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Carbonate component chemostratigraphy and depositional history of the Ordovician Decorah Formation, Upper Mississippi Valley

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ABSTRACT

The Decorah Formation of eastern Iowa was deposited on an open-marine subtidal shelf near storm wave base. Maximum transgression is represented in organic-rich strata of the Guttenberg Member. Brachiopod-derived marine carbonate isotopic compositions from the Decorah are approximately $\delta^{13}C$ = +1‰ and $\delta^{18}O$ = –3.5‰; these data are consistent with a recently recognized long-term secular increase in the $\delta^{18}O$ of Middle Ordovician marine carbonates. Decorah carbonates lithified in early diagenetic modified-marine phreatic environments. Isotopic data from diagenetic components show that the Spechts Ferry Member lithified in a more fluid-dominated diagenetic system than the immediately overlying Guttenberg Member, which was characterized by a rock-dominated system. Whole-rock carbonate $\delta^{13}C$ shifts in the Decorah Formation are carried by micritic components. A positive shift in the Guttenberg to micrites with $\delta^{13}C$ values up to +2.5‰ indicates that some of the micrite isotopic signal is primary and not of benthic origin and/or that early diagenetic marine phreatic fluids in the organic-rich Guttenberg were affected by bacterial methanogenesis. Subtidal shallowing-upward depositional cycles in the Decorah are internally characterized by micrites with stratigraphically upward trends toward ^{13}C depletion as a consequence of increasing diagenetic water/rock ratios. Decoupling between coeval carbon isotopic signals carried by open-marine brachiopod carbonate and those of organic carbon and micrite indicates that the positive carbon isotopic excursion in the Guttenberg resulted from an episode of increased photosynthetic productivity near the sea surface. This event was a consequence of quasiestuarine circulation associated with marine transgression during deposition of the Guttenberg Member. Results from this study suggest that the extinct organic-walled microfossil *Gloeocapsomorpha prisca*, the principal source of organic carbon in the Decorah Formation, was a phytoplanktic organism.

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INTRODUCTION

Rock strata of the Decorah Formation of the Upper Mississippi Valley have been the focus of intensive sedimentary research because contained organic-rich units represent unaltered, thermally immature correlates of rocks that have generated petroleum in many sedimentary basins around the world (Hatch et al., 1987; Jacobson et al., 1988), and because they contain the type sections of closely spaced chemically correlated K-bentonites that have been traced across much of the eastern United States and Europe (Kolata et al., 1986, 1987; Haynes, 1994; Huff et al., 1992). The recognition of a positive $\delta^{13}C$ excursion of several parts per mil recorded in coexisiting kerogen and carbonate fractions of oil-prone shales in the Decorah Formation (Hatch et al., 1987; Jacobson et al., 1988) raised important questions about the depositional history of the unit. As noted by Hatch et al. (1987), differences in the magnitudes of the organic and carbonate $\delta^{13}C$ excursions could be related to many factors, including episodes of high organic productivity and/or increased preservation of organic matter, changes in sea level and seaway circulation, changes in temperature, salinity, and atmospheric P_{CO_2}, and the possible obscuring effects of carbonate diagenesis. In addition, the organic-rich strata containing the positive $\delta^{13}C$ excursion contain abundant remains of the extinct organic-walled microfossil *Gloeocapsomorpha prisca* (Jacobson et al., 1988). The biologic affinity and paleoenvironmental significance of *G. prisca* has been controversial (Reed et al., 1986; Hoffman et al., 1987; Jacobson et al., 1988; Stasiuk and Osadetz, 1990; Foster et al., 1990; Stasiuk et al., 1993); arguments have been advanced for existence as a phytoplanktic organism or as a benthic heterotroph.

This report on our investigations of carbonate component stable isotope chemostratigraphy and detailed sedimentology is intended to help develop constraints on environmental interpretations that can be applied to the Decorah Formation. In addition to field studies of many exposed sections, intensive laboratory studies (Ludvigson et al., 1990a, 1990b, 1991, 1992a, 1992b) were performed on the Cominco Millbrook Farms SS-9 core (Iowa Geological Survey Bureau W-27581), an important reference section in eastern Iowa used in the discovery of the $\delta^{13}C$ excursion in the Decorah Formation (Hatch et al., 1987).

RESEARCH METHODS

Field and core logging studies included descriptions of lithologic changes at the centimeter to decimeter scale. Core splits selected for carbonate component microsampling were first stabilized by epoxide resin and cut into serial thin sections and thin slabs (about 1 mm thick) perpendicular to bedding. Brachiopods sampled from shale outcrops of the Spechts Ferry Member (North Guttenberg Roadcut section of Sloan et al., 1987) came from bulk shale samples that were treated with Stoddards solvent, washed and screened, hand sorted by species, and mounted in epoxide plugs that were micropolished and cut into thin sections. Rock thin sections and slabs were mounted on oversize (50 mm × 75 mm) microscope slides and micropolished for cathodoluminescence (CL) and transmitted light petrography. CL petrography was performed with a Nuclide ELM-2A cathodoluminoscope using an accelerating voltage of 10 kV and a beam current of 0.5 mA operating in a rarefied helium atmosphere.

Powdered carbonate samples ranging from 0.5 to 5 mg were extracted with a microscope-mounted drill assembly using a 0.5-mm-diameter tungsten carbide dental burr. Powders drilled from microsample sites on polished thin slab surfaces were split for coordinated stable isotopic and trace element analyses. Stable isotopic analyses of carbonate components were performed at the University of Michigan Stable Isotope Laboratory. Samples were roasted in vacuum at 380 °C for 1 h to remove volatile organic contaminants. Samples were reacted with anhydrous H_3PO_4 at 72 °C in a CarboKiel reaction device coupled to the inlet of a Finnigan MAT 251 gas ratio mass spectrometer. All values are reported relative to the Peedee belemnite (PDB) standard, with reported precision better than ±0.05‰ for both carbon and oxygen.

Trace element splits of 0.2 or 0.4 mg powdered carbonate were dissolved in 1 ml ultrapure 10% HNO_3 solution, filtered through 0.22 μm Millipore HATF, and excess acidity was neutralized using Alltech IC-OH filters. Solutions were spiked with a known concentration of Mg, and were analyzed by ion chromatography using a Waters ion chromatograph. Cations were eluted using a Waters IC Pak-C M/D column with a 0.1 mM EDTA and 3 mM HNO_3 mobile phase at a 1.0 ml/min flow rate, and detected with a Waters 431 conductivity detector. The solid carbonate detection limit for Mg in the spiked microsamples is ≤ 24 ppm, although with error propagation it is considered to be ≤ 75 ppm (0.003 ppm sensitivity).

Electron probe microanalyses of calcite cement zones in Decorah grainstones were performed on an automated ARL-SEMQ microprobe housed in the Department of Geological and Atmospheric Sciences at Iowa State University. Operating conditions for calcite analyses consisted of an accelerating voltage of 15 kV, a beam current of 30 nA, a defocused beam diameter of 20 μm, and counting times of 100 s. Detection limits for Ca, Mg, Mn, and Fe are all considered to be ≤ 170 ppm.

