

## A PROFILE OF THE MID-CARADOC (ORDOVICIAN) CARBON ISOTOPE EXCURSION AT THE MCGREGOR QUARRY, CLAYTON COUNTY, IOWA

G.A. Ludvigson, B.J. Witzke, C.L. Schneider, E.A. Smith,  
N.R. Emerson, S.J. Carpenter, and L.A. González

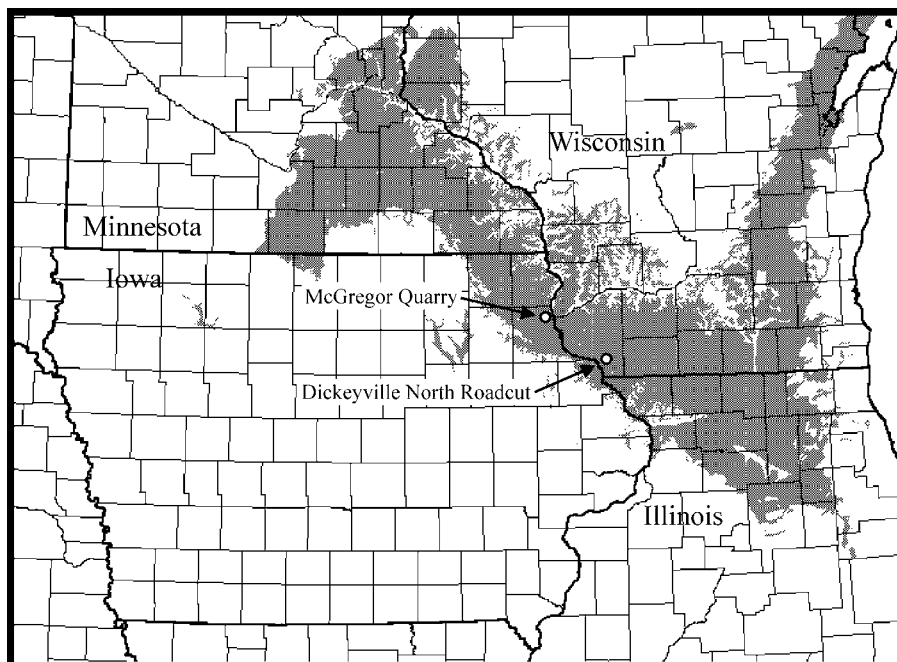
### Abstract

Carbonate  $\delta^{13}\text{C}$  profiles of a mid-Caradoc carbon isotope excursion are compared between three exposed stratigraphic sections: the McGregor Quarry in Clayton County, Iowa, the Dickeyville North Roadcut section in Grant County, Wisconsin, and the Eureka Roadcut section in St. Louis County, Missouri.

### Introduction

The Earth Sciences remain in a period of discovery of carbon isotope excursions, geologically brief episodes of changes in the  $^{13}\text{C}/^{12}\text{C}$  ratios of inorganic and organic carbon in stratigraphic successions of sedimentary rocks, recording global perturbations in the carbon cycle (Kump and Arthur, 1999). A

positive carbon isotope excursion first recognized in the Middle Ordovician Decorah Formation of eastern Iowa (Hatch et al., 1987; Ludvigson et al., 1996) has since been recognized in correlative carbonate strata in Pennsylvania (Patzkowsky et al., 1997) and Estonia (Ainsaar et al., 1999). Widespread appearance of this chemostratigraphic event, along with a coincident decrease in  $\delta^{13}\text{C}_{\text{carbonate}} - \delta^{13}\text{C}_{\text{organic matter}}$  values ( $\Delta^{13}\text{C}$ ) during the excursion (Patzkowsky et al., 1997; Kump and Arthur, 1999) suggest that the event was global in extent, recording a brief drawdown of atmospheric  $\text{pCO}_2$  resulting from increased



