = Carimona.

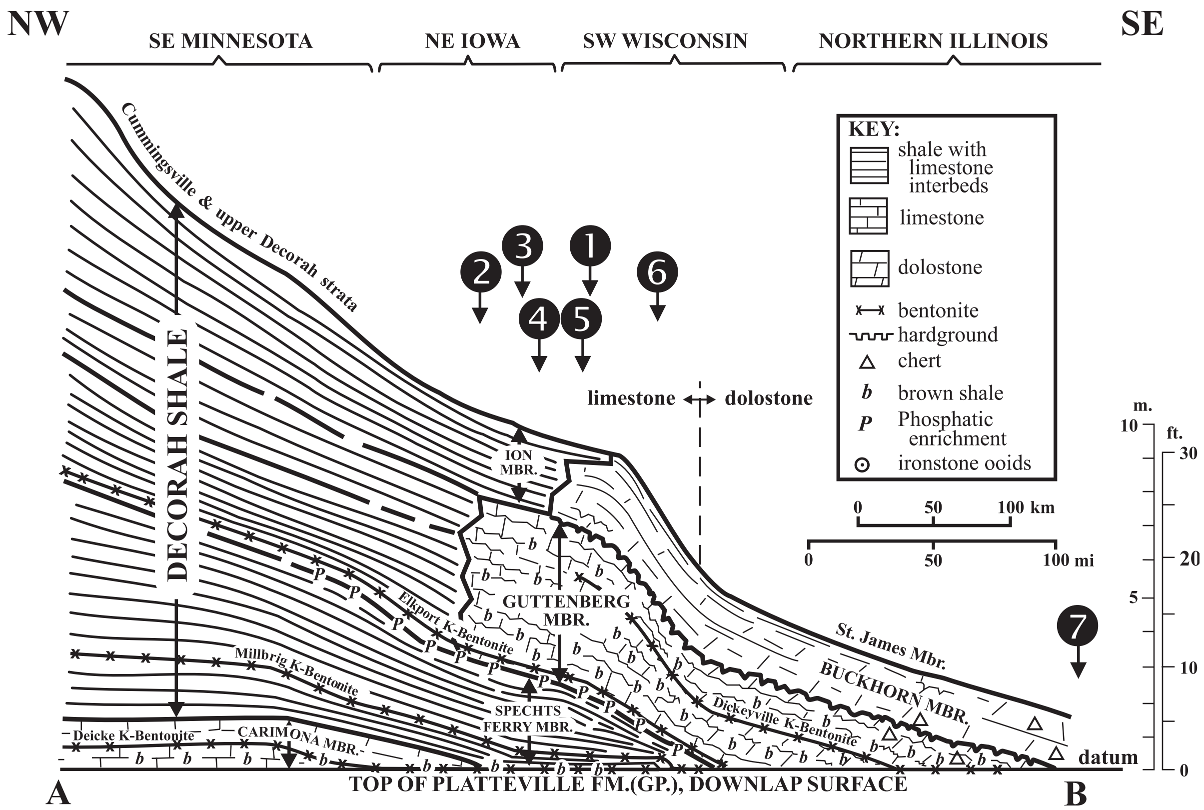

Fig. 3. Generalized stratigraphic cross section of the Decorah Formation from southeast Minnesota to northern Illinois. The location of the line of section is shown in Fig. 1. Numbered localities from Fig. 1 are interpolated into their approximate position on this line of section. Modified from Ludvigson et al. (1996).

A brief report by Ludvigson et al. (2000) on isotope profiles from exposed stratigraphic sections in northeast Iowa, southwest Wisconsin, and eastern Missouri showed that the positive carbon isotope excursion of the Guttenberg interval can be widely traced around the mid-continent United States, but also suggested that additional positive carbon isotope excursions are present below the underlying Deicke K-bentonite bed (Fig. 2; dated at 454 ± 0.5 Ma). This study further explores geographic and stratigraphic variations in Ordovician carbon isotopic records contained in several long curated drillcores from Iowa and Illinois.

2. Geologic setting

The succession of carbonate and shale strata included within the Platteville and Decorah formations in eastern Iowa and the Mississippi Valley area spans the middle part of the Mohawkian Series (Turinian and Chatfieldian stages) of the Upper Ordovician (equivalent to mid-Caradoc of global chronology). The carbonate-dominated Platteville Formation in eastern Iowa includes three members (Pecatonica, McGregor, Quimbys Mill; Fig. 2), and a similar succession (with additional dolomite facies) is recognized in the Platteville Formation of Minnesota (Mossler, 1985). Platteville strata significantly thin northwestward across Iowa (to less than 6-m thick; Witzke and Kolata, 1988). Thicker correlative strata in Illinois are assigned to five formations (Pecatonica, Mifflin, Grand Detour, Nachusa, Quimbys Mill) within the Platteville Group (Templeton and Willman, 1963; Willman and Kolata, 1978). In eastern Missouri, correlative strata of the Plattin Group include a succession of five formations (Pecatonica, Bloomsdale, Beckett, Hager, Macy; see Thompson, 1991). Platteville strata show a progressive southward thickening in the Mississippi Valley, delineating a "Sauk-type regional isopachous pattern" (Witzke and Kolata, 1988), the same thickening pattern seen in strata of the Sauk Megasequence (Cambrian–Lower Ordovician).

Above the Platteville, the Galena Group includes a thick succession of widely traceable carbonate and shale strata. Regional thickness patterns contrast with those of the Platteville, and the Galena Group thickens northward in the Mississippi Valley (the "Galena structural reorganization" of Witzke and Kolata, 1988). The lower part of the Galena Group is termed the Decorah Formation (or Subgroup). Shale and carbonate strata of the Decorah Formation in eastern Iowa comprise three members (Spechts Ferry, Guttenberg, Ion). Northwestward in Iowa and Minnesota, these members lose their lithologic distinction as the formation becomes shale-dominated (Decorah Shale; Fig. 3). The Ion Member loses its shaly character southward, where correlative carbonate-dominated units are included in the Dunleith or Kimmswick formations in southern Iowa, Missouri, and Illinois. The Decorah Subgroup of Illinois includes only the Spechts Ferry and Guttenberg formations (Willman and Kolata, 1978).

The Platteville and Decorah Formations in eastern Iowa are interpreted to comprise a complex stack of six or seven stratigraphic sequences. Each sequence is bounded by widespread hardground surfaces and/or thin phosphatic units, which correspond with episodes of sediment starvation or condensation in the epicontinental (cratonic) seaway. Several of these "planar omission surfaces" were interpreted by Kolata et al. (2001, p. 1073) as regionally significant subtidal drowning or flooding surfaces (DS1–DS4; see Fig. 1) that formed during episodes of pronounced and persistent relative sea-level rise and carbonate sediment starvation. Some of these starved surfaces are of vast regional extent, spanning distances of up to 1000 km within the continental interior. We concur with the interpretations of Kolata et al. (2001) in recognizing the regional stratigraphic significance of these surfaces, which lack evidence of subaerial exposure and likely formed coincident with the spread of cooler nutrient-rich bottom waters. Choi and Simo (1998) interpreted one of these widespread surfaces (their sequence bounding SB3 surface which is surface DS4 of Kolata et al., 2001) to represent subaerial exposure and erosion in Wisconsin.

Like many relatively thin Paleozoic cratonic marine deposits, stratal relationships within the Platteville–Decorah interval have proven difficult to constrain. However, the fortuitous presence of several K-bentonites (altered volcanic ashes) has been of considerable help in delineating stratal geometries within the Decorah succession (Kolata et al., 1998; Leslie and Bergström, 1997). Stratal patterns of thinning and pinch-out that have been interpreted variously to either reflect regional stratigraphic onlap or downlap. The stratigraphic convergence across eastern Iowa and southwestern Wisconsin of several K-bentonites in the Decorah Formation outlines a region of relative sediment condensation (Figs. 3 and 4). This convergence and thinning is not coincident with the margins of the Wisconsin Arch (Fig. 1) or any other known structural feature, but extends across large areas of eastern and central Iowa as well (a 300-km-wide belt within the middle-shelf region of Witzke and Bunker, 1996).

Ludvigson et al. (1996) interpreted the top of the Platteville Formation (DS1 surface of Kolata et al., 2001) to mark a regional downlap surface. The Decorah K-bentonites converge southward along this surface, and strata of the Spechts Ferry and Guttenberg members progressively pinch out and lap this surface to the southeast across southern Wisconsin and northern Illinois (Fig. 3). Similar patterns of regional downlap are identified along certain hardground surfaces within the Platteville Formation of eastern Iowa (see later discussion), but the regional stratigraphic relationships of the entire Platteville succession remain incompletely known.

The Platteville–Decorah interval of the Upper Mississippi Valley is subdivided into a succession of stratigraphic sequences that show similar stratigraphic and lithologic features. (1) As noted above, each sequence is bounded by a widespread hardground surface (omission surface) or thin zone of phosphatic enrichment. Many of these hardgrounds are ferruginous (oxidized pyrite) or blackened (phosphatic and pyritic crusts), and some of these surfaces show a complex history of multiple superimposed hardgrounds, omission fillings, and boring/burrowing. Previously termed corrosion surfaces by earlier workers (e.g., Templeton and Willman,

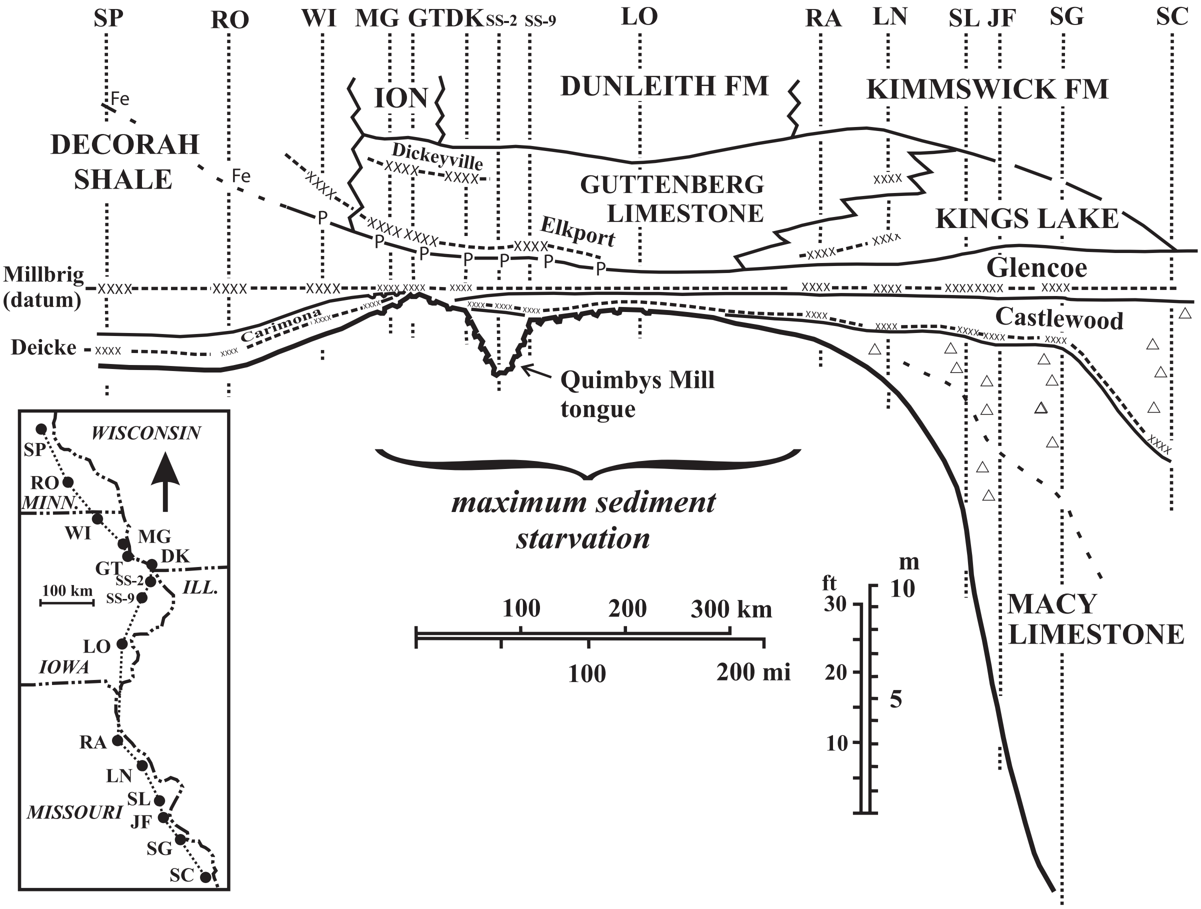

Fig. 4. Regional north–south stratigraphic cross section of Platteville–Decorah strata from St. Paul, Minnesota to SC, Missouri. Note the condensation of strata in the eastern Iowa area. Stratigraphic datum is the Millbrig K-bentonite bed, formally defined as the Turinian–Chatfieldian boundary. Localities are SP—St. Paul; RO—Rochester; WI—Winneshiek County exposures; GT—Guttenberg; MG—McGregor (Pikes Peak); SS-2 core; SS-9 core; LO—Louisa County cores; RA—Ralls County; LN—Lincoln County; SL—St. Louis County; JF—Jefferson County; SG—Ste. Genevieve; SC—Scott County. For sections see Kolata et al. (1986) and Thompson (1991). Abbreviations: ××× = K-bentonite horizon; P = phosphatic; Fe = ooidal ironstone; △ = cherty.