Organic carbon contents of cored samples were determined at Chevron Oil Field Research Company in La Habra, California, by Rock-Eval pyrolysis using a Rock-Eval II instrument as described in Jacobson et al. (1988). Whole-rock carbonate $\delta^{13}C$ was determined by Chevron Oil Field Research Company. Samples were washed in distilled water and vacuum roasted for 1 h at 375 °C to remove organic matter. Samples were then reacted in 100% H_3PO_4 at 50 °C and the carbon isotopic ratios of evolved CO_2 gas were determined on a Finnigan MAT 250 mass spectrometer. Results are reported in the normal δ ‰ notation (Craig, 1957) relative to the Chicago PDB standard. Precision on carbon data was ±0.07‰ 1σ.

Organic carbon isotopic data were obtained in two different laboratories, one at Chevron Oil Field Research Company and the other at the U.S. Geological Survey in Denver (Hatch et al., 1987). The new data from La Habra came from ground rock samples treated with 18% HCl to remove carbonate. The organic matter was then filtered and dried: ~1 mg of organic matter was used to determine stable carbon isotope ratios on a Finnigan Delta-E MAT stable isotope mass spectrometer. A value of –0.17‰ has been added to the previously published carbon isotope data of Hatch et al. (1987) to account for different carbon isotope values of the NBS-22 oil standard used by the different laboratories (U.S. Geological Survey Denver, Colorado, and Chevron Oil Field Research Company, La Habra, California [–29.58‰ and –29.75‰, respectively]).

GALENA GROUP DEPOSITION IN THE UPPER MISSISSIPPI VALLEY

The Decorah Formation is the basal unit of the Galena Group carbonate succession in the Upper Mississippi Valley (see Witzke and Bunker, this volume). The unit is dated as early Rocklandian (Middle Ordovician; *Phragmodus undatus* Zone; Witzke, 1992; Leslie and Bergstrom, 1993), equivalent to the mid-Caradocian of Europe (Sloan, 1987). The Galena Group was deposited within a subequatorial Middle Ordovician epeiric sea. Paleogeographic reconstruction of the Middle Ordovician Laurentian continent by Witzke (1990) placed the paleoequator and related humid zone near the Transcontinental Arch, and showed continental subaerial paleoenvironments associated with the arch, the Canadian shield, and the Taconic orogenic belt.

Galena Group strata record a major marine transgression onto the central craton area of North America, and are characterized primarily by clean skeletal carbonate rocks deposited in subtidal open-marine settings. However, the Decorah Formation is characterized by a significant component of siliciclastic marine sediments (primarily illite and kaolinite clays) from nearby source terranes on the emergent Transcontinental Arch (Witzke, 1980). Shale content in the Decorah diminishes to the southeast away from the source areas, and the unit becomes carbonate dominated across most of eastern Iowa and adjacent Illinois. In eastern Iowa, the Decorah Formation is divided, in ascending order, into the Spechts Ferry, Guttenberg, and Ion Members (Witzke, 1983). The Spechts Ferry is primarily a gray-green shale unit about 1.5 to 3 m thick with minor carbonate interbeds. The Guttenberg is a limestone unit from 3 to 6 m thick with minor brown and green shale partings, and the Ion ranges from 0 to 9 m in thickness and consists of interbedded limestone and gray-green shale.

The middle carbonate-dominated interval of the Decorah in eastern Iowa, the Guttenberg Member, includes brown shales that are extremely organic-rich with total organic carbon (TOC) ranging up to 51.7%, and records the positive $\delta^{13}C$ excursion (Fig. 1). Above the Decorah, Galena Group strata are progres-

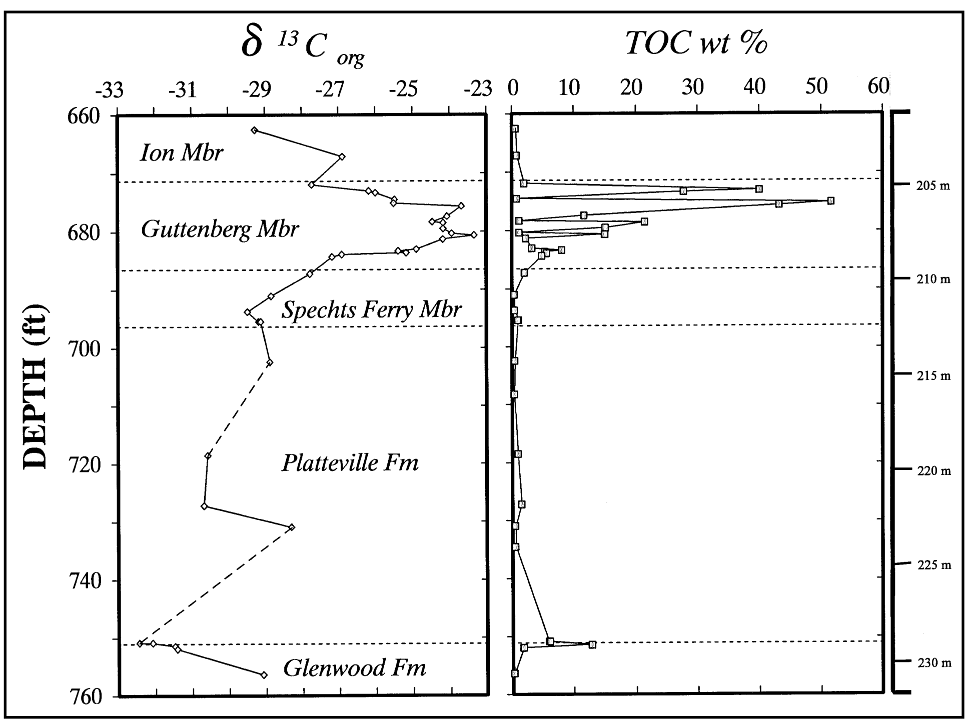

Figure 1. Organic carbon $\delta^{13}C$ and total organic carbon (TOC) profile of the Cominco Millbrook Farms SS-9 core (sec 29, T84N, R1E; Jackson Co., IA), showing the positive carbon isotope excursion and increase in organic carbon in the Guttenberg Member of the Decorah Formation. Data from Hatch et al. (1987) are augmented by newer data from Chevron Oil Field Research Company.

sively less argillaceous, and the general upward decrease in clay content reflects marine inundation of source terranes as seaways completely flooded the Transcontinental Arch.

SEDIMENTOLOGIC AND PALEONTOLOGIC CONSTRAINTS ON PALEOBATHYMETRY OF THE DECORAH FORMATION

Varying opinions have been advanced concerning the depositional environments and paleobathymetry of strata in the Decorah Formation. Witzke and Kolata (1988) interpreted qualitative sea-level cycles for the Middle and Upper Ordovician succession in the Upper Mississippi Valley, and recognized a eustatic cycle they named the Decorah subcycle of the Galena cycle.