**Figure 1.** Location map showing the McGregor Quarry and the Dickeyville North Roadcut sections. The Eureka, Missouri, roadcut section is located to the southwest of St. Louis in east-central Missouri. Shaded area shows Ordovician outcrop belt.

marine organic carbon burial. Recent analysis of the carbon isotopic chemistry of chlorophyll-based photosynthetic biomarkers in the discovery site in eastern Iowa, the Cominco Millbrook Farms SS-9 drillcore (IGSB site W-27581) by Pancost et al., (1998, 1999), shows the same  $\Delta^{13}\text{C}$  values detected by

Patzkowsky et al. (1997) in Pennsylvania, further supporting the idea that the event recorded a global drawdown in atmospheric pCO<sub>2</sub>.

We recently embarked on an effort to characterize changes in the local expression of this carbon isotope excursion along a transect perpendicular to the ancient shoreline (Ludvigson et al., 2000; Smith et al., 2000). This transect extends from stratigraphic sections in southeastern Minnesota through eastern Iowa into western Illinois, ending in southeastern Illinois. The rock strata containing the excursion interval have been proposed to starve out in offshore settings along this cross section line by Ludvigson et al. (1996) and Kolata et al. (1998). While most of this work has involved studies of curated drillcores, we have also collected from exposed sections that contain widely-correlated volcanic ash beds of the Hagan K-bentonite complex, including the 454±0.5 Ma Deicke and 453.7±1.3 Ma Millbrig K-bentonites (Kolata et al., 1998). Studies of these sections permit refined chronostratigraphic correlations that have enabled us to assess local changes in the expression of the carbon isotope excursion (Smith et al., 2000). Among the surface sections that we have collected are the McGregor Quarry section adjacent to Pikes Peak State Park, the Dickeyville North Roadcut section in southwest Wisconsin, and the Eureka Roadcut section in southern Missouri. Comparisons between the lithostratigraphy and carbon isotope profiles of these sections are the subject of this paper.

All isotope analyses reported in this paper were performed at the Paul H. Nelson Stable Isotope Laboratory in the Department of Geoscience at The University of Iowa. Ludvigson et al. (1996) showed that the δ<sup>13</sup>C excursion signal in this interval resides in micritic components, and for this study, powdered carbonate samples were milled by dental drill bit from micritic domains in hand samples. Powdered carbonate samples were reacted with anhydrous phosphoric acid at 74 °C in a Kiel III automated carbonate reaction device coupled to the inlet of a Finnigan MAT 252 stable isotope ratio mass spectrometer. The analytical precision of reported δ<sup>13</sup>C values relative to the PDB standard is better than 0.05 ‰.

### The McGregor Quarry Section

The McGregor Quarry section exposes all of the Decorah Formation and its bounding units (Fig. 2). High wall exposures of the Platteville Formation were sampled along a talus cone in the southern part of the quarry, and the Decorah Formation and overlying strata of the Dunleith Formation were sampled above a bench at the top of the Platteville. The best exposures of the Spechts Ferry Member of the Decorah Formation are only accessible on life-threatening slopes, and thus the sampling frequency in this interval was lower than in other units in the section.

Uppermost Platteville strata below the Deicke K-bentonite in the McGregor Quarry show baseline δ<sup>13</sup>C values between -2 to -1.5 ‰ (Fig. 2). Carbonate beds immediately above the Deicke show an abrupt negative shift to a value less than -3 ‰, followed by a positive shift in the interval below and immediately above the Millbrig K-bentonite. As noted in other sections in the area (Ludvigson et al., 1996), the interval of the Spechts Ferry Member often includes a negative carbon isotope excursion, and this is also evident in the section at the McGregor Quarry. Above this negative excursion is an interval showing an abrupt positive excursion reaching to δ<sup>13</sup>C values above +1 ‰ in the uppermost beds of the Spechts Ferry Member and at the base of the Guttenberg Member, just above the position of the Elkport K-bentonite (Fig. 2).