1963), some of these hardgrounds show putative evidence of carbonate dissolution. (2) Additional hardground surfaces are recognized within many (but not all) of these sequences, underscoring the relatively condensed nature of regional sedimentation and recurring sediment starvation.

(3) The lithologies within each sequence are dominated by mud-rich carbonate fabrics (sparse mudstones to wackestones) or sparsely skeletal calcareous clay shales. The fine-grained aspect and normal-marine fauna of these sediments suggest deposition in relatively quiet subtidal marine environments. (4) Skeletal packstones are recognized in each sequence, most commonly as lenses and stringers. The packstones and shell coquinas are interpreted to result from episodic storm current activity during deposition. Some sequences show a general upward increase in packstone beds, suggesting a shallowing-upward succession. (5) Each sequence contains thin brown organic shale partings of local to regional extent. The preservation of organic matter in shales (medium to dark chocolate brown) and in brown carbonate mudstones (sometimes fetid) suggests that deposition occurred beneath bottom-waters that were dysoxic to

anoxic at least episodically. Organic productivity blooms may also be involved in the formation of certain organic-rich lithologies (with up to 50% TOC).

(6) Many of the sequences show significant fluctuations in stable carbon isotope ratios during their deposition, with relative $\delta^{13}C$ excursions of +0.5‰ to +2.5‰ VPDB observed in five of the sequences. It remains to be seen whether these excursions reflect global oceanic or local epeiric processes. (7) Each sequence is incompletely developed over regions of the continental interior, and certain stratigraphic units are locally or regionally absent at the position of the bounding hardground surfaces. The basal parts of some sequences condense, converge, and starve out across the region in an interpreted downlap relationship. In addition, the upper parts of some sequences may also be absent locally, missing at the position of the regional hardground surfaces. In some cases, entire sequences may be absent along these surfaces. For example, the entire Quimbys Mill and Carimona sequences are missing (between the Glencoe and Grand Detour) in parts of eastern Iowa. Likewise, the Carimona, Glencoe, and Guttenberg sequences are completely absent across parts of northern Illinois (Fig. 3) above the Quimbys Mill. The stacking and lapping of sequences with respect to the various bounding surfaces create complex regional stratigraphic relationships. The complex stratal geometries have not yet been worked out for all sequences, but known and hypothesized stratigraphic relationships are discussed for each sequence, as follows.

2.1. Platteville sequences

We subdivide the Platteville Formation (or Group) of Iowa into four or five stratigraphic sequences in this report, whereas Choi and Simo (1998) placed the Platteville succession of Wisconsin within two sequences (S1 and S2). These varying interpretations are not considered to be seriously at odds, but may be more of an artifact of how the various depositional cycles (parasequence sets) within the Platteville are grouped together. Choi and Simo (1998) include the lower Platteville Pecatonica Member within a separate sequence from overlying Platteville strata, and we strongly concur. Overlying Platteville strata of the McGregor and Quimbys Mill members in Wisconsin were assigned to a single sequence (S2), comprised of five or six widely recognizable depositional cycles (Choi and Simo, 1998, p. 450). Each of these cycles shows broad-scale geographic facies changes, and each is "typically bounded by omission surfaces" (ibid.). Our subdivisions within the Platteville merely recognize some of these omission surfaces as sequence boundaries. The higher-order sequence stratigraphic subdivisions that we propose for several Platteville intervals reflect our interpretations of the magnitude and geographic significance of certain bounding surfaces and the nature of stratal geometries with respect to these surfaces. Surfaces that display widespread stratal onlap or downlap and constrain regional disconformities (missing strata) are considered to be sequence boundaries for the purposes of this report.

2.2. Pecatonica sequence

The Pecatonica sequence makes up the basal part of the Platteville Formation (or Group), and its deposition marks the expansion of carbonate facies in the region (above the condensed Glenwood Shale in eastern Iowa). Choi and Simo (1998) include the Glenwood Shale and Pecatonica Member within the same stratigraphic sequence in Wisconsin, although Witzke and Bunker (1996) recognized the Glenwood in Iowa as a separate coarsening- and shallowing-upward cycle. Phosphatic enrichment (apatite clasts, hardground crusts) is common in the lower part of the Pecatonica, with brown shales locally present in eastern Iowa. A number of local to regional hardgrounds are developed within the carbonate mudstone-wackestone succession (see Choi and Simo, 1998). Wavy-bedded nodular mudstones with brown shale partings (like facies seen in the McGregor and Guttenberg members) are developed across parts of eastern Iowa. The top of the Pecatonica is marked by a remarkably widespread ferruginous and phosphatic hardground surface (often developed as a closely spaced pair of hardgrounds). Willman and Kolata (1978, p. 25) wrote, "the corrosion surface that consistently marks the top [of the Pecatonica] ... is very flat, and there is no evidence of erosional scour. Although a withdrawal of the seaway is not indicated, the surface appears to represent a major interruption in sedimentation''. Distinctive red-brown burrow networks are common beneath the upper hardground.

The upper Pecatonica includes cross-bedded skeletal packstones (Oglesby interval) southward in the region (Willman and Kolata, 1978), consistent with an upward-shallowing succession. However, Oglesby strata are not recognized northward in the Mississippi Valley. The entire Pecatonica sequence is absent beneath strata of the Mifflin sequence over large areas of northeast and east-central Missouri as well as locally in northern Illinois (Thompson, 1991; Templeton and Willman, 1963). Offshore Pecatonica carbonate strata likely share shoreward facies relationships with upper Glenwood shales across Minnesota (Mossler, 1985).

2.3. Mifflin sequence

The Mifflin sequence includes the Mifflin Formation (Platteville Group) in Illinois, the lower half of the McGregor Member in Iowa, Wisconsin, and Minnesota (sometimes termed the Mifflin member or submember), and the Bloomsdale–lower Beckett formations of Missouri (Thompson, 1991). These strata are dominated by wavy-bedded nodular lime mudstones and wackestones across most of the region. A general upward increase in clay and shale content may reflect overall depositional shallowing. Brown shale partings are developed in the basal Mifflin sequence of eastern Iowa, above the bounding Pecatonica hardground. Multiple hardground surfaces are developed in the upper Mifflin sequence of eastern Iowa and northern Illinois, some regionally persistent (Templeton and Willman, 1963, p. 80). The top of the Mifflin sequence in eastern Iowa is drawn at widespread complex hardground surface, and in Illinois ''a consistently sharp contact'' marks the top of the Mifflin (Templeton and Willman, 1963).

Mifflin strata overstep the Pecatonica edge across eastern Missouri, where basal transgressive strata include oolitic and ''lithographic'' limestones of the Brickeys Member (Thompson, 1991). These basal strata are not recognized northward in Iowa. Templeton and Willman (1963, p. 80) interpreted a westward-expanding diastem in the upper sequence between Missouri and Minnesota indicated by the irregular westward wedging-out of upper Mifflin and lower Grand Detour members.

2.4. Grand Detour and Nachusa sequences

The Grand Detour sequence includes the Grand Detour Formation of Illinois, the upper McGregor Member (Grand Detour submember) in Iowa, Wisconsin, and southern Minnesota, and the Beckett–Hager formations in Missouri. Carbonate facies are similar to those of the Mifflin sequence, although the interval is generally less argillaceous and more dolomitic. Brown and red-brown shale partings are identified in eastern Iowa and Illinois. Skeletal packstones are most common in the upper part (Willman and Kolata, 1978), possibly reflecting an upward-shallowing succession. Multiple hardgrounds are recognized in the Grand Detour sequence of Iowa and Illinois. A complex hardground surface is developed at the top of the sequence across eastern Iowa.

Templeton and Willman (1963, p. 89) indicated that the uppermost Grand Detour is locally transitional with the overlying Nachusa Formation, but a ''sharp break separates the Grand Detour and upper Nachusa strata'' in parts of western Illinois. Strata correlative with the Nachusa Formation are apparently absent across all of Iowa and Minnesota (Templeton and Willman, 1963), suggesting that the Grand Detour–Quimbys Mill hiatus may be of considerable magnitude in that area. However, regional relationships between strata of the Grand Detour and Nachusa formations are not known with certainty. It is not yet clear whether Nachusa strata should be included within an expanded Grand Detour sequence (gradational contact), or whether the Nachusa should be considered as a separate sequence (sharp disconformable contact). Relationships in Missouri make the latter suggestion more likely, where the Victory Member (Hager Formation) marks a position that correlates at or near the top of the Grand Detour Formation of Illinois (ibid.). The Victory Member is a distinctive white carbonate mudstone unit, in part with algal laminations and fenestral structures, that may record regressive peritidal deposition; its top is usually corroded and truncated (Thompson, 1991, p. 166). The Victory marker bed is absent northward into northeast Missouri and Iowa, and the Grand Detour sequence significantly thins in that direction. The lower Macy Formation (Hook Member) of Missouri is correlative with the Nachusa Formation of Illinois (ibid.).

2.5. Quimbys Mill sequence

The Quimbys Mill sequence includes the Quimbys Mill Formation in Illinois, the Quimbys Mill Member in Iowa and Wisconsin, and the upper Macy Formation (Zell Member) of Missouri. Quimbys Mill strata are generally absent across most of Iowa and the Upper Mississippi Valley, although a thin (5–40 cm) mudstone unit with characteristic conchoidal fracture is locally noted in that area that may represent westward lapping of a greatly thinned Quimbys Mill sequence. The Quimbys Mill sharply overlies the Nachusa in northern Illinois (Templeton and Willman, 1963), and it overlies a complex hardground surface on the upper McGregor Member (Grand Detour) in parts of eastern Iowa (Fig. 5). The Quimbys Mill sequence (including Zell Member) dramatically thickens southward in Missouri and Illinois (Fig. 4). The Quimbys Mill interval is characterized by brown carbonate mudstones with minor wackestone and packstone units. Numerous medium to dark brown organic shale partings occur within the succession in the northern area, but green-gray shale partings are characteristic southward in Missouri (Thompson, 1991). Couplets of limestone and brown shale are correlatable across areas of eastern Iowa (Fig. 5), suggestive of generally quiet subtidal deposition. The local presence of laminated mudstones and coralline units in northern Illinois (Witzke and Kolata, 1988) and a general upward increase in packstone frequency in eastern Iowa (Fig. 5) suggest an overall shallowing-upward succession for the Quimbys Mill.