Cisne and coworkers (Cisne and Rabe, 1978; Rabe and Cisne, 1980; Cisne et al., 1982, 1984; Cisne and Chandlee, 1982; Cisne, 1985; Cisne and Gildner, 1988) developed a paleoenvironmental model for Ordovician units including the Decorah Formation in the Galena Group. They based their interpretations on carefully measured sections, systematically collected macrofossils, and correlated bentonites. Using statistical treatment of their data to quantify sedimentation rates, they suggested that sea-level changes relative to the continent included two components for the Decorah: (1) a rise of ~10 m that occurred over 10 m.y., and (2) an overprint by pulses of 1 m rises and falls that represented about 0.1 to 1.0 m.y. each. Their interpretation is directionally consistent with sea-level curves independently derived by Witzke and Kolata (1988) from the Iowa-Illinois area, and pertains to the strata containing the carbon isotope excursion of Hatch et al. (1987).

Cisne (1985) and Cisne and Gildner (1988) interpreted absolute water depth during Decorah sedimentation at about 2 m in eastern Iowa (expanded to about 10 m by Cisne; 1989, personal commun., Jacobson); they suggested that the high stratigraphic resolution and long range correlation within the Decorah reflects tectonic quiescence, spatial homogeneity, and tidelessness within the epeiric sea.

We suggest a differing bathymetric interpretation, based on sedimentary features that are inconsistent with deposition in water that shallow. Recognition of these features is based on our bed by bed sedimentologic logging of many exposed sections, and these are illustrated specifically for the Cominco Millbrook Farms SS-9 core (Fig. 2). We interpret the sedimentology of the Decorah Formation within the context of bathymetrically related tempestite proximality trends on the Galena Group carbonate ramp, and the stratigraphic distribution of articulated crinoids, benthic algae, burrowing fabrics, and early diagenetic features in the succession. Proximality trends refer to depth-controlled gradients in the sedimentology of storm-related shelf deposits, ranging from proximal coquinites or sands deposited above storm wave base to distal mud burial layers deposited below storm wave base (Aigner and Reineck, 1982; Brett et al., 1986; Easthouse and Driese, 1988; Baarli, 1988; Brett et al., 1993).

Although the Decorah is dominated by thinly bedded fossiliferous siliciclastic and carbonate muds indicating subtidal deposition below fair-weather wave base, they are punctuated by discrete echinoderm-brachiopod-bryozoan packstone-grainstone units with lenticular starved symmetrical megaripple bedforms. These beds are interpreted as tempestite deposits recording bottom agitation and winnowing of muds during storm events. A plot of the stratigraphic frequency of tempestite beds through the Decorah (Fig. 2) shows a distinct minimum within the Guttenberg Member compared to immediately overlying and underlying units. If constant rates of background (mud, skeletal grains) sedimentation are assumed, the drop in tempestite frequency implies that the Guttenberg records a deepening during which benthic environments were seldom above storm wave base.

Discussion

Estimates of the absolute water depths for normal (fair weather) wave base and storm wave base in ancient marine deposits are fraught with interpretive difficulties, and are influenced by many factors including different paleoclimates, configurations of seaways, and wind direction, constancy, and fetch. Nevertheless, depth ranges for these important bathymetric indicators can be estimated from modern shelf environments to provide approximate scalar dimensions for framing subsequent discussions (Brett et al., 1993). As is frequently the case, the lack of modern well-studied epeiric sea bottoms places a further limitation on these analogies. Aigner and Reineck (1982) reported active storm sediment transport to depths greater than 20 m, and the summaries of Swift (1985) and Swift and Niedoroda (1985) on the mid-Atlantic U.S. shelf suggested active storm sediment transport to depths greater than 132 m. Clifton (1988) reported depths of 5 to 10 m for normal fair-weather wave base, and 20 to 150 m for storm wave base on the modern central California shelf. In our opinion, these are realistic estimates with respect to deposition within the Decorah Formation. Deposition within normal fair-weather wave base is characterized by continuously agitated, or shoal-water environments. Sedimentary deposits formed above normal wave base are typically mud free because of continuous winnowing. Carbonate sediments characteristic of this environmental setting would be massive, cross-bedded grainstones. As such, all units within the Decorah Formation were deposited in muddy subtidal environments well below normal wave base.

In our view, several well-documented paleontological features of the Guttenberg carbonates also argue for deposition in relatively deep water. The preservation of articulated echinoderm faunas within the Guttenberg (Fig. 2; Kolata, 1986) is suggestive of “smothered bottom” fossil assemblages that were rapidly buried by muds settling from suspension clouds, characteristic of distal tempestite facies in benthic realms below storm wave base (Brett et al., 1986).

Receptaculitid calcareous green algae are common skeletal constituents in many carbonate units in the Galena Group. They