Multiple positive δ<sup>13</sup>C peaks have previously been noted in the Guttenberg Member (Ludvigson et al., 1996), and the high stratigraphic sampling frequency in this interval at the McGregor Quarry shows a systematic organization into two well-defined positive peaks with values greater than +1 ‰, separated by a negative shift reaching to a value less than 0 ‰ PDB (Fig. 2). The two positive peaks occur below the position of a possible bentonite occurrence in the upper Guttenberg Member (?Dickeyville? K-bentonite). Upward from this position, δ<sup>13</sup>C values undergo a steady decline in baseline values from about 0 to -1 ‰ (Fig. 2). The uppermost beds of the Ion Member appear to show an abrupt positive shift of about 1 per mil that interrupts this mostly steady decline in δ<sup>13</sup>C values.

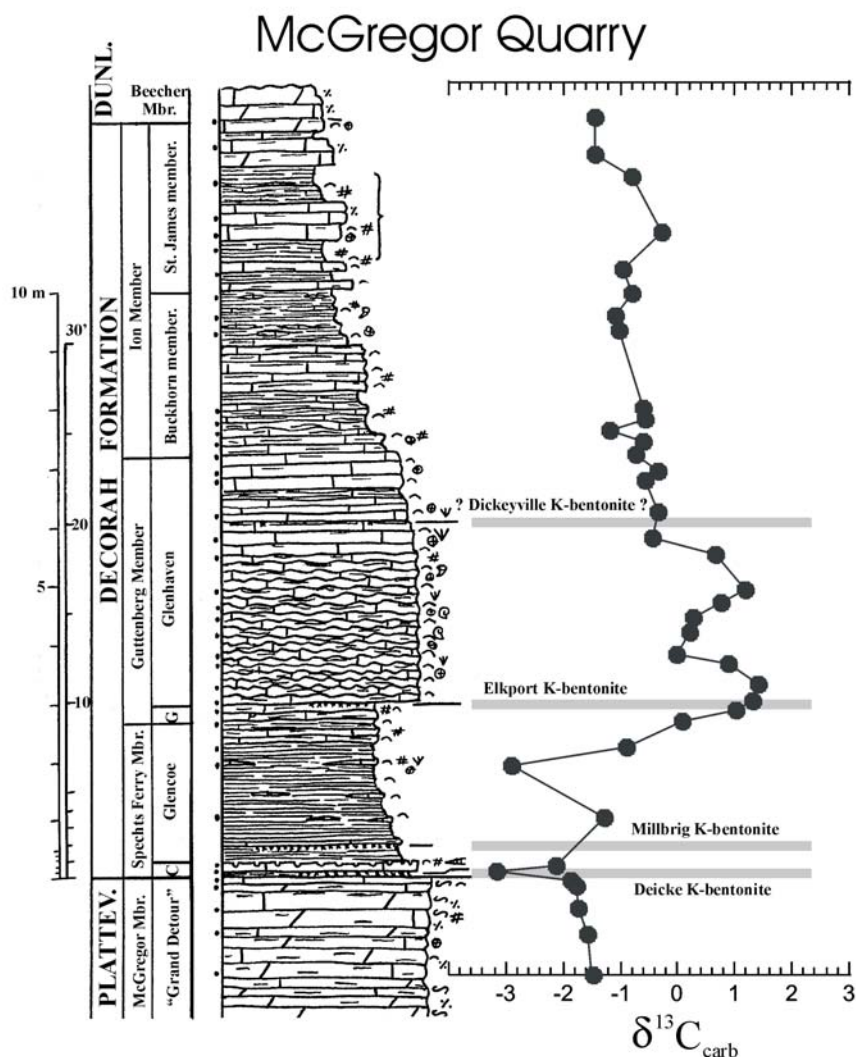


Figure 2. Graphic log of the McGregor Quarry section, showing a matching carbon isotope profile of sampled carbonate beds.