The Quimbys Mill Member in east-central Iowa is of varying thickness, and progressive thinning is related to loss of lower units, not truncation of upper strata (Fig. 5). Templeton and Willman (1963) also interpreted the local absence of lower, not upper, Quimbys Mill strata in Illinois, and Willman and Kolata (1978, p. 33) suggested that “the westward disappearance [of the Quimbys Mill] appears to be depositional rather than erosional.” Progressively younger beds lap the major hardground surface at the top of the McGregor Member in eastern Iowa, and the entire Quimbys Mill sequence terminates westward along this surface (possibly forming a lobate western margin; Fig. 5). These stratigraphic relationships are interpreted to form a downlap succession across a regionally expansive starved subtidal hardground surface. Nachusa strata also apparently starve out westward along this same surface. Although no evidence of subaerial exposure is recognized along this surface, a major diastem is indicated, probably of submarine origin. Unlike the southeastward stratal downlap interpreted for the overlying Decorah Formation, the Quimbys Mill downlap apparently is oriented to the northwest (and possibly Nachusa as well). Such contrasting stratigraphic patterns help to differentiate the Platteville and Galena groups (Witzke and Kolata, 1988).

A major ferruginous hardground surface is developed at the top of the Quimbys Mill in northern Illinois, and “in many places phosphatic pellets are abundant on the surface” (Willman and Kolata, 1978, p. 33). This is drowning surface DS1 of Kolata et al. (2001), which is recognized across a vast area of the central and eastern United States. In eastern Iowa and Missouri, the top of the Quimbys Mill (Zell) is a planar surface below the Deicke K-bentonite. This surface merges with the basal Quimbys Mill and upper Grand Detour hardground surfaces across most of Iowa, marking a major diastem between Platteville and Decorah strata.

2.6. Spechts Ferry (Carimona, Glencoe) sequences

As discussed earlier, the Decorah succession is interpreted to downlap surface DS1 southward from Minnesota to northern Illinois (Fig. 3). The Spechts Ferry Member (or Formation) comprises the lower Decorah interval, bounded below by surface DS1 and above by surface DS3 (of Kolata et al., 2001) at the base of the Guttenberg Member. The Spechts Ferry is the basal interval of the Galena Group and is subdivided into two intervals (Kolata et al., 1986): (1) a lower limestone and shale package known as the Carimona beds/member (in Minnesota, Wisconsin, northern Iowa, northern Illinois) or Castlewood beds/member (in southern Iowa, southern Illinois, Missouri), with the Deicke K-bentonite at or near the base; and (2) an upper shale-dominated unit termed the Glencoe beds/member, which contains the Millbrig K-bentonite (Figs. 2 and 5). These two intervals are separated regionally by surface DS2 of Kolata et al. (2001). Surface DS2 probably separates two sequences regionally, here termed the Carimona and Glencoe sequences. Nevertheless, surface DS2 is

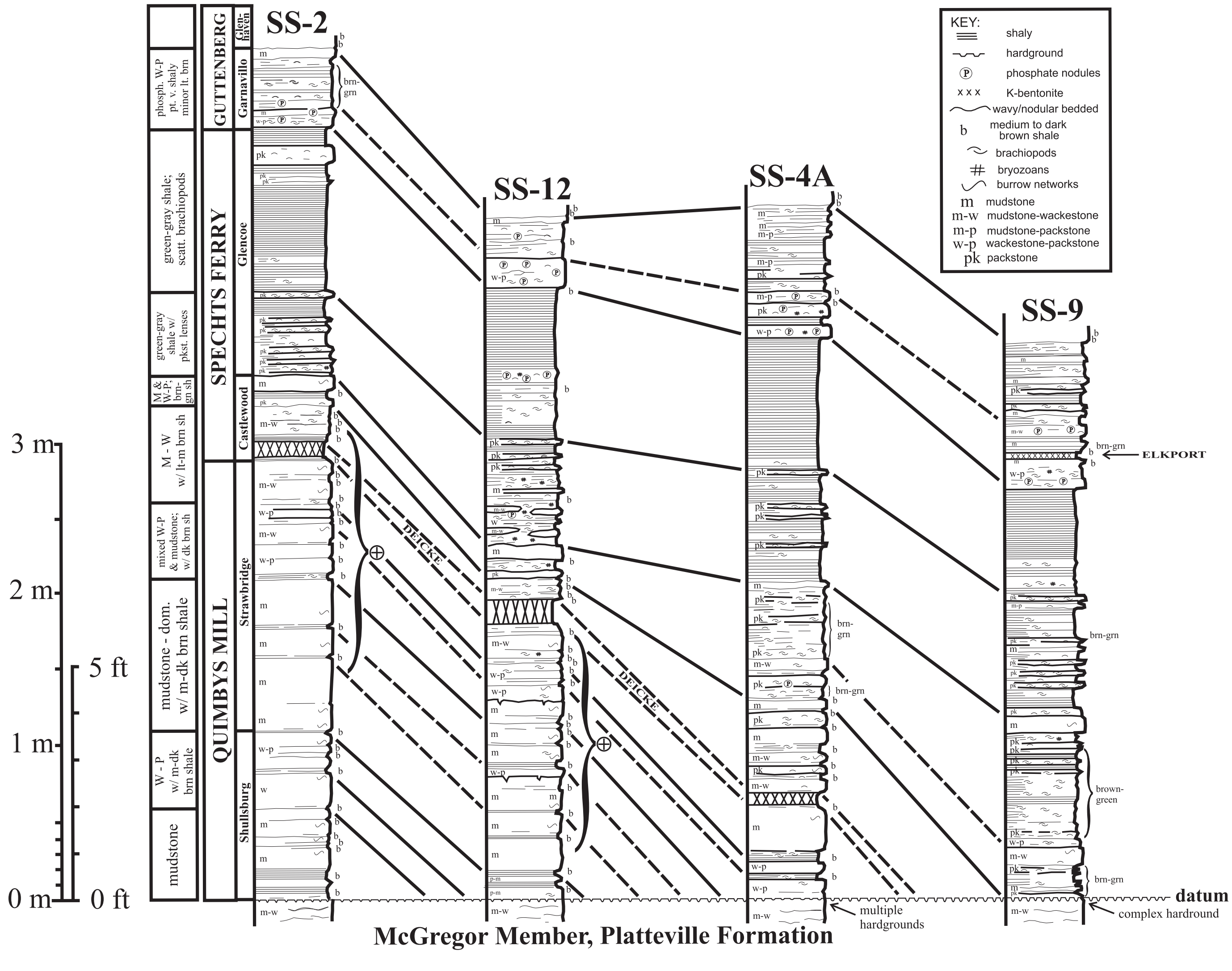

Fig. 5. Stratigraphic cross section of the Platteville–Decorah contact interval in Jackson County, Iowa, showing downlap of Quimbys Mill and Spechts Ferry strata onto a submarine disconformity surface. The position of the Quimbys Mill positive carbon isotope excursion intervals in the SS-2 and SS-12 cores is shown by the brackets to the right of the graphic logs. Abbreviations: m = mudstone; m-w = mixed mudstone and wackestone; pk = packstone; w-p = mixed wackestone and packstone; b = brown shale interbeds; m-dk = medium to dark; lt-m = light to medium; brn = brown; grn = green.

not developed as a ferruginous or phosphatic hardground over most of the Upper Mississippi Valley area. It is generally marked by a sharp contact between Glencoe shaly packstones and a widespread upper Carimona/Castlewood mudstone bed in eastern Iowa. However, DS2 is locally expressed as a bored pyritic hardground at the top of the Carimona in northeast Iowa (Witzke et al., 2000), and a prominent phosphatic hardground is recognized locally at the top of the Castlewood in western Illinois (see later discussion in Section 4.8).

Templeton and Willman (1963, p. 107) suggested a southward disappearance across northeast Iowa of several widely traceable limestone beds within the Carimona sequence. The Carimona interval thins southeastward along surface DS1 in the Upper Mississippi Valley, pinching out across parts of northeast Iowa. Carimona strata are entirely absent along surface DS1 in parts of eastern Iowa (as at Guttenberg and type Spechts Ferry) and northern Illinois. The Carimona sequence reappears southward in eastern Missouri and western Illinois above DS1, where it comprises a separate lithostratigraphic package assigned to the Castlewood Member. The Castlewood significantly thickens southward (Fig. 4). Castlewood and Carimona strata generally are dominated by carbonate mudstones and wackestones, but skeletal packstones and shales are also significant. Brown shale partings are widely recognized in the Carimona sequence.

The Glencoe interval (upper Spechts Ferry) is shale-dominated across the region, characterized by green-gray calcareous shales with thin skeletal packstone beds (primarily brachiopod-rich). The shale interval thickens northward into the lower Decorah Shale of Minnesota (Figs. 3 and 4). The Glencoe thins southward across northeast Iowa and southwest Wisconsin, and it is absent across areas of northern Illinois. The Glencoe interval is present across much of eastern Missouri and western Illinois, but it is greatly thinned (to absent?) at some localities (see later discussion in Section 4.8). The Glencoe is interpreted to regionally downlap surface DS2, and, where the Carimona sequence is absent, the Glencoe overlies a merged DS1–DS2 surface. The Glencoe records the maximum progradation of Decorah shale lithologies, derived from source areas on the Transcontinental Arch (Witzke, 1980). The Glencoe interval is sharply overlain by strata of the Guttenberg sequence; the contact marks “drowning surface” DS3 of Kolata et al. (2001).

2.7. Guttenberg sequence

The Guttenberg Member (or Formation) of the Upper Mississippi Valley is characterized in its type area by wavy- to nodular-bedded limestones with organic-rich brown shale partings (Ludvigson et al., 1996). The limestones are dominated by mudstone lithologies, but skeletal wackestones and packstones are locally interbedded, especially upward in the succession. The base of the Guttenberg sequence is marked by a thin but widespread phosphatic interval (Garnavillo beds/member), which contains common to abundant apatite grains and nodules within a mudstone to shaly packstone interval (Fig. 5). This phosphatic unit is regionally widespread (Missouri, Illinois, Iowa, Wisconsin) at the base of the Guttenberg carbonates above surface DS3, and it can be traced into the shale-dominated facies of Minnesota as well. Surface DS3 is generally not a recognizable hardground surface, primarily because it is developed on Glencoe shale facies (and not on carbonate strata). The phosphatic Garnavillo bed is interpreted to be the condensed transgressive interval of the Guttenberg sequence.

A more grain-rich carbonate facies southward in Illinois and Missouri, the Kings Lake Formation, was once thought to pre-date Guttenberg deposition (Templeton and Willman, 1963), but it is considered here to be a southern facies tract within the Guttenberg sequence (Fig. 4). Ludvigson et al. (1996) and Witzke and Bunker (1996) included shaly strata of the Ion Member within the shallowing-upward portion of the same large-scale transgressive–regressive cycle that includes the Guttenberg Member. We now exclude Ion strata (and their carbonate facies equivalents in the lower Dunleith and Kimmswick formations) from the Guttenberg sequence for two reasons. First, a prominent hardground surface is recognized at the top of the Guttenberg across much of Iowa, Illinois, and Missouri (Kolata et al., 1986). This surface was shown as regional drowning surface DS4 by Kolata et al. (2001). This surface is correlated with a condensed zone of oolitic ironstone or phosphatic enrichment within the Decorah Shale succession of northwest Iowa and Minnesota beyond the Guttenberg carbonate edge. Second, a diastem above the Guttenberg in the southern area has been suggested (Templeton and Willman, 1963, p. 117), further supporting stratigraphic separation at the top of the Guttenberg.