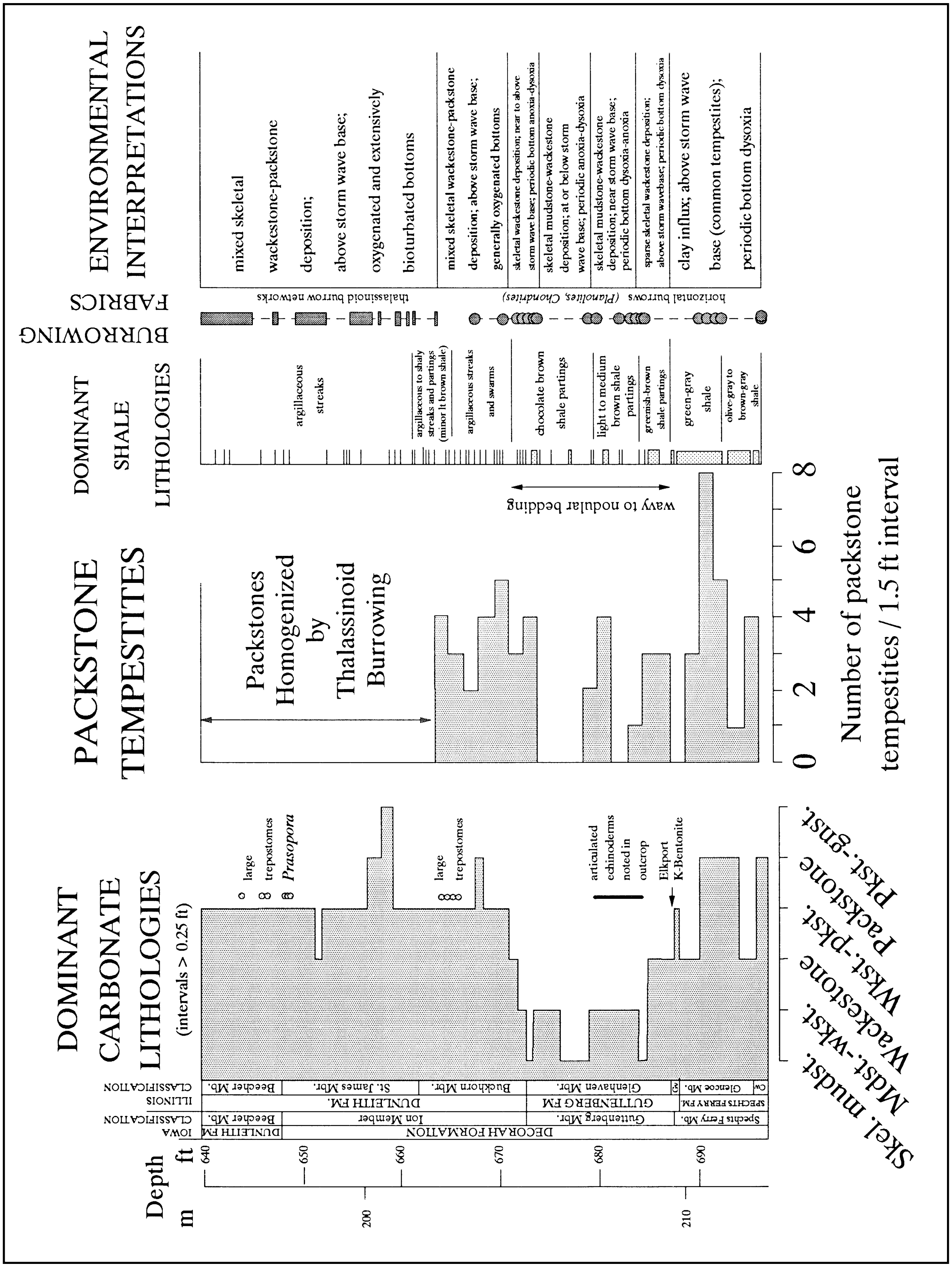

Figure 2. Sedimentologic log of the Cominco Millbrook Farms SS-9 core, showing the positions of dominant carbonate lithologies and tempestite frequency. Plots are also included showing dominant shale lithologies, burrowing fabrics, and environmental interpretations of specific intervals. Also note the stratigraphic positions of articulated echinoderm faunas, the stratigraphic extent of wavy to nodular bedding, and the position of the Elkport K-Bentonite.

are largely missing from carbonate strata in the Decorah, first appearing in the Buckhorn Member of the Dunleith Formation of Illinois (Templeton and Willman, 1963), equivalent to the lower Ion Member of the Decorah Formation in Iowa (Fig. 2). In addition, exhaustive point-counting by Bakush (1985) showed that dasycladacean green algae (*Vermiporella*) are common skeletal constituents in many Galena Group carbonates, but they are not present in any of the carbonate units within the Decorah. The presence of dasyclad algae demonstrates that benthic environments were within the zone of effective solar light penetration (Beadle, 1988). Conversely, their absence in the Decorah argues against very shallow water depths, and suggests deposition below the photic limit for dasyclads. Reported maximum depths for dasyclads are down to 90 m (Fagerstrom, 1987; Brett et al., 1993).

Other sedimentary and diagenetic fabrics support the interpretation of general deepening and development of bottom anoxia during the deposition of the Guttenberg Member. Burrowing fabrics are particularly instructive. The thin-bedded aspect of much of the Decorah, particularly the Guttenberg, permitting the resolution of individual sedimentation units of millimeter to centimeter thickness, is lost upward through the Ion Member (Fig. 2), where development of vertically extensive thalassinoid burrow networks homogenize the sediment, and burrows host selective dolomitization of carbonate fabrics. These amalgamated sediments contrast sharply with the underlying thinly bedded Guttenberg characterized by horizontal burrows, including *Planolites* and *Chondrites*. *Chondrites* networks are considered evidence for dysoxic sedimentation (Bromley and Ekdale, 1984), and the change in burrowing patterns suggests that deposition of the Spechts Ferry and Guttenberg strata coincided with at least periodic development of oxygen-stressed benthic environments, which implies deeper water where vertical circulatory replenishment of dissolved oxygen was less likely. Following the scheme of Byers (1977), the upward transition to thalassinoid networks in the Ion Member is interpreted to signify the development of continuous benthic oxygenation, and the consequent vigorous activity of benthic infauna.

Early diagenetic fabrics in the wavy to nodular-bedded muddy carbonates of the Guttenberg Member have important implications for the deposition of the unit. These bedding styles closely resemble those in the underlying Platteville Formation (Fig. 2) that were interpreted by Byers and Stasko (1978) to be products of early submarine diagenesis in low-energy subtidal environments. Contrasts between the lack of compactional fabrics of skeletal components in the nodular beds and their extreme compaction in immediately adjacent beds in the Guttenberg clearly demonstrate the early origin of the fabric, and high-angle to concentric septarian-like vein fills in some of the nodular mudstone beds further attest to the diagenetic origin of the bedding style. Paleozoic limestones with generally similar fabrics have been interpreted as pelagic deposits (Tucker, 1974; Jenkyns, 1986). Byers (1983, 1987) has further commented on the similarities between the depositional and diagenetic features of the Galena Group carbonates and those of pelagic Cretaceous chalks.

In summary, sedimentary features place the Guttenberg interval of the Decorah in much deeper shelf environments than those envisioned by Cisne and coworkers, perhaps several tens of meters to 100 m in depth relative to higher beds, where storm deposits and benthic algae indicate shallower water by perhaps tens of meters, but still possibly 20 to 40 m in depth by modern shelf analogue.

SEQUENCE STRATIGRAPHY OF THE DECORAH CLASTIC WEDGE

The stratal geometry of the Decorah Formation, and the Guttenberg Member in particular, provide important constraints for framing discussion of depositional history. The areal extent of the Guttenberg in Illinois was mapped by Herbert (1949), who showed that the unit is limited to western Illinois, attains its maximum thickness in the westernmost part of that state, and forms an elongate rock body along a north-northeast to south-southwest axis (Fig. 3). Witzke's (1983) work in Iowa

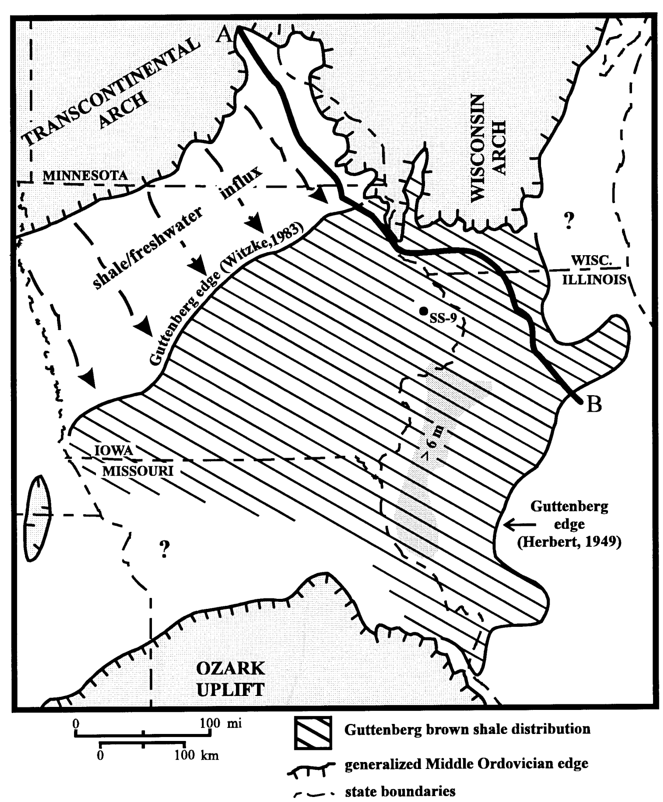

Figure 3. General distribution of Guttenberg Member (Formation in Illinois) and associated organic brown shales. Guttenberg edge after Witzke (1983) and Herbert (1949), modified following Kolata (pers. comm., 1995). Outline within cross-ruled area shows general region where Guttenberg is greater than 6 m (20 ft) in thickness (after Herbert, 1949). Decorah shale influx off Transcontinental Arch. See Figure 4 for cross section along line A-B.

showed that the Guttenberg passes northwestward into shale facies along a northeast-southwest line paralleling the Transcontinental Arch (Fig. 3). Collectively, these works show that the Guttenberg occupies a 300–600-km-wide belt that parallels the more nearshore Decorah shale belt, indicating a systematic spatial relationship to an eroded strandline on the Transcontinental Arch (Fig. 3).