### The Dickeyville North Section, Southwest Wisconsin

The Dickeyville North Roadcut Section (locality 40 of Kolata et al., 1986) exposes uppermost strata of the Platteville Formation and much of the Decorah Formation (Fig. 3). In this section, uppermost Platteville strata have baseline  $\delta^{13}C$  values of a little less than  $-1$  ‰, about the same as in the McGregor Quarry section. Unlike the profile in the McGregor Quarry, the profile from the Dickeyville section shows no negative shift in  $\delta^{13}C$  values at the position of the Deicke K-bentonite. Instead, an abrupt positive shift in  $\delta^{13}C$  values begins just below the Deicke, and continues to a position just above the Millbrig K-bentonite (Fig. 3). This lower positive carbon isotope excursion interval is a common feature observed in many profiles (Smith et al., 2000) that we have sampled.

Dickeyville North Section, Grant Co., Wisconsin  
6-8-2000

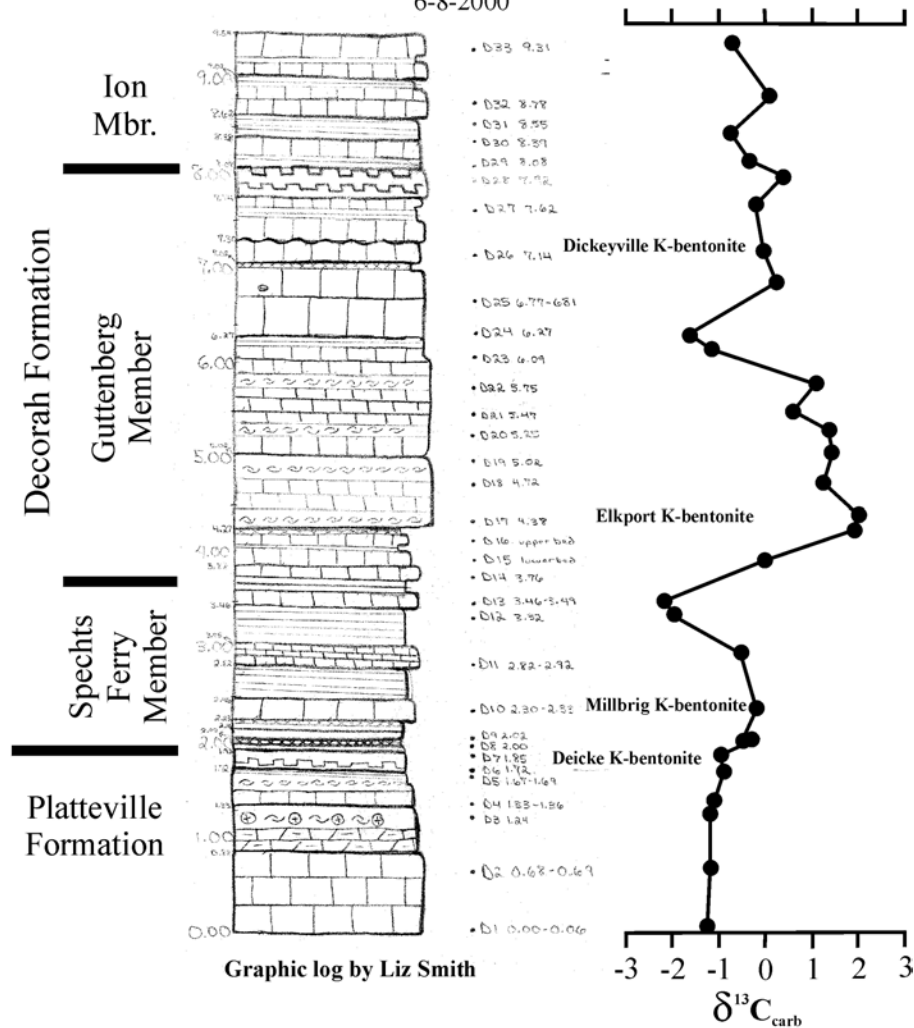


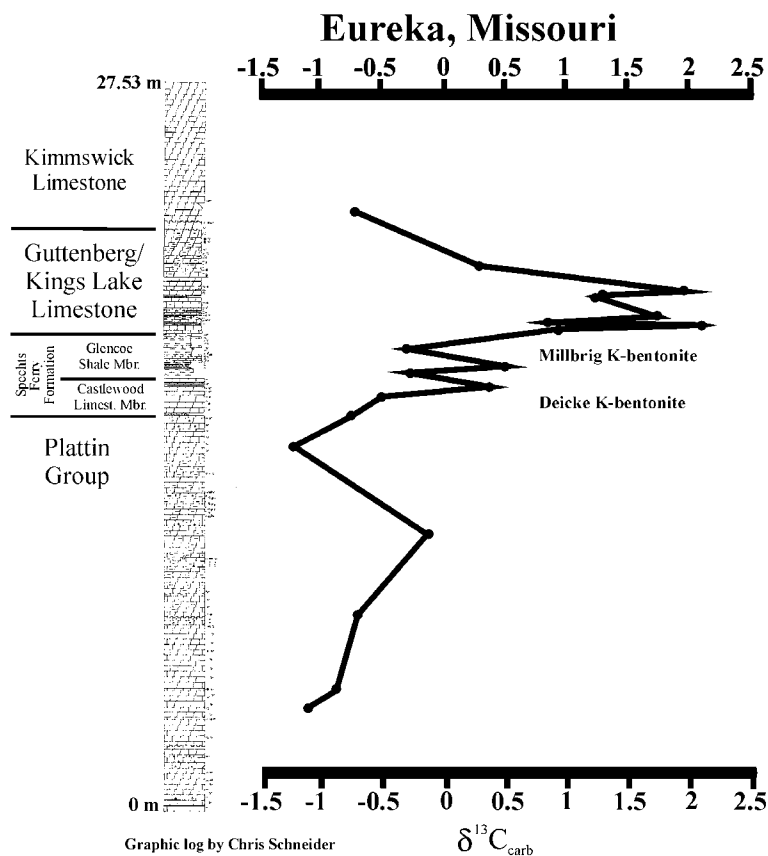
Figure 3. Graphic log of the Dickeyville North Roadcut section, showing the carbon isotope profile of sampled carbonate beds.

As was the case in the McGregor Quarry section, a negative shift to  $\delta^{13}\text{C}$  values less than  $-2\text{‰}$  occurs in the Spechts Ferry Member at the Dickeyville section, followed by a positive excursion to peak values of about  $+2\text{‰}$  (Fig. 3). The dual positive peaks seen at the McGregor Quarry section are not evident at the Dickeyville section. Instead, a broad-shouldered positive excursion is succeeded by a negative shift to  $\delta^{13}\text{C}$  values less than  $-1\text{‰}$  below the Dickeyville K-bentonite. Above the Dickeyville K-bentonite, the profile returns to baseline values mostly between  $-1$  to  $0\text{‰}$  PDB (Fig 3).

The Eureka, Missouri, Roadcut Section

Longer-range correlation of the carbon isotope excursion within the North American midcontinent region is shown by comparison to the  $\delta^{13}\text{C}$  profile at Eureka, Missouri. The Eureka, Missouri roadcut section (locality 217 of Kolata et al., 1996; archived collection stored as IGSB site W-31225) exposes the Spechts Ferry Formation, and the Kings Lake/Guttenberg limestones and their bounding units (Fig. 4;