2.8. Post-Guttenberg sequences

Ion Member shaly carbonate strata and correlative purer carbonate strata within the Dunleith Formation (Buckhorn and St. James members) are widely distributed in the Upper Mississippi Valley. This interval contains a succession of pyritic and phosphatic hardground surfaces that are recognized in parts of Illinois, Iowa, Minnesota, and Wisconsin. Brown shales interbed with this interval in parts of eastern Iowa (Fig. 2), resembling earlier sequences of the Decorah–Platteville succession. A decrease in argillaceous and shale content in the overlying Beecher Member marks regional expansion of mud-rich carbonate facies. This regional facies shift is interpreted to record seaway expansion onto shale source areas, although Decorah shale deposition continued in shoreward areas of Minnesota and northwestern Iowa coincident with carbonate deposition of the lower Dunleith Formation in more offshore areas of the interior sea. Regional seaway expansion and further drowning of siliciclastic source areas on the Transcontinental Arch and adjacent parts of the Canadian Shield is suggested for the middle Dunleith Formation (Rivoli Member), which marks the end of Decorah shale deposition throughout the region. The regional expansion of carbonate facies is recorded at several stratigraphic positions within the Galena Group. These facies shifts likely correspond to episodes of transgressive deepening and foundering of siliciclastic source areas, subdividing the Galena Group into several additional stratigraphic sequences (Witzke, 1999; Fanton et al., 2002).

3. Methods

In order to collect chemostratigraphic profiles at high stratigraphic resolution, this study utilized long drillcores with full penetrations of the Platteville and Decorah Formations in which carbonate units are preserved in the original limestone fabrics. The selected cores also penetrated bounding strata, and sampling in these units helped define stratigraphic baseline $\delta^{13}C$ values. Selected cores at the Iowa Geological Survey's Rock Library and the Illinois State Geological Survey's Geological Sample Library were logged and sampled at high stratigraphic resolution using an electric drill with 0.75-cm diameter dental carbide drill bit. All commercial well drilling technology in the United States of America tracks drilling depths in feet, and all of the curated cores are stored, retrieved, measured, and annotated using depth in feet. In order to preserve the integrity of these primary data, we report core sample depth intervals in feet, with ancillary meter scales in our illustrations. Core surfaces were abraded to expose fresh rock surfaces in order to avoid inadvertent cross-contamination between samples. Powdered rock samples of about 1 g were milled from drillcore segments, preferentially selecting for fine-grained carbonate mud matrix following the report of Ludvigson et al. (1996) that this component best captures the chemostratigraphic record. Milled powders from each sample position were mixed and stored in 2-ml microcentrifuge tubes.

Carbonate $\delta^{13}C$ analyses were performed on splits of about 5–10 μg of powdered sample that were removed from microcentrifuge tubes by scalpel, roasted for 1 h in vacuo at 380 °C to remove volatile contaminants, and reacted with anhydrous phosphoric acid at 72 °C in a Finnigan Kiel III carbonate reaction device coupled to the inlet of a Finnigan MAT 252 stable isotope mass spectrometer at the Paul H. Nelson stable isotope laboratory at the University of Iowa. Analytical results are reported in standard delta notation in per mil deviations relative to the Vienna Pee Dee belemnite (VPDB) carbon isotope standard, with precision for carbon isotope analyses better than ± 0.05‰.

4. Results

4.1. New data from the Cominco Millbrook Farms SS-9 drillcore (locality 1)

The Cominco Millbrook Farms SS-9 drillcore (drilled in 1975; Iowa Geological Survey site W-27581; Sec. 29, T84N, R1E in Jackson County, Iowa) was one of the discovery sites for the Guttenberg carbon isotope excursion (Hatch et al., 1987), and is shown as locality 1 in Figs. 1 and 3. Published carbonate carbon isotopic profiles from this reference section from Ludvigson et al. (1996) and Pancost et al. (1999) are compared in Fig. 6. Both studies reported the same peak $\delta^{13}C$ values in the same stratigraphic position for the Guttenberg excursion, but produced profiles with differing chemostratigraphic details, apparently resulting from differing sampling positions. For example, a prominent negative shift in $\delta^{13}C$ values in the upper part of the Spechts Ferry Shale (Fig. 6) reported by Ludvigson et al. (1996) occurs in an interval that was not sampled by Pancost et al. (1999). Likewise, a positive shift in carbon isotopic values in the Platteville Formation (Fig. 6) reported by Pancost et al. (1999) occurs in an interval that was not sampled by Ludvigson et al. (1996). Taken together, the two published profiles suggest that a sensible, higher-resolution chemostratigraphic record is embedded in the stratigraphic section that was not captured by these earlier studies. In order to test this hypothesis, the stratigraphic interval of the Spechts Ferry Shale and bounding strata was resampled at higher stratigraphic resolution from the 680- to the 700-ft-depth levels to test for a more intricate structure in the chemostratigraphic record. The results of this newer work are shown in the inset profile in Fig. 6, and show that while the isotopic results from the earlier published reports can be replicated, neither of the earlier studies sampled at sufficiently high resolution to capture the detailed structure of the chemostratigraphic record. While all three different studies captured the rising limb of the positive Guttenberg carbon isotope excursion through this interval, the presence of abrupt negative shifts in $\delta^{13}C$ values as secondary features embedded within this interval of overall increasing $\delta^{13}C$ values was not fully recognized until now. Of special note is the abrupt 2‰ negative shift in $\delta^{13}C$ values at the precise position of the Platteville–Decorah sequence boundary. The significance of this chemostratigraphic feature will be discussed later.

4.2. Big Spring #4 drillcore (locality 2)

The Big Spring # 4 drillcore (drilled in 1989; Iowa Geological Survey site W-30096; Sec. 20, T95N, R6W in Clayton County, Iowa) was sampled for this study from the 440- to the 529-ft-depth levels, including strata of the Pecatonica and McGregor members of the Platteville Formation, all of the Decorah Formation, and strata of the Beecher and Eagle Point members of the Dunleith Formation (Fig. 7). This drill site is located very near the proximal depositional limit of the Guttenberg Limestone, and is shown as locality 2 in Figs. 1 and 3.

This comparatively lengthy time series of carbon isotopic ratios from the basal Platteville carbonates ranging upward into the Dunleith carbonates (Fig. 7) is one of increasing $\delta^{13}C$ values, starting at a lower baseline value of around -2‰ and rising to an upper baseline value of about -0.5‰ VPDB. A simple linear regression of the profile yields an upward increase in $\delta^{13}C$ values of 0.013‰/ft (0.042‰/m) of stratigraphic section. Superimposed on that longer-term trend are more short-term positive and negative excursions. These include two positive excursions in the McGregor Member of the Platteville Formation, in the lower Mifflin beds (up to about 0‰) and the lower Grand Detour beds (up to about 0‰), a negative excursion in the upper Grand Detour beds (down to about -3‰), and two positive excursions in the Decorah Formation, in the Spechts Ferry Member (up to about $+0.5$‰), and the Guttenberg Member (up to about $+1.5$‰).

4.3. Elkader A1 drillcore (locality 3)

The New Jersey Zinc A1 drillcore located near Elkader, Iowa (drilled in 1963; Iowa Geological Survey site W-27254, Sec. 8, T92N, R5W in Clayton County, Iowa), was sampled for this study from the 150- to the 235.9-ft-depth levels, including strata of the McGregor Member of the Platteville Formation, all of the Decorah Formation, and strata of the Beecher and Eagle Point members of the Dunleith Formation (Fig. 8). This drill site is in a slightly more distal position than the Big Spring #4 drill site, and is shown as locality 3 in Figs. 1 and 3.

As in the previous case, the long-term time series of carbon isotopic ratios in this core is one of gradually upward increasing $\delta^{13}C$ values, rising to an upper baseline value of about -0.5‰ VPDB (Fig. 8). Superimposed on the long-term trend are shorter-term positive and negative excursions. These include

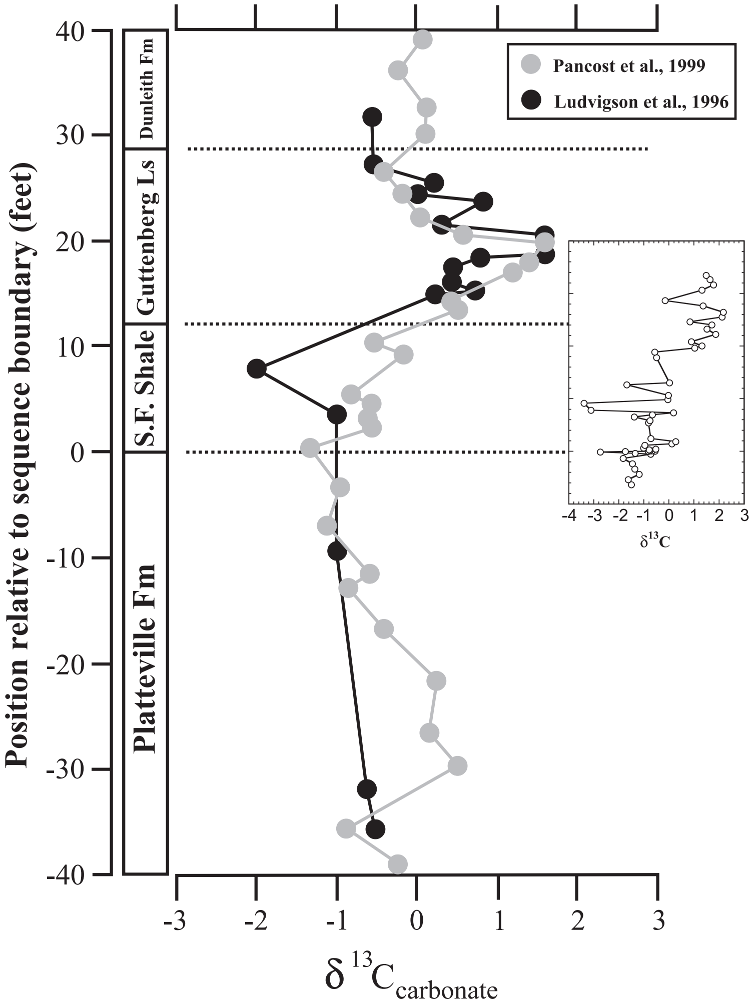

Fig. 6. Carbon isotopic profiles from locality 1, the Cominco Millbrook Farms SS-9 drillcore in Jackson County, Iowa. Discrepancies between reported depths from chemostratigraphic profiles published in Ludvigson et al. (1996) and Pancost et al. (1999) were reconciled by calibrating stratigraphic thicknesses to the Platteville–Spechts Ferry contact. The inset box to the right shows a new higher-resolution profile of the Spechts Ferry Shale and parts of the bounding stratigraphic units in the SS-9 drillcore, collected at even more closely spaced intervals than the two earlier studies.

the same positive excursions in the McGregor Member of the Platteville Formation, in the lower Mifflin beds (up to about +0.5‰) and the lower Grand Detour beds (up to about 0‰), a negative excursion in the upper Grand Detour beds (down to about −2‰), and two distinct positive excursions in the Decorah Formation, in the lower Spechts Ferry (up to about 0‰) and Guttenberg (up to about +1.5‰) intervals. These two positive ^{13}C excursions in the Decorah Formation are separated by an abrupt negative shift in δ^{13}C values in the upper Spechts Ferry Member (down to about −2‰).