A stratigraphic cross section along an onshore-offshore transect (Fig. 4) shows that the Decorah clastic wedge thins away from clastic sources on the Transcontinental Arch. Clinoform geometry and discrete episodes of sediment progradation are revealed by the configuration of chemically fingerprinted and correlated K-bentonites (Kolata et al., 1986, 1987). The downlap of strata containing these ash beds onto and along the top of the underlying Platteville Formation (Deicke, Dickeyville) is especially noteworthy. This relationship indicates that the southeastward depositional limits of immediately underlying portions of the Decorah Formation can be attributed to sediment starvation in deeper offshore environments. There are local tectonic complications to this regional interpretation in portions of northern Illinois, however, where the Guttenberg includes packstone-grainstone facies suggestive of deposition in shallow settings (Kolata et al., 1986; Witzke and Kolata, 1988). Similar relations regarding offshore sediment starvation have been recognized in other Devonian and Mississippian cycles in the Iowa area (Witzke and Bunker, this volume).

Witzke and Kolata (1988) recognized a "Decorah subcycle" within a larger Galena cycle of deposition. More recent analyses show that higher orders of cyclicity can be recognized on a regional scale (Witzke and Bunker, this volume). Analysis of tempestite frequency in the Cominco Millbrook Farms SS-9 core shows a maximum in the upper part of the Spechts Ferry Member, suggesting an upward shallowing, followed by an upward decrease in tempestite frequency into the Guttenberg, suggesting deepening paleobathymetry (Fig. 2).

Paleobathymetric relations are further amplified by the stratal geometries shown in Figure 4. In the Guttenberg and Ion Members of northeast Iowa, offshore carbonates pass north-

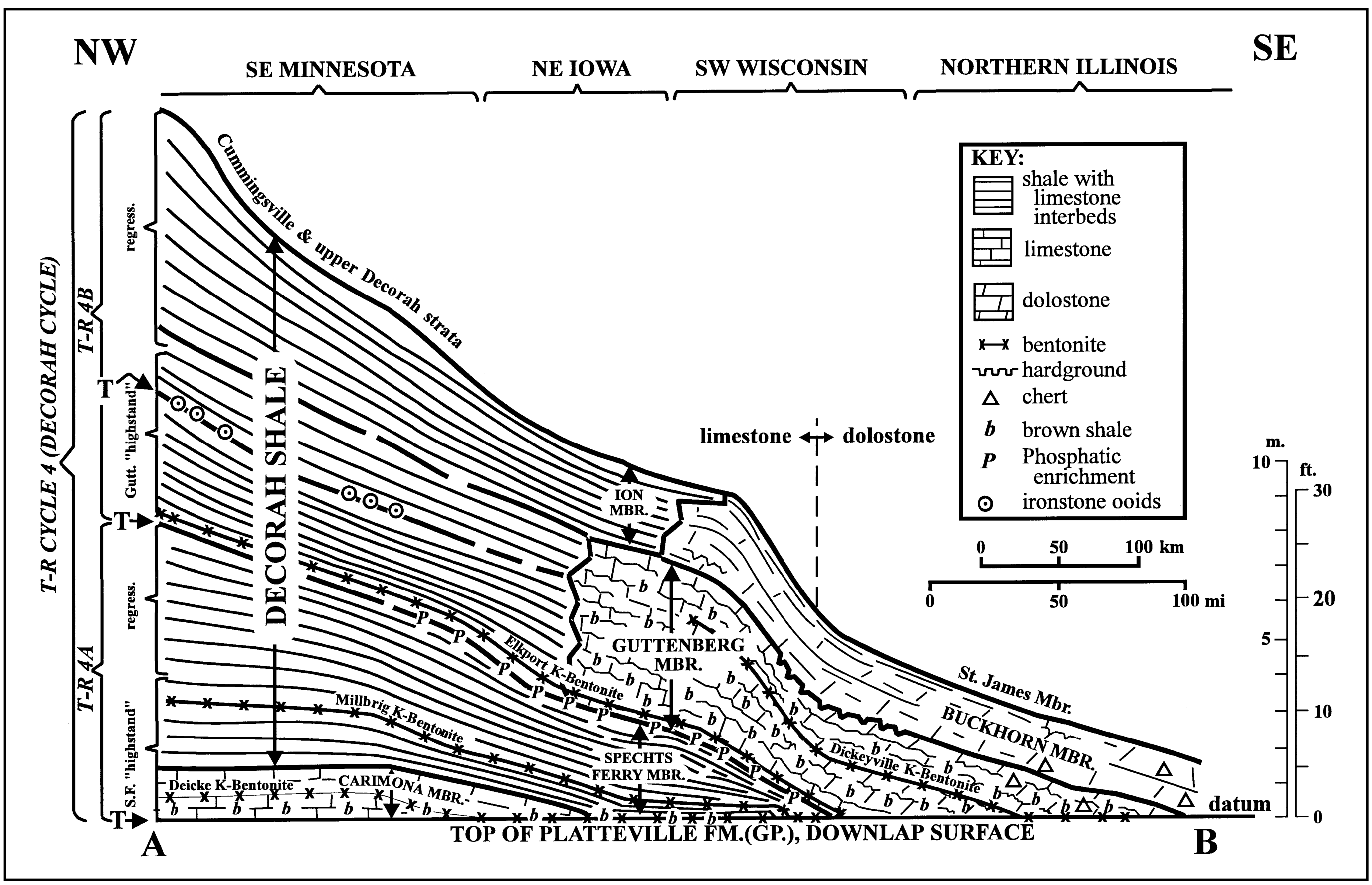

Figure 4. Generalized stratigraphic cross section, Decorah depositional cycle, southeast Minnesota to northern Illinois. See Figure 3 for location of cross section line A-B. Stratigraphy is based in part on sections from Templeton and Willman (1963), Willman and Kolata (1978), Kolata et al. (1986), and recent studies. Transgressive-regressive (T-R) cycles after Witzke and Bunker (this volume). Transgressive surfaces are labeled (T); deepest facies (maximum transgression) are interpreted above the middle Guttenberg. Phosphatic enrichment marks condensed sedimentation at the base of cycle 4B.

westward into more nearshore marine shale units. Episodes of shale progradation in this succession record regression attending the seaward advance of the paleoshoreline. The Spechts Ferry and Ion Members are both progradational packages indicating such seaward advance. The landward stepping of the carbonate-shale boundary at the onset of Guttenberg deposition, however, records a retrogradational geometry indicating an abrupt transgression. The Spechts Ferry–Guttenberg contact and correlative positions in the more nearshore marine shale belt are marked by phosphatic enrichment (Fig. 4), as lags of skeletal and nodular authigenic apatite, recording condensed sedimentation at the position of this abrupt landward stepping of sedimentary facies.