stratigraphic terminology after Thompson, 1991). In this section, uppermost strata of the Plattin Group have variable  $\delta^{13}\text{C}$  values that range between less than  $-1$  to a little less than  $0$  ‰ PDB (Fig. 4). A positive excursion in  $\delta^{13}\text{C}$  values begins below the position of the Deicke K-bentonite and extends upward to the position of the Millbrig K-bentonite, with peak values of about  $+0.5$  ‰ (Fig. 4). As in the other sections discussed above, a negative shift, in this case to  $\delta^{13}\text{C}$  values of about  $-0.5$  ‰, occurs in the upper part of the Glencoe Shale Member of the Spechts Ferry Formation, and is immediately succeeded by the major positive shift in  $\delta^{13}\text{C}$  values, with peak values ranging up to  $+2$  ‰ in the lower part of the Kings Lake/Guttenberg interval (Fig. 4). Multiple positive peaks are present in this interval at Eureka, although from the present stratigraphic sampling density, it is unclear whether these shifts are organized into systematic, well-organized trends (Fig. 4). In the upper part of the Kings Lake/Guttenberg interval,  $\delta^{13}\text{C}$  values decrease back to baseline values less than  $-0.5$  ‰ in the basal Kimmswick Limestone.



**Figure 4.** Graphic log of the Eureka, Missouri roadcut section, showing the carbon isotope profile of sampled carbonate beds.

Figure 4). Multiple positive peaks are present in this interval at Eureka, although from the present stratigraphic sampling density, it is unclear whether these shifts are organized into systematic, well-organized trends (Fig. 4). In the upper part of the Kings Lake/Guttenberg interval,  $\delta^{13}\text{C}$  values decrease back to baseline values less than  $-0.5$  ‰ in the basal Kimmswick Limestone.

## Discussion

The similarity of the carbon isotope profile at Eureka, Missouri to those we have described from the Upper Mississippi Valley (McGregor and Dickeyville sections) raises questions about the validity of the Kings Lake Limestone of Missouri as a genetically distinct unit, and proposed unconformable relationships with overlying strata of the Guttenberg Limestone (as originally proposed by Herbert, 1949, and outlined in Kolata et al., 1986, and Thompson, 1991, p. 172-182). The most distinctive feature shared between all three sections is the major positive shift in  $\delta^{13}\text{C}$  values at the contact between the Spechts Ferry interval and the immediately overlying carbonates. This chemostratigraphic correlation suggests that the “Kings Lake Limestone” at Eureka is a direct time-stratigraphic correlate to the lower part of the Guttenberg Member at the McGregor and Dickeyville sections.

Carbon isotope profiles from all three sections show that a lower positive carbon isotope excursion of lesser magnitude is present in the strata between the Deicke and Millbrig K-bentonites, and immediately overlying strata (figs. 2, 3, and 4). This lower positive  $\delta^{13}\text{C}$  excursion is always separated from the major positive  $\delta^{13}\text{C}$  excursion to maximum values (which begins at about the position of the Elkport K-bentonite) by a negative shift in values in the Spechts Ferry interval. Our continuing studies in cored sections show that this lower positive excursion reaches maximum values of up to  $+1.5$  ‰ in sections

where the overlying positive excursion reaches maximum values of up to +2.5 ‰. In many sections, the onset of the lower excursion begins well below the position of the Deicke K-bentonite (Smith et al., 2000). The sequence stratigraphic significance of the Carimona-Castlewood carbonates below the shales of the Spechts Ferry is a continuing focus of this research. This interval may be bounded by an underlying sequence boundary, as suggested by Ludvigson et al. (1996).

### Acknowledgments

This research supported by NSF grant EAR-0000741. The work of Smith as a summer NSF-REU intern at The University of Iowa was supported by NSF grant EEC-9912191. Special thanks to Steve Jacobson for collaborating on field collection of the Eureka, Missouri section in 1989. Interactions and collaboration with Matt Saltzman helped revive interest in this research. Long-term dialogue and timely field guidance from our colleague Dennis Kolata has been immensely helpful. We thank Bill Bunker, Jack Gilmore, and Matt Goolsby of the Iowa Geological Survey Bureau for logistical support on this project.