4.4. Cominco SS-12 drillcore (locality 4)

The Cominco P. Hueneke SS-12 drillcore (drilled in 1976; Iowa Geological Survey site W-27584; Sec. 18, T87N, R4E in Jackson County, Iowa) was sampled for this study from the 290- to the 358.9-ft-depth levels, including strata of the McGre-

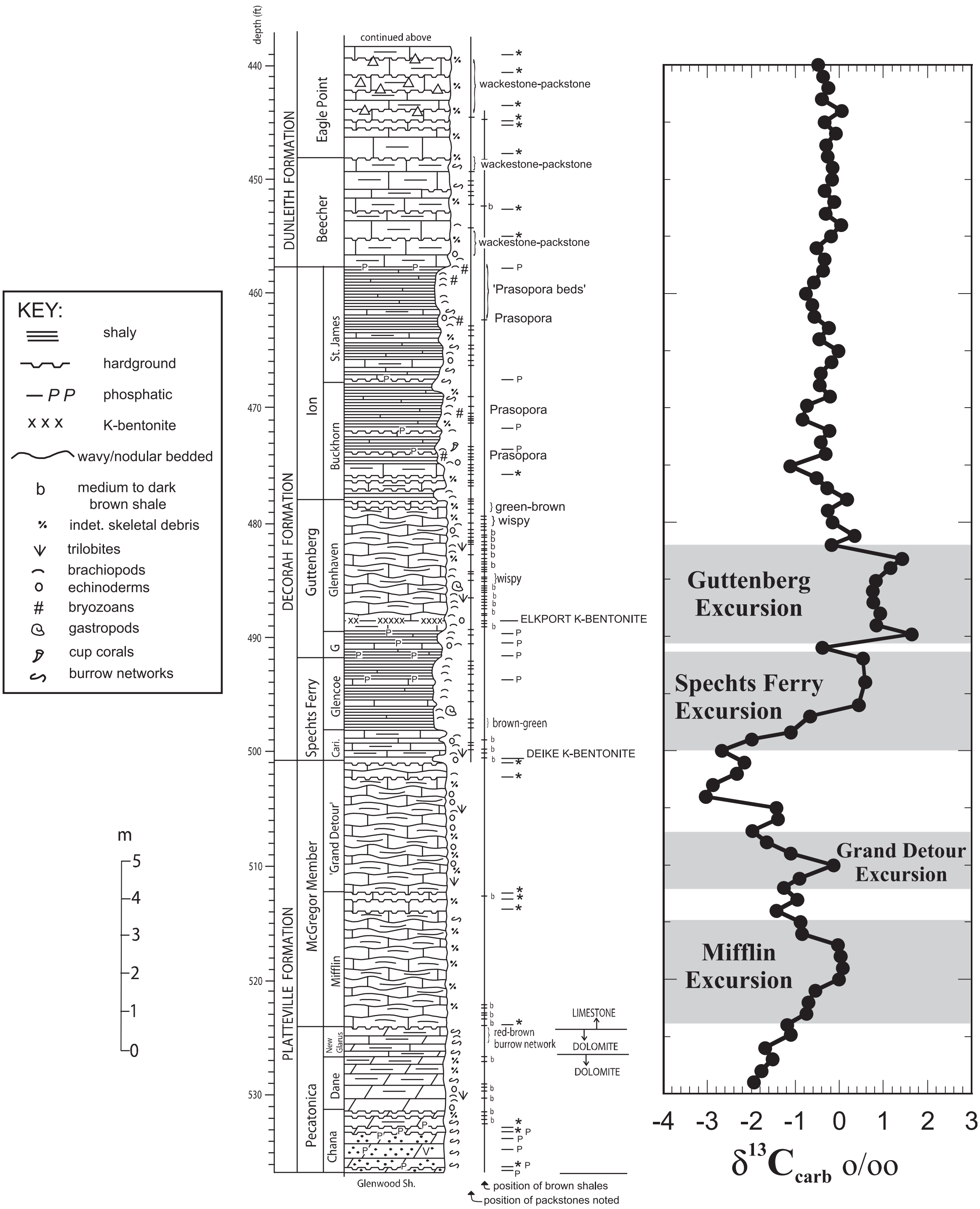

Fig. 7. Graphic log and δ^{13}C profile of locality 2, the Big Spring No. 4 drillcore in Clayton County, Iowa.

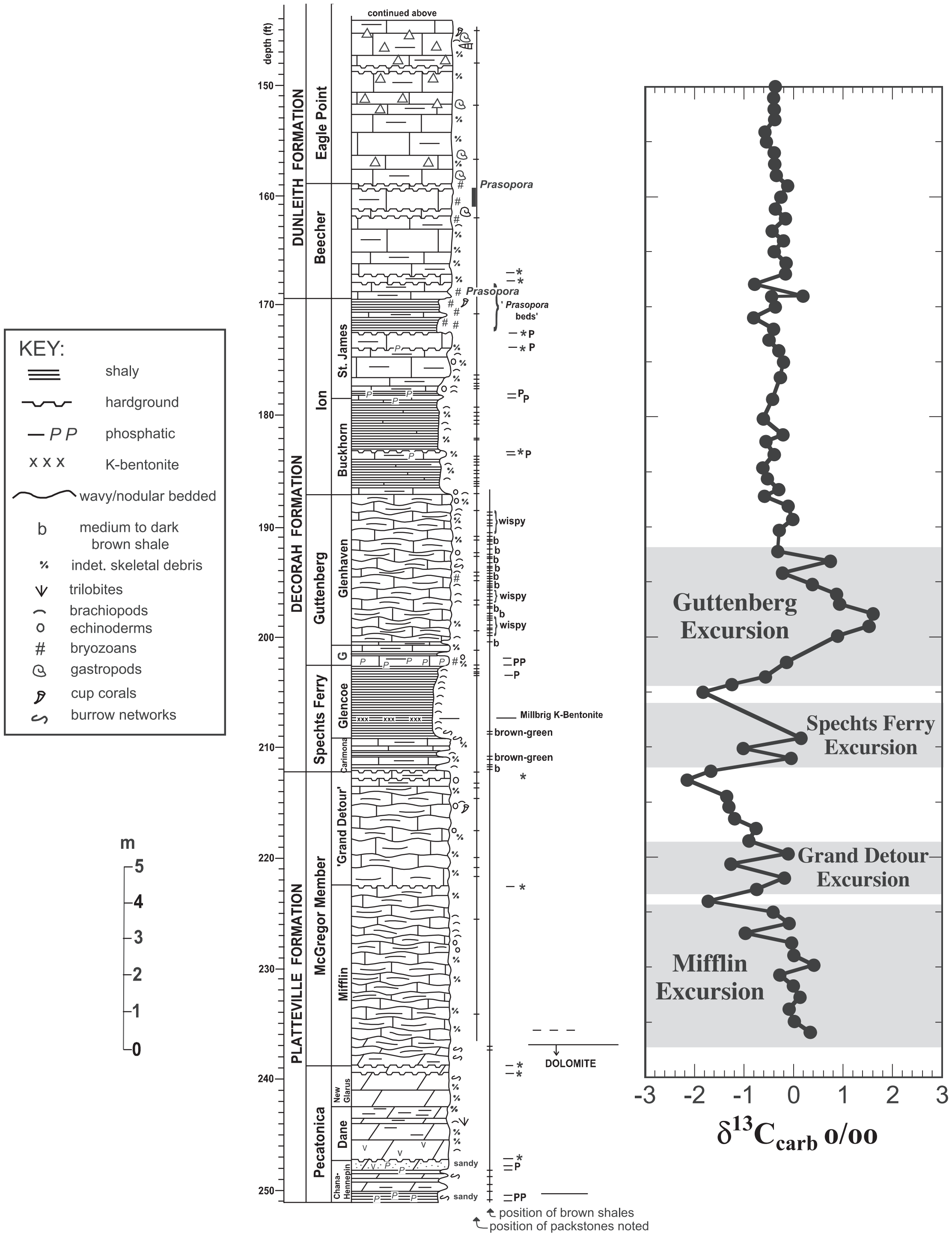

Fig. 8. Graphic log and δ^{13}C profile of locality 3, the Elkader A1 drillcore in Clayton County, Iowa.

gor and Quimby's Mill members of the Platteville Formation, all of the Decorah Formation, and strata of the Buckhorn, St. James, Beecher, and Eagle Point members of the Dunleith Formation (Fig. 9). This drill site is located near the Cominco SS-9 discovery site for the Guttenberg excursion, and is shown as locality 4 in Figs. 1 and 3.

As in the previous cases, $\delta^{13}C$ values in this core gradually increase upward to an upper baseline of about −0.5‰, with superimposed positive and negative excursions (Fig. 9). These include positive excursions in the Platteville Formation, in the lower Grand Detour beds of the McGregor Member (up to about −0.3‰) and the Quimbys Mill Member (up to about +1‰), separated by a negative excursion in the upper part of the Grand Detour beds (down to about −1.5‰). As before, two distinct positive excursions occur in the Decorah Formation, in the lower Spechts Ferry Member (up to about +2‰) and the Guttenberg Member (up to about +2.5‰). The positive excursions in the Quimbys Mill and Spechts Ferry intervals are separated by an abrupt negative shift in $\delta^{13}C$ values to as low as −2.2‰.

4.5. Cominco SS-2 drillcore (locality 5)

The Cominco Poll SS-2 drillcore (drilled in 1973; Iowa Geological Survey site W-27574; Sec. 36, T85N, R3E in Jackson County, Iowa) was sampled for this study from the 696- to the 751.9-ft-depth levels, including strata of the McGregor and Quimby's Mill members of the Platteville Formation, all of the Decorah Formation, and strata of the Buckhorn and St. James members of the Dunleith Formation (Fig. 10). This drill site is also located near the Cominco SS-9 discovery site for the Guttenberg excursion, and is shown as locality 5 in Figs. 1 and 3.

The pattern of long-term upward increase in $\delta^{13}C$ values appears to be present in this core as well, with an upper baseline value increasing to about 0‰ VPDB (Fig. 10). Superimposed on this trend are more short-term excursions in the Platteville Formation, including the falling limb of the positive excursion in the lower Grand Detour interval (peak values up to about −0.2‰) and a positive excursion in the upper Quimbys Mill interval (up to about +1.5‰), separated by a negative excursion in the upper Grand Detour interval (down to −1.5‰). As before, positive excursions in the Decorah Formation occur in the lower Spechts Ferry interval (up to about 0‰) and the Guttenberg interval (up to about +2.5‰). Positive excursions in the Quimbys Mill and Spechts Ferry intervals are separated by an abrupt negative shift in $\delta^{13}C$ values to as low as −2‰.

4.6. Harris No. 1 drillcore (locality 6)

The Northern Natural Gas V. Harris No. 1 drillcore (drilled in 1961; Iowa Geological Survey site W-13816; Sec. 1, T73N, R4W in Louisa County, Iowa) was sampled for this study from the 834- to the 895-ft-depth levels, including strata of the Pecatonica and McGregor members of the Platteville Formation, all of the Decorah Formation, and strata of the Buckhorn and St. James members of the Dunleith Formation (Fig. 11). This drill site is located west of the axis of maximum thickness of the Guttenberg Limestone Member of the Decorah Formation (Fig. 1), and very near the downlap edge of the Spechts Ferry Shale Member (Fig. 3), and is shown as locality 6 in Figs. 1 and 3.