These relations have led to the recognition of two separate higher order cycles within the Decorah cyle (Tippecanoe I cycle 4 of Witzke and Bunker, this volume). They are cycle 4A consisting of the Carimona (largely a Minnesota unit; see Sloan, 1987) and Spechts Ferry Members, and cycle 4B consisting of the Guttenberg and Ion Members in Iowa. As developed in subsequent discussions, the recognition of this sequence boundary within the Decorah Formation has implications for interpreting the chemostratigraphy of the unit.

DIAGENETIC PROCESSES IN DECORAH CARBONATES

Petrographic and geochemical studies of carbonate cement sequences, coupled with studies of the petrography and comparative geochemistry of other carbonate components, yield insights into the paleohydrologic and early diagenetic processes responsible for lithification of the Decorah Formation, and the extent to which these processes might have influenced the chemostratigraphy of the unit.

Petrographic observations of the Decorah-Platteville sequence boundary

The broader context of the Decorah-Platteville sequence boundary is discussed by Witzke and Bunker elsewhere in this volume (see their discussion of Tippecanoe I cycles 3B and 4A). Certain aspects of the petrography of this surface in the Cominco Millbrook Farms SS-9 core are noteworthy, and pertain to the environmental interpretation of the sequence boundary. Uppermost Platteville strata in the SS-9 core are sparsely skeletal carbonate mudstones-wackestones containing scattered crinoid, trilobite, brachiopod, ostracode, and bryozoan grains. These rocks are unconformably overlain by argillaceous strata of the basal Spechts Ferry at the 696.8 ft (212.4 m) level. A brachiopod packstone just above the base of the Spechts Ferry contains abundant detrital quartz silt and scattered well-rounded quartz sand grains, components that are generally lacking in background carbonate sediments of the Galena Group of eastern Iowa, but are commonly noted in condensed intervals immediately overlying hardgrounds in the succession. Lithoclasts of upper Platteville lithologies ranging from 5 mm to 3 cm in diameter extend up to 4 cm above the contact. The outermost rims of these rounded clasts are irregularly impregnated to a thickness of about 1 mm by opaque sedimentary iron sulfides, chiefly as aggregates of pyrite framboids ranging from 5 to 25 µm in diameter.

The micritic matrix in the Platteville clasts, and in the uppermost 4 cm of the Platteville Formation is mostly nonluminescent, with irregularly speckled luminescent domains up to 100 µm in diameter. This pattern is replaced downward by uniformly luminescent micrites, and also contrasts with uniformly luminescent micrites in the immediately overlying skeletal packstones of the basal Spechts Ferry, as well as all other micrites observed in the Decorah Formation. The nonluminescent micrites just below this sequence boundary closely resemble a much thicker interval of nonluminescent micrites described by Ludvigson (1989) from a Devonian limestone unit shown to have undergone early meteoric phreatic diagenesis in an oxidizing environment developed below a subaerially exposed sequence boundary (Plocher et al., 1992). The nonluminescent micrites just below the Decorah-Platteville sequence boundary could possibly suggest that a period of subaerial exposure separated deposition of these two units, although further study is needed to evaluate the environmental significance of this surface.

Petrographic observations and element chemistry of Decorah cements

Starved megaripple packstone-grainstone bedforms encased in Decorah mudrocks contain interparticle void spaces filled by blocky equant calcite cements. Cathodoluminescence (CL) photomicroscopy shows that these cements are characterized by constructive crystal growth zonations in luminescent intensity. Cements nucleated around, and are syntaxial to echinoderm ossicles, with cement crystal dimensions ranging from 300 to 1,000 µm. Anhedral to subhedral microdolomite inclusions (dimensions ranging from 5 to 10 µm; see Lohmann and Meyers, 1977) are abundant within echinoderm ossicles and the cements immediately adjacent to them. At the scale of serial thin sections and thin slabs cut from core splits, interparticle cement CL zonation patterns persist throughout a given grainstone bed, but are unique to each tempestite unit. Microprobe transects of cement growth sequences show that Mg contents steadily decreased during crystal growth (from about 5,000 down to 2,000 ppm), and that changes in Mn contents control CL intensity (from 6,000 down to 500 ppm), with Fe contents consistently below 500 ppm.

Recognition of unique cementation histories specific to each tempestite bed in the Decorah Formation imposes an important constraint on the diagenetic processes responsible for the lithification of the unit. These observations preclude cementation in a hydrologic system of vigorous cross-formational fluid flow, like that observed in carbonate sequences cemented in meteoric phreatic or mixed marine-meteoric ground-water flow systems (Meyers and Lohmann, 1985; Frank and Lohmann, 1995). Conversely, Decorah cements are more likely to have crystallized from modified marine phreatic pore fluids, with solute transport dominated by diffusional processes rather than fluid advection. This idea is further supported by field observations of mud-filled *Trypanites* borings into the top of tempestite packstone-grainstone beds in the Decorah, demonstrating very early cementation at or just below the sea floor.

Petrographic observations of intercalated nodular micrites and shales in the Guttenberg Member

The transmitted light and CL petrography of wavy to nodular bedded lime mudstones and interbedded brown shales of the Guttenberg yield important insights into the origin of this bedding style. At the thin-section scale, nodular carbonate interbeds laterally wedge out into equivalent thinly laminated brown shales. The contacts between carbonate-cemented nodules and the surrounding shales are gradational along diffuse boundaries ranging to 500 µm in thickness. Thin-shelled brachiopod and trilobite grains (0.1 to 0.5 mm thick) are scattered throughout. The sparsely skeletal lime mudstone nodules contain 5% to 10% by volume subspherical organic-walled microssils of *Gloeocapsomorpha prisca* in three-dimensional preservation (25 to 50 µm in diameter; aspect ratio 1:1). By comparison, the thinly laminated brown shales consist almost exclusively of flattened, compressed organic-walled microfossils (bedding-parallel dimensions of 100 to 125 µm; aspect ratio 5:1) of *G. prisca* (also see Jacobson et al., 1988). These petrographic observations indicate that the wavy to nodular bedded sedimentary fabric of the Guttenberg limestone originated from very early nodular micritic cementation of organic-rich muds, before the development of significant sediment compaction. Similar nodular-bedded mud-rich facies in Ordovician strata of eastern Iowa may have developed in primary sediments of organic-rich brown shales, with the characteristic nodular bedding entirely related to early diagenetic processes (Ludvigson et al., 1992a; see Raatz and Ludvigson, this volume). In thicker intervals of brown shale lacking carbonate nodule interbeds (to 3 cm thick; at 679.2 ft [207 m] level in SS-9 core), primary shale laminations show variations in the abundance of equant 20-µm-diameter calcite particles that could possibly be primary detrital components. Compressed organic-walled microfossils in the brown shales are all nonluminescent, and the contained calcite particles are uniformly luminescent, as with all other fine-grained carbonate in the Decorah.