### References

- Ainsaar, L., Meidla, T., and Martma, T., 1999, Evidence for a widespread carbon isotopic event associated with late Middle Ordovician sedimentological and faunal changes in Estonia: *Geological Magazine*, v. 136, p. 49-62.
- Hatch, J.R., Jacobson, S.R., Witzke, B.J., Risatti, J.B., Anders, D.E., Watney, W.L., Newell, K.D., and Vuletich, A.K., 1987, Possible late Middle Ordovician organic carbon isotope excursion: Evidence from Ordovician oils and hydrocarbon source rocks, mid-continent and east-central United States: *American Association of Petroleum Geologists Bulletin*, v. 71, p. 1342-1354.
- Herbert, P., 1949, Stratigraphy of the Decorah Formation in western Illinois, unpublished Ph.D. Dissertation, University of Chicago, 80 p.
- Kolata, D.R., Frost, J.K., and Huff, W.D., 1986, K-bentonites of the Ordovician Decorah subgroup, Upper Mississippi Valley: Correlation by chemical fingerprinting: *Illinois State Geological Survey, Circular 537*, 30 p.
- Kolata, D.R., Huff, W.D., and Bergström, S.M., 1996, Ordovician K-bentonites of eastern North America: *Geological Society of America Special Paper 313*, 84 p.
- Kolata, D.R., Huff, W.D., and Bergström, S.M., 1998, Nature and regional significance of unconformities associated with the Middle Ordovician Hagan K-bentonite complex in the North American midcontinent: *Geological Society of America Bulletin*, v. 110, p. 723-739.
- Kump, L.R., and Arthur, M.A., 1999, Interpreting carbon-isotope excursions: carbonates and organic matter: *Chemical Geology*, v. 161, p. 181-198.
- Ludvigson, G.A., Jacobson, S.R., Witzke, B.J., and González, L.A., 1996, Carbonate component chemostratigraphy and depositional history of the Ordovician Decorah Formation, Upper Mississippi Valley, in Witzke, B.J., Ludvigson, G.A., and Day, J., eds., *Paleozoic Sequence Stratigraphy: Views from the North American Craton*: *Geological Society of America, Special Paper 306*, p. 67-86.
- Ludvigson, G.A., Witzke, B.J., Carpenter, S.J., Saltzman, M.R., González, L.A., and Schneider, C.L., 2000, Use of carbon isotope chemostratigraphy for refining the sequence stratigraphic architecture of offshore subtidal carbonates: An Example from the Ordovician: *American Association of Petroleum Geologists, Program for Annual Meeting*, v. 9, p. A89.

*Geological Society of Iowa*

- Pancost, R.D., Freeman, K.H., Patzkowsky, M.E., Wavrek, D., and Collister, J.W., 1998, Molecular indicators of redox and marine photoautotroph composition in the late Middle Ordovician of Iowa, U.S.A.: *Organic Geochemistry*, v. 29, p. 1649-1662.
- Pancost, R.D., Freeman, K.H., and Patzkowsky, M.E., 1999, Organic-matter source variation and the expression of a late Middle Ordovician carbon isotope excursion: *Geology*, v. 27, p. 1015-1018.
- Patzkowsky, M.E., Slupik, L.M., Arthur, M.A., Pancost, R.D., and Freeman, K.H., 1997, Late Middle Ordovician environmental change and extinction: Harbinger of the Late Ordovician or continuation of Cambrian patterns?: *Geology*, v. 25, p. 911-914.
- Smith, L.A., Ludvigson, G.A., Witzke, B.J., Schneider, C.L., Emerson, N.R., Carpenter, S.J., and González, L.A., 2000, Calibration of the mid-Caradoc carbon isotope excursion with volcanic ash bed chronology of the Hagan K-bentonite complex: *Geological Society of America, Abstracts with Programs*, v. 32, no. 7, p. A457.
- Thompson, T.L., 1991, Paleozoic succession in Missouri: Part 2 Ordovician System: Missouri Department of Natural Resources, Division of Geology and Land Survey, Report of Investigations No 70, 282 p.