The comparatively lengthy succession of chemostratigraphic samples in this core clearly shows a long-term upward increase in $\delta^{13}C$ values, starting with lower baseline values of about −2‰ in the Pecatonica interval, and ranging upward to baseline values of about 0‰ in the Buckhorn interval (Fig. 11). A simple linear regression of the profile yields an upward increase in $\delta^{13}C$ values of 0.039‰/ft (0.128‰/m) of stratigraphic section. Superimposed on the longer-term trend are positive excursions in the Mifflin interval (up to about −0.5‰), the rising limb of a positive excursion in the uppermost beds of the Grand Detour beds (up to about +1‰), a positive excursion in the Spechts Ferry interval (up to about +0.5‰), and a positive excursion (up to about +2‰) in the Guttenberg interval. A glaring discrepancy between this chemostratigraphic succession and those found in localities 2, 3, 4, and 5 is in the ^{13}C profile in the Grand Detour beds of the McGregor Member of the Platteville Formation. In the other sampling localities, a positive excursion to peak values of about 0‰ occurs in the lower part of this interval, whereas in the V. Harris No. 1 core, a unique positive excursion to peak values of about +1‰ occurs at the top of this interval. The lack of

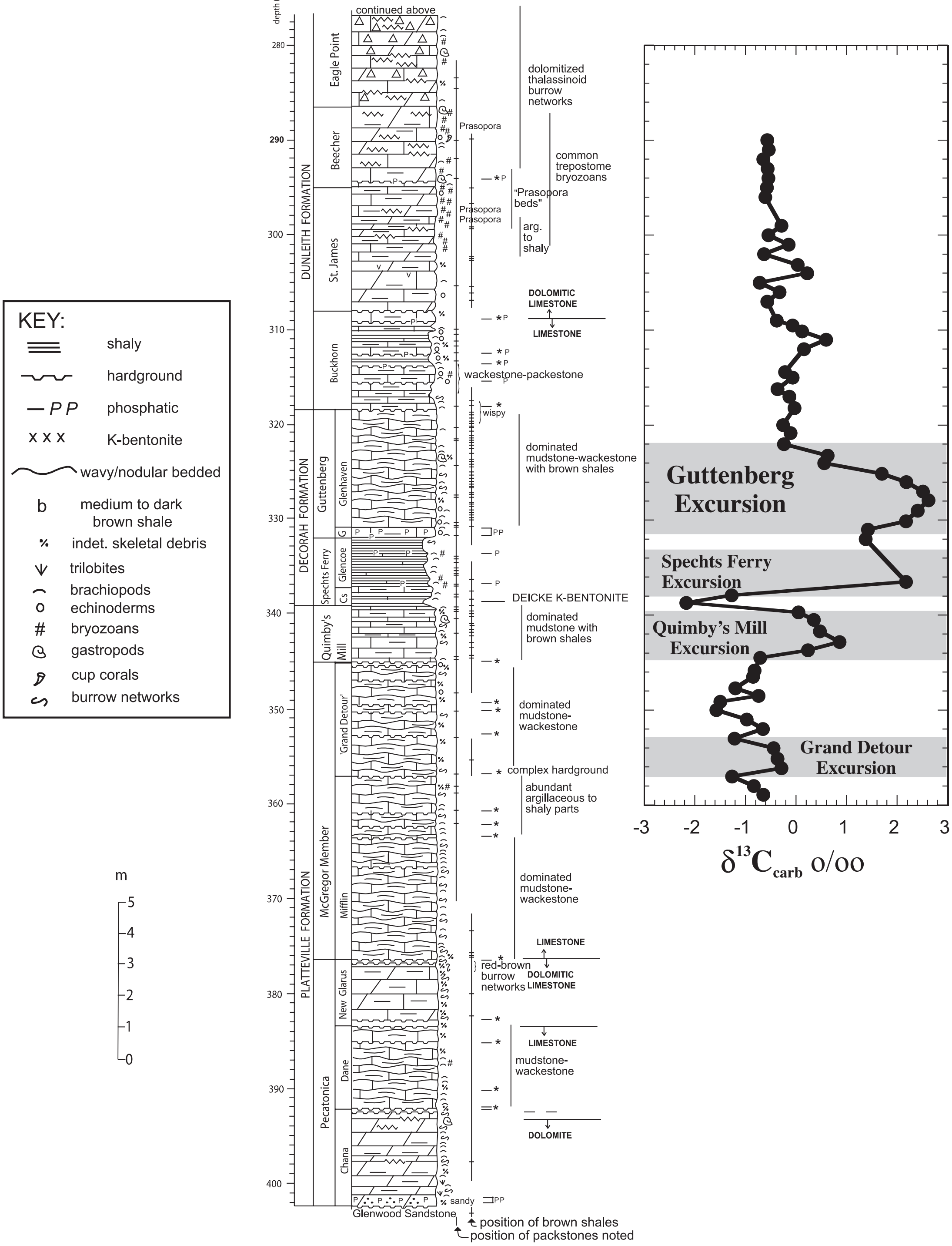

Fig. 9. Graphic log and δ^{13}C profile of locality 4, the Cominco SS-12 drillcore in Jackson County, Iowa.

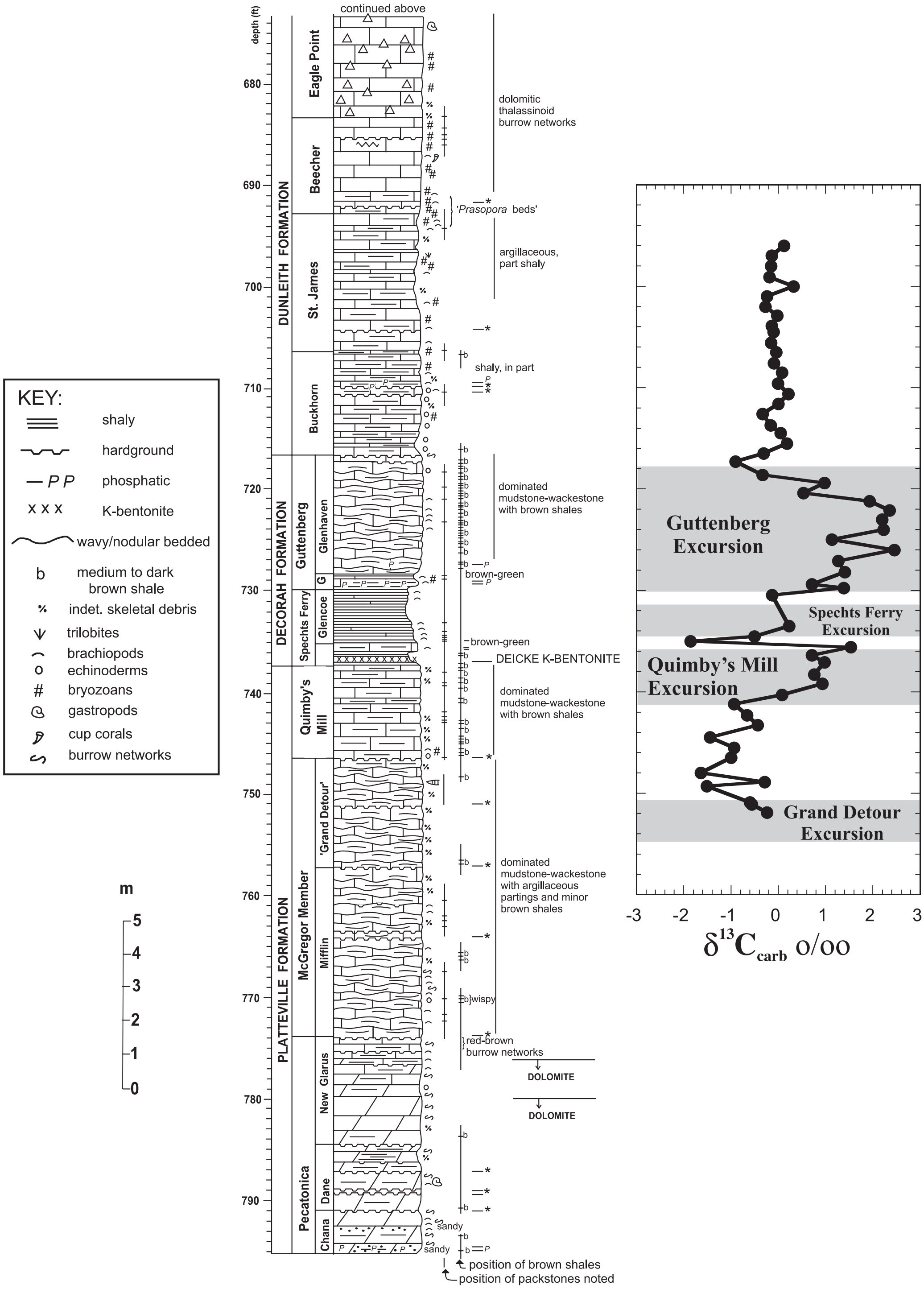

Fig. 10. Graphic log and δ^{13}C profile of locality 5, the Cominco SS-2 drillcore in Jackson County, Iowa.

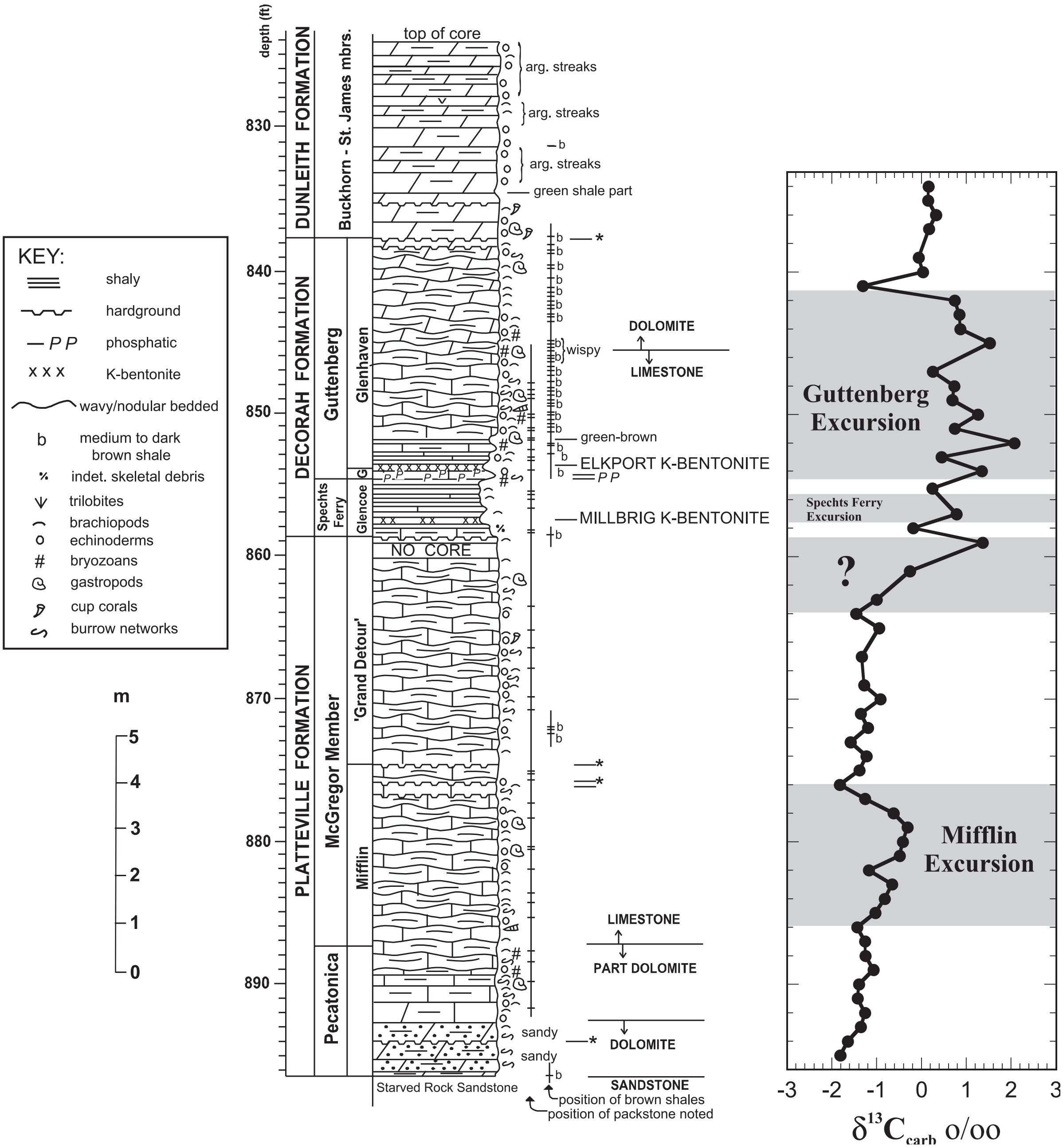

Fig. 11. Graphic log and δ^{13}C profile of locality 6, the Harris No. 1 drillcore in Louisa County, Iowa.

a positive excursion in the lower Grand Detour interval and lack of a negative excursion in the upper Grand Detour interval (to δ^{13}C values as low as -3‰) are unique to this locale.

4.7. Sample #1 drillcore (locality 7)

The Miller G.W. Sample #1 (drilled in 1939; Illinois State Geological Survey site C28; Sec. 11, T15N, R3W) drillcore in Sangamon County, Illinois (Shaw and Sargent, 1989) was sampled for this study from the 2340- to the 2430-ft-depth levels, including strata of the Quimbys Mill Formation, the Spechts Ferry Formation, and the Moredock facies of the Kimmswick Limestone (Fig. 12). This drill site is located outward beyond the downlap limits of the Guttenberg Limestone Member of the Decorah Formation, and is shown as locality 7 in Figs. 1 and 3.