STABLE ISOTOPIC AND TRACE ELEMENT RESULTS

Brachiopod skeletal calcite

Original marine calcite compositions in Paleozoic limestones have been estimated from well-preserved brachiopod shells and marine cements (Popp et al., 1986; Veizer et al., 1986; Lohmann and Walker, 1989). Brachiopods are abundant and well preserved in Decorah strata (Rice, 1987; Sloan et al., 1987), and are used here to estimate original isotopic compositions of Rocklandian marine calcite.

Brachiopod calcite from the Spechts Ferry Member has $\delta^{18}O$ values that range between about –6‰ to –3.5‰, and $\delta^{13}C$ values that range between about –2‰ to +1‰ (Fig. 5). Brachiopod calcite from the Guttenberg Member has $\delta^{18}O$ values that range between about –7‰ to –5‰ and $\delta^{13}C$ values that range between about –0.5‰ to +1‰ (Fig. 5). Positive linear covariant isotopic trends with differing slopes are apparent from brachiopod populations in the Spechts Ferry and Guttenberg Members (Fig. 5). These two trends converge in compositional field A in Figure 5, with a $\delta^{13}C$ value of ~+2‰, and a $\delta^{18}O$ value of ~–3‰. Ludvigson et al. (1990b) suggested that the covariant $\delta^{18}O$ and $\delta^{13}C$ trends reflected proportional solid-phase mixing between isotopically depleted luminescent intraskeletal diagenetic calcite and original nonluminescent brachiopod skeletal calcite, with field A representing the brachiopod-derived isotopic composition of marine calcite in the Decorah Formation.

That interpretation implied, however, that no pure end-member marine skeletal calcites were sampled, and further suggested that brachiopods sampled from the Guttenberg had higher proportions of diagenetic calcite (i.e., ≥ 50%) than those of the Spechts Ferry (i.e., ≥ 20%). Coordinated $\delta^{13}C$ and Mg concentration data from brachiopod shells and other carbonate components in the Decorah Formation (Fig. 6), however, do not support this interpretation. Brachiopod calcites from both the Guttenberg and Spechts Ferry members contain up to 12,000 ppm Mg, although those of the Spechts Ferry show the more depleted $\delta^{13}C$ values are associated with Mg contents that drop to as low as 1,000 ppm (Fig. 6).

Elevated concentrations of Mg are characteristic of original components in marine limestones, and Mg contents are depleted in diagenetic calcites through water-rock interactions during diagenesis (Veizer, 1983). Therefore, the coordinated isotopic and trace element data suggest that, if anything, brachiopods of the Spechts Ferry are hosts to greater proportions of diagenetic calcite than those of the Guttenberg. Accordingly, original marine calcite values from the Guttenberg and Spechts Ferry are interpreted to coincide with the ^{18}O- and ^{13}C-enriched end members of the linear covariant isotopic trends for each respective unit. The estimated composition of brachiopod calcite in the Spechts Ferry is in compositional field B of Figure 5, with a $\delta^{13}C$ value of ~+1‰ and a $\delta^{18}O$ value of –3.5‰. For the Guttenberg, the estimated composition of brachiopod calcite is in compositional field C of Figure 5, with a $\delta^{13}C$ value of +1‰ and a $\delta^{18}O$ value of –5‰.

Other carbonate components

Carbonate components from the Spechts Ferry have $\delta^{18}O$ values that range between about –7.5‰ to –3.5‰ and $\delta^{13}C$ val-

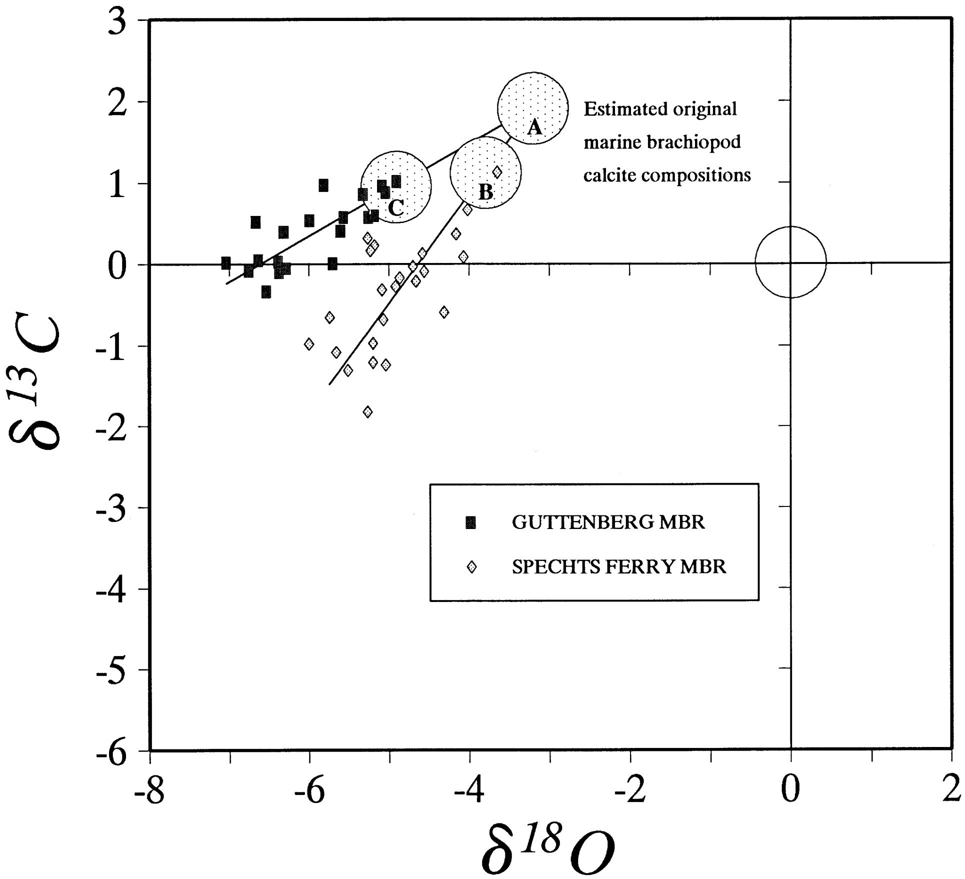

Figure 5. Carbon and oxygen isotope plot of brachiopod skeletal calcite sampled from the Spechts Ferry and Guttenberg Members of the Decorah Formation. Note the differing slopes of covariant trends from each unit. The linear correlation trends for each population were calculated as the major axes of ellipses that describe each data set. Field A is located at the intersection of these two linear trends, at the Rocklandian marine carbonate composition estimated by Ludvigson et al. (1990b). Note, however, that field A occurs outside the actual data range. Fields B and C are the estimated marine carbonate compositions for the Spechts Ferry and Guttenberg members, respectively. Data shown for the Spechts Ferry are from the 692.2 ft (211 m) level of the SS-9 core and from specimens of *Pionodema* and *Strophonema* separated from shale outcrops. Data shown from the Guttenberg are from the 684.5 ft (208.6 m) level of the SS-9 core.

ues that range between about –4‰ to +1‰ (Fig. 7a). Carbonate components from the Guttenberg have $\delta^{18}O$ values that range between about –7.5‰ to –4‰ and $\delta^{13}C$ values that range between about –1‰ to +2.5‰ (Fig. 7b).