A gradual upward increase in $\delta^{13}C$ values is also evident in this core, with baseline values from the lower sampled interval of about 0‰ ranging upward to about +0.5‰ at the top of the sampled interval (Fig. 12). A prominent positive carbon isotope excursion occurs in the Quimbys Mill interval, with $\delta^{13}C$ values up to about +2.75‰ VPDB. Another positive carbon isotope excursion occurs in the Castlewood interval, with $\delta^{13}C$ values ranging up to about +1‰, and punctuated by three abrupt negative shifts in $\delta^{13}C$ values to as low as −0.5‰. Of special note is the complete absence of any Guttenberg strata, and despite very dense chemostratigraphic sampling across this interval, the complete absence of the positive Guttenberg carbon isotope excursion (Fig. 12). As is shown in Fig. 3, the Guttenberg interval is completely starved out at this locale.

4.8. New stratigraphic observations on the Platteville–Decorah sequence boundary

The presence of a pronounced positive carbon isotope excursion in the Quimbys Mill carbonates in the Cominco SS-12 and SS-2 drillcores (localities 4 and 5 in Figs. 1, 3, 9, and 10)) and their complete absence in the nearby Cominco SS-9 drillcore (locality 1 in Figs. 1, 3, and 6)) posed significant questions about the nature of the Platteville–Decorah boundary in eastern Iowa. Could diagenetic overprinting have possibly removed the record of the Quimbys Mill carbon isotope excursion in the SS-9 core? First, there are no Quimbys Mill strata in the SS-9 core. Moreover, earlier diagenetic studies of carbonate beds in the Cominco SS-9 drillcore by Ludvigson et al. (1996) produced data showing standard deviations in $\delta^{13}C$ values that ranged between 0.08‰ and 0.45‰, extracted by repetitive microsampling of micritic components in each stratigraphic rock sample. This lack of significant variability indicates that little, if any, diagenetic overprinting has occurred in relation to the original micritic $\delta^{13}C$ values, and Ludvigson et al. (1996) interpreted the data as well-preserved isotopic records of early submarine diagenesis in subtidal carbonates. The differences in drillcore records are not related to diagenetic complications.

In order to further examine the discrepancies between the apparent chemostratigraphic records in the SS-12 and SS-2 drillcores with that of the SS-9 drillcore noted above, detailed stratigraphic logging of the interval in question was undertaken in these cores, along with a supplemental intervening cored stratigraphic section (the Cominco Saunders SS-4A; drilled in 1975; Iowa Geological Survey site W-27576; Sec. 35, T84N, R2E in Jackson County, Iowa). The results of this logging and stratigraphic synthesis are portrayed in Fig. 5.

The positive Quimbys Mill carbon isotope excursion interval occurs in carbonate mudstones with interbedded brown shales in the upper part of the unit (Fig. 5). Reconnaissance petrography of these laminated and sparsely burrowed skeletal carbonate mudstones (at the 338.9-, 339.6-, 342.4-, and 344.7-ft levels in the SS-12 core) shows a noteworthy abundance of detrital quartz silt. The Quimbys Mill strata, the overlying Deicke K-bentonite bed, and lower portions of the overlying Carimona carbonates all downlap onto a complex hardground surface over the lateral distance of a few tens of kilometers. Localities 4 and 5 were the only sampled sections in Iowa that captured the Quimbys Mill excursion. In light of these observations, it appears that these closely spaced cores penetrated the depositional edge of a lobe of Quimbys Mill carbonate strata that prograded into Iowa from a depositional center to the east.

Ludvigson et al. (1996, p. 74) briefly commented on the petrography of the Platteville–Decorah sequence boundary in the Cominco Millbrook Farms SS-9 drillcore (locality 1, Figs. 1 and 3), and further details are presented here. The contact is a complex hardground surface (Fig. 5) consisting of a stack of discrete millimeter to centimeter-scale skeletal packstones that engulf hardground clasts of underlying Platteville skeletal wackestones (Fig. 13). The packstone beds have sharp unit contacts at the thin section scale, and are each characterized by unique deposi-

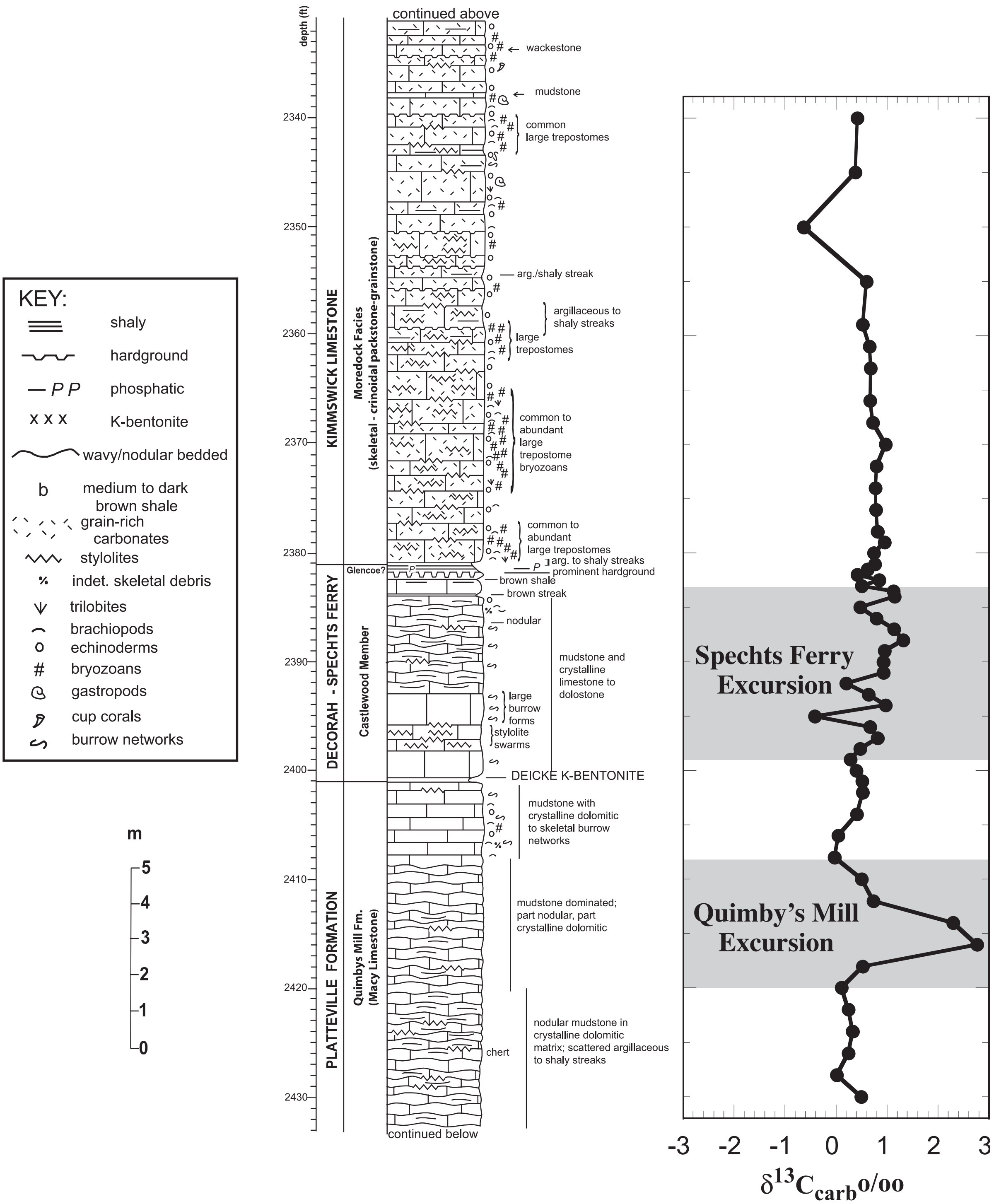

Fig. 12. Graphic log and δ^{13}C profile of locality 7, the C28 drillcore in Sangamon County, Illinois.

tional and diagenetic characters. Packstone A is immediately underlain by a pyrite-impregnated surface (Fig. 13), and contains a brown shaly matrix. Packstone B is a more coarse-grained whole shell brachiopod-bearing unit with euhedral–subhedral dolomite rhombs (up to 0.25-mm wide) floating in the matrix. Packstone C is a brachiopod-echinoderm unit with a modal abundance of $\geq 50\%$ detrital quartz silt. The B–C surface is draped by brown shale, and packstone C also contains brown shale infiltrate. Packstone D is another coarse-grained whole-shell brachiopod-bearing unit with abundant brown shale infiltrate and euhedral dolomite rhombs floating in the matrix. Packstone E is another unit with high modal abundance of detrital quartz silt ($\geq 50\%$) and discrete thin layers of interbedded brown shale. Packstone F is another coarse-grained whole shell brachiopod-bearing unit with abundant brown shale infiltrate. Hardground clasts of skeletal wackstones are variably impregnated by opaque sedimentary iron sulfides

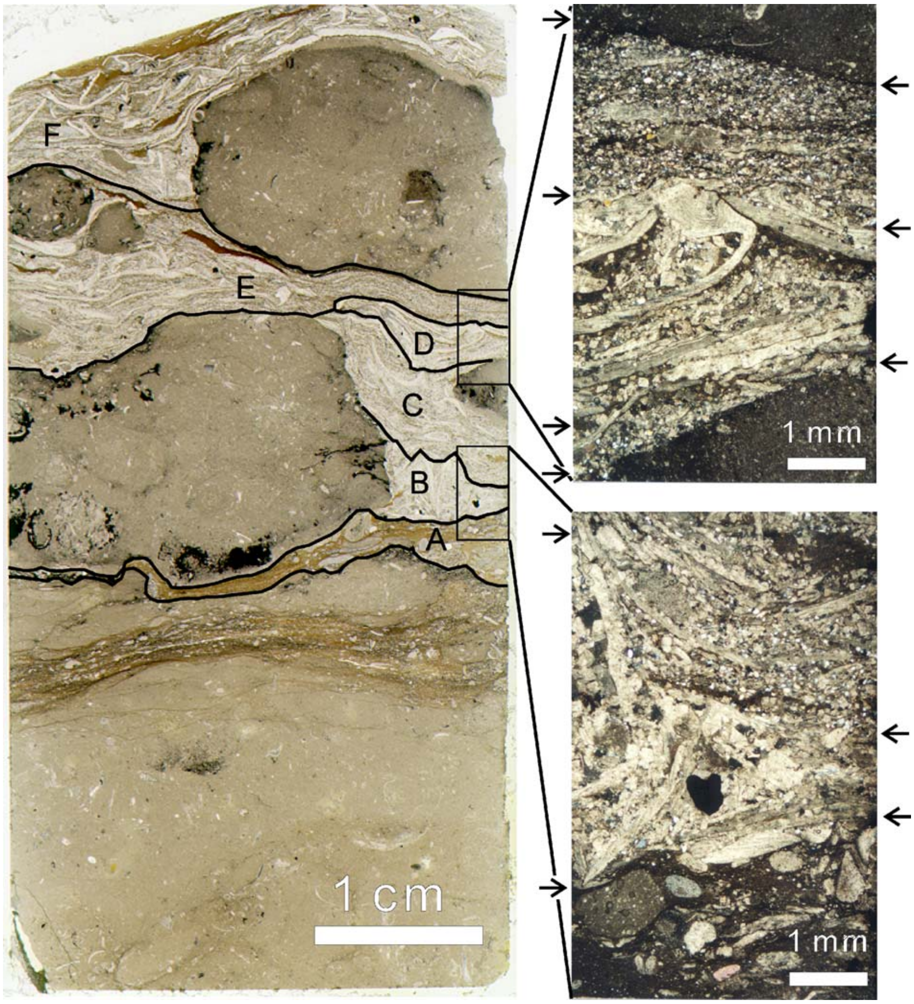

Fig. 13. Microstratigraphy of the Platteville–Decorah formational contact at locality 1, the Cominco Millbrook Farms SS-9 drillcore. To the left is a scanned image of a thin section of the contact interval. Boundaries between packstones A–F are annotated on the image. To the lower right is a thin section photomicrograph (cross-polarized light) of the A–B and B–C packstone boundaries marked by arrows on the side. To the upper right is a thin section photomicrograph of the C–D and D–E packstone boundaries marked by arrows on the side. (For color see online version).

around their margins. The amalgamation of discrete thin packstone units above this hardground surface suggests extreme condensation of units above the hardground surface.

5. Discussion

5.1. Stratigraphic and paleogeographic patterns of the isotope data

The five positive carbon isotope excursions reported here amend earlier simpler conceptions of mid-Caradoc carbon isotope chemostratigraphy in which only a single event (Guttenberg positive excursion) was previously noted. Moreover, the peak $\delta^{13}C$ magnitudes of these excursion events vary considerably over the sampled geographic area in Iowa and Illinois. These results indicate that considerable caution should be exercised in formulating interregional chemostratigraphic $\delta^{13}C$ correlations of Late Ordovician strata without similar high resolution stratigraphic sampling and the availability of other independent chronostratigraphic constraints.

The gradual stratigraphically upward increases in $\delta^{13}C$ values in Upper Ordovician strata reported here are consistent with earlier reports by Ludvigson et al. (1990), Qing and Veizer (1994), Ludvigson et al. (1996), and Veizer et al. (1999) of longer-term secular changes in the isotopic compositions of Ordovician marine carbonates. The five higher-frequency carbon isotopic excursions identified in this report are embedded within a longer-term interval of dramatic global change recorded by the Ordovician chemostratigraphic record, an interval that culminated in a later Ashgill continental glaciation at high southern latitudes (Veizer et al., 1999).

Stratigraphic baseline $\delta^{13}C$ values also show significant geographic variations along the north–south sampling transect (Fig. 1), with progressive ^{13}C enrichment to the south. While baseline values in the Platteville–Decorah interval are difficult to estimate because of the closely spaced isotope excursions, they are more easily estimated in the Ion Member of the Decorah Formation and its lateral equivalents, the Buckhorn and St. James members of the Dunleith Formation. In northern Iowa, baseline $\delta^{13}C$ values from this interval range between −1‰ and 0‰ (Figs. 7–10), while in southern Iowa they are very near 0‰ (Fig. 11). Even further to the south, the laterally equivalent Moredock facies of the Kimmswick Limestone has baseline values of about +0.5‰ (Fig. 12). This regional $\delta^{13}C$ gradient in the Upper Mississippi Valley region was reported by Ludvigson et al. (2001), and is consistent with a broader Turinian continental-scale $\delta^{13}C$ gradient identified by Holmden et al. (1998), with isotopically heavier values occurring closer to the continental margin.

The peak $\delta^{13}C$ values in the Quimbys Mill, Spechts Ferry, and Guttenberg positive carbon isotope excursions also appear to increase in a southward direction. In east-central Iowa, the peak $\delta^{13}C$ values in the Quimbys Mill excursion range between +1‰ and +1.5‰ (Figs. 7 and 8), whereas farther to the south in central Illinois, the Quimbys Mill excursion reaches peak $\delta^{13}C$ values of up to +2.75‰ (Fig. 12). In the sections from northern Iowa, the peak $\delta^{13}C$ values in the Spechts Ferry excursion range between 0‰ and +0.5‰ (Figs. 7 and 8), while farther to the south in the eastern Iowa sections, peak values range between +0.2‰ and +2.2‰ (Figs. 9–11), and in central Illinois they peak at +1.3‰ (Fig. 12). Peak $\delta^{13}C$ values in the Guttenberg excursion reach up to +1.5‰ in the northern Iowa sections (Figs. 7 and 8), and from +2.0‰ up to +2.6‰ in the sections farther to the south in eastern Iowa (Figs. 9–11). Ludvigson et al. (2000) reported peak $\delta^{13}C$ values greater than +2‰ from this interval in the exposed stratigraphic section at Eureka, Missouri (Fig. 2).

5.2. Carbon isotope excursions and coincident episodes of sediment starvation

As shown in Figs. 2, 3, and 5, the positive carbon isotope excursions of the Quimbys Mill, Spechts Ferry, and Guttenberg intervals occur in stratigraphic units that downlap to offshore submarine disconformities, and are condensed to absent in parts of the Upper Mississippi Valley. Kolata et al. (1998) have shown that some of these submarine disconformities can be widely traced through Ordovician carbonate strata across the eastern United States, suggesting that the processes responsible for shutting off carbonate accumulation operated at the geographic scale of the epeiric sea. Is this relationship purely coincidental, or do episodes of sedimentary organic carbon sequestration with resulting positive carbon isotope excursions and cessations of carbonate accumulation in offshore settings of the epeiric sea share a common cause? Studies of the Cominco SS-9 core (locality 1) are especially instructive in this regard. We have shown that the Quimbys Mill excursion interval is absent in this section, even though it was penetrated in the nearby SS-2 and SS-12 drillcores (Fig. 5). Petrographic studies of the surface of sediment starvation and overlying amalgamated packstones in the SS-9 core (Fig. 13) show three features that invite further comment: (1) the presence of abundant detrital quartz silt in packstones C and E; (2) the presence of brown shale infiltrates in the amalgamated packstones; and (3) impregnation of the surface beneath packstone A, and of the margins of hardground clasts by sedimentary iron sulfides.

As noted previously, reconnaissance petrography of laminated skeletal carbonate mudstones from the Quimbys Mill interval in the SS-12 core showed that dispersed detrital quartz silt is a prominent component in these rocks, in all likelihood an eolian constituent (Delgado, 1983). The presence of abundant detrital quartz silt in the amalgamated packstone units C and E (Fig. 13) suggests the possibility that these units could be extremely condensed correlates to portions of the Quimbys Mill Member.

Infiltrates of brown shale in the amalgamated packstones at the base of the Decorah Formation in the SS-9 core are of special interest because of the report by Pancost et al. (1998) that organic matter from this interval contains high molecular abundances of aryl isoprenoids. The aryl isoprenoids are fossil biomarkers for green sulfur bacteria, a group of obligate anaerobes requiring photic zone euxinia. The sedimentary context of organic biomarkers for euxinic water masses in close juxtaposition with the deposits of an aerobic shelly benthos suggests that euxinic conditions alternated with benthic environments that otherwise supported an aerobic macrobiota. The presence of sedimentary iron sulfide impregnations of the sculpted hardground surface, and of the exteriors of hardground clasts (Fig. 13) also are consistent with the idea of episodic euxinia during the development of this sediment-starved surface.

Kolata et al. (2001) reported that widespread Turinian–Chatfieldian carbonate hardground omission surfaces DS1, DS2, DS3, and DS4 (see Fig. 2) are drowning surfaces that converge in the Sebree Trough, a paleobathymetric feature (located over the failed Reelfoot Rift) through which oxygen-poor, phosphate-rich ocean waters were routed into the epeiric sea. Condensed graptolitic shales that accumulated in the Sebree Trough are characterized by lack of carbonate accumulation, development of hardground surfaces, substrate erosion, and phosphogenesis (ibid.). Witzke (1987) and Raatz and Ludvigson (1996) suggested that dysoxic or anoxic waters from the oxygen minimum zone in the open ocean were drawn as bottom currents into the Late Ordovician epeiric sea as part of a quasiestuarine circulation system. Raatz and Ludvigson (1996) suggested that the inflowing bottom currents entered the epeiric sea through the area of western Kentucky and Tennessee, and Kolata et al. (2001) specifically identified the Sebree Trough as the inlet through which bottom currents were drawn from below a pycnocline into the epeiric sea, and deflected by counterclockwise gyre into the Upper Mississippi Valley region. These paleoceanographic dynamics might in part be responsible for the regional condensation of Turinian–Chatfieldian strata in the eastern Iowa area (Fig. 4).

Petrographic and geochemical observations on the hardground surface at the base of the Decorah Formation in the SS-9 core discussed above (Figs. 5 and 13) are relevant to ideas on the general origins of regional hardground omission surfaces in the Ordovician of the Upper Mississippi Valley. The downlapped interval in Fig. 5 merges surfaces DS1 and DS2 of Kolata et al. (2001) with the complex hardground beneath the Quimbys Mill Member of the Platteville Fm (Fig. 2). In this particular instance, the abrupt termination and sediment starvation of two separate sedimentary sequences is interpreted to relate to the episodic impingement of euxinic water masses on the sea floor. The position of this hardground surface corresponds to a very abrupt and well-defined negative excursion in $\delta^{13}C$ values of 2‰ over a stratigraphic thickness of 5.18 cm (see inset plot in Fig. 6). The coarser-level sampling of Pancost et al. (1999) also showed a negative $\delta^{13}C$ shift at this position, the very same sample that also showed the peak molecular abundance of organic biomarkers for euxinic conditions (Pancost et al., 1998). These data suggest that extremely abrupt negative shifts in $\delta^{13}C$ values in these Ordovician stratigraphic sequences of subtidal carbonates could be geochemical markers for condensed intervals recording euxinic events during which carbonate accumulation was greatly attenuated.

The carbon isotopic effect of ^{13}C depletion by sulfate-reducing bacteria in diagenetic carbonates (Curtis et al., 1972) is well known in the geological literature, and the abrupt negative $\delta^{13}C$ shifts associated with pyrite-impregnated hardgrounds reported here could possibly be related to bacterial sulfate reduction effects on the isotopic composition of dissolved inorganic carbon in diagenetically active fluids, either within a benthic euxinic water mass or in shallow marine phreatic pore fluids below the sediment–water interface. In addition to the abrupt negative shift in $\delta^{13}C$ values at the Platteville–Decorah contact shown in Fig. 6, another abrupt negative $\delta^{13}C$ shift of about 3‰ occurs in the same section near the top of the Carimona carbonates (compare Figs. 5 and 6), coinciding with the position of DS2 of Kolata et al. (2001). Other abrupt negative shifts in $\delta^{13}C$ values occur at the position DS3 of Kolata et al. (2001) at locality 2 (Fig. 7), at the position of DS1 of Kolata et al. (2001) at locality 4 (Fig. 9), and DS2 of Kolata et al. (2001) at locality 5 (Fig. 10). These results suggest that a centimeter-scale $\delta^{13}C$ record of episodic incursions of euxinic water masses during marine flooding events might possibly be developed in the section. These negative $\delta^{13}C$ shifts might possibly be regarded as very localized diagenetic signals that developed at the position of drowning surfaces in the epeiric sea, and not from broader changes in the marine carbon cycle. Relationships between the Mifflin and Grand Detour carbon isotope excursions and the stratigraphic architecture of the Platteville Formation are not yet understood well enough to determine whether similar phenomena occurred in that interval.

6. Conclusions

Earlier conceptions of Turinian–Chatfieldian carbon isotope chemostratigraphy in the Upper Mississippi Valley region, in which a single positive $\delta^{13}C$ excursion occurs at the position of the Guttenberg Limestone, are now amended by the recognition of four additional excursion events in the Mifflin, Grand Detour, Quimbys Mill, and Spechts Ferry intervals. These five positive carbon isotope excursions are superimposed on a longer-term trend toward increasing background $\delta^{13}C$ values, by up to 2‰ over the span of the Pecatonica–Dunleith interval. A regional north–south $\delta^{13}C$ gradient is also reported, with lighter values to the north and heavier values to the south, both in background and peak excursion $\delta^{13}C$ values. The Quimbys Mill, Spechts Ferry, and Guttenberg positive carbon isotope excursions occur in subtidal carbonate strata that are bounded by submarine disconformities, and completely starve out in deeper, more offshore settings. Closely spaced chemostratigraphic sampling of carbonate strata bounding these disconformity surfaces suggests that abrupt negative $\delta^{13}C$ shifts of up to several per mil may be associated with them, possibly recording the incursion of euxinic bottom waters during marine flooding events.

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