Micrites. Stratigraphic changes in the isotopic composition of micritic components are the most noteworthy aspects of these data. At each stratigraphic sampling position, micrites plot in unique tightly constrained compositional fields in carbon-oxygen isotope space. At the 692.2 ft (211 m) level in the SS-9 core, the most extensively sampled horizon in the Spechts Ferry Member, micrite has $\delta^{18}O$ values that range between about –5‰ to –4‰ and $\delta^{13}C$ values that range between about –4‰ to –2.5‰, generally plotting in compositional field 2 of Figure 7c. Luminescent brachiopod calcite sampled at this stratigraphic position also plots within the same field in carbon and oxygen isotope space (cf. Fig. 7, a and c). At the 684.5 ft (208.6 m) level in the SS-9 core, below the peak of the positive $\delta^{13}C$ excursion in the Guttenberg Member (see Fig. 1), micrite has $\delta^{18}O$ values that range between about –5.5‰ to –4.5‰ and $\delta^{13}C$ values range between about +0.4‰ to +0.75‰, generally plotting within compositional field 4 of Figure 7d. At the 679.4 ft (207 m) level, in strata from the peak of the positive $\delta^{13}C$ excursion (Fig. 1), micrite has $\delta^{18}O$ values that range between about –5.1‰ to –4.75‰ and $\delta^{13}C$ values that range between about +1.5‰ to +2.5‰ (Fig. 7b), coinciding with compositional field 6 of Figure 7d.

Echinoderms. Echinoderm grains microsampled from the Spechts Ferry at the 692.2 ft (211 m) level in the SS-9 core have $\delta^{18}O$ values that range between about –7.5‰ to –5‰ and $\delta^{13}C$ values that range between about –2‰ to –0.5‰. The car-

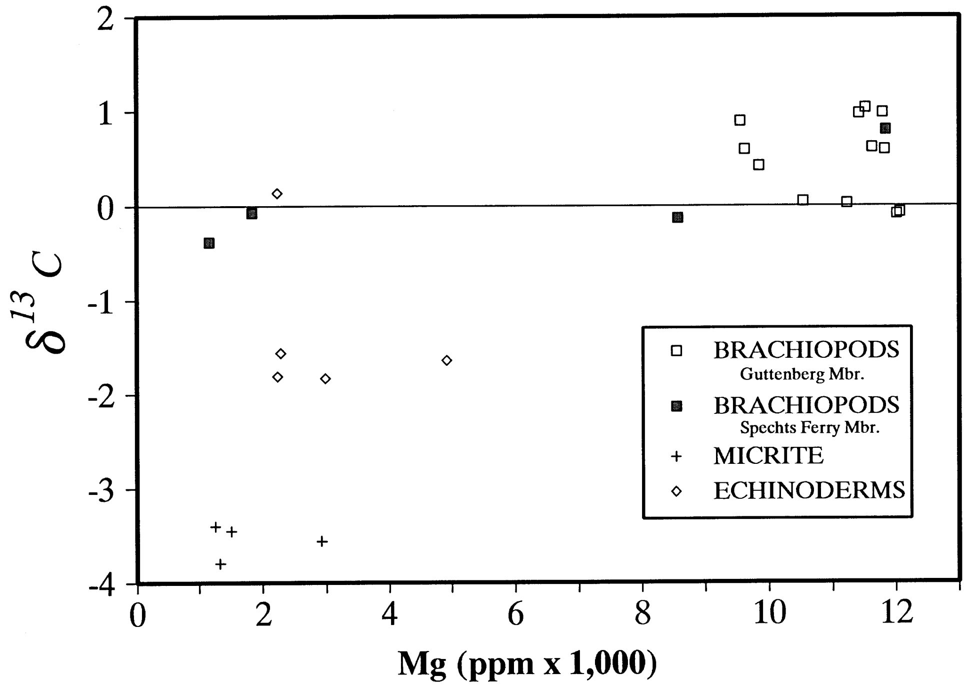

Figure 6. Plot of coordinated $\delta^{13}C$ and Mg contents of carbonate components in the Spechts Ferry and Guttenberg members of the SS-9 core. Brachiopods are enriched in ^{13}C and Mg relative to other components. Note that brachiopod calcite analyses from the Spechts Ferry include more depleted ^{13}C and Mg compositions relative to those of the Guttenberg. Data for the Spechts Ferry are from the 692.2 ft (211 m) level, and data from the Guttenberg are from the 684.5 ft (208.6 m) level of the SS-9 core.

bon and oxygen isotopic values of crinoid grains from the Spechts Ferry plot within an elongate field with a negative slope, encompassing the area within and between fields 1 and 3 in Figure 7c. The only microsample of intergranular spar recovered from the Decorah Formation was drilled at this stratigraphic level, and plots at the ^{13}C-enriched, ^{18}O-depleted end member of the crinoid grain field for the Spechts Ferry, in compositional field 3 of Figure 7c.

Echinoderm grains from the Guttenberg at the 684.5 ft (208.6 m) level in the SS-9 core have $\delta^{13}C$ values that range between about –6.5‰ to –4‰ and $\delta^{13}C$ values that range between about –0.25‰ to +0.75‰ (Fig. 7b). The carbon and oxygen isotopic values from these crinoid grains in the Guttenberg plot within an elongate field with a positive slope, coinciding with compositional field 5 of Figure 7d.

Magnesium contents of carbonate components. A plot of coordinated carbon isotope and Mg concentrations in carbonate components from the Decorah Formation (Fig. 6) shows several salient features. As noted before, brachiopods sampled from the Guttenberg uniformly have Mg contents in the 10,000 to 12,000 ppm range, and those from the Spechts Ferry (at the 692.2 ft [211 m] level in the SS-9 core) show a trend toward Mg depletion. Other carbonate components, all from the Spechts Ferry at the 692.2 ft (211 m) level in the SS-9 core, show trends toward further $\delta^{13}C$ and Mg depletion. Mg contents in echinoderm grains range from about 2,000 to 5,000 ppm, and micrites range from 1,000 to 3,000 ppm.

Discussion

Secular variation in stable isotopic compositions of Ordovician marine carbonates. At the time of Ludvigson et al.'s (1990a, 1990b) intitial reports of work on brachiopods from the Decorah Formation, their new $\delta^{18}O$ values (–3.8‰ to –3‰) represented the most positive oxygen isotopic compositions yet detected in North American Middle Ordovician open-marine carbonates. Widely cited published summaries on secular variation in the oxygen and carbon isotopic composition of Phanerozoic marine carbonates (James and Choquette, 1983; Popp et al., 1986; Lohmann, 1988; Lohmann and Walker, 1989) noted Middle Ordovician values of $\delta^{18}O$ = –6.5‰ to –5.5‰, based on analyses of marine cements and other components in the Whiterockian Antelope Valley Limestone of Nevada (Ross et al., 1975) and Caradocian brachiopods from New York (Popp et al., 1986). Marshall and Middleton (1990) noted brachiopod $\delta^{18}O$ compositions of –3‰ in younger Caradocian marine carbonates from Europe, results that were comparable to those from the Decorah. The concurrence of these results, and comparison with other published data led Ludvigson et al. (1990a, 1990b) to propose that widely varying $\delta^{18}O$ compositions reported from the Middle-Late Ordovician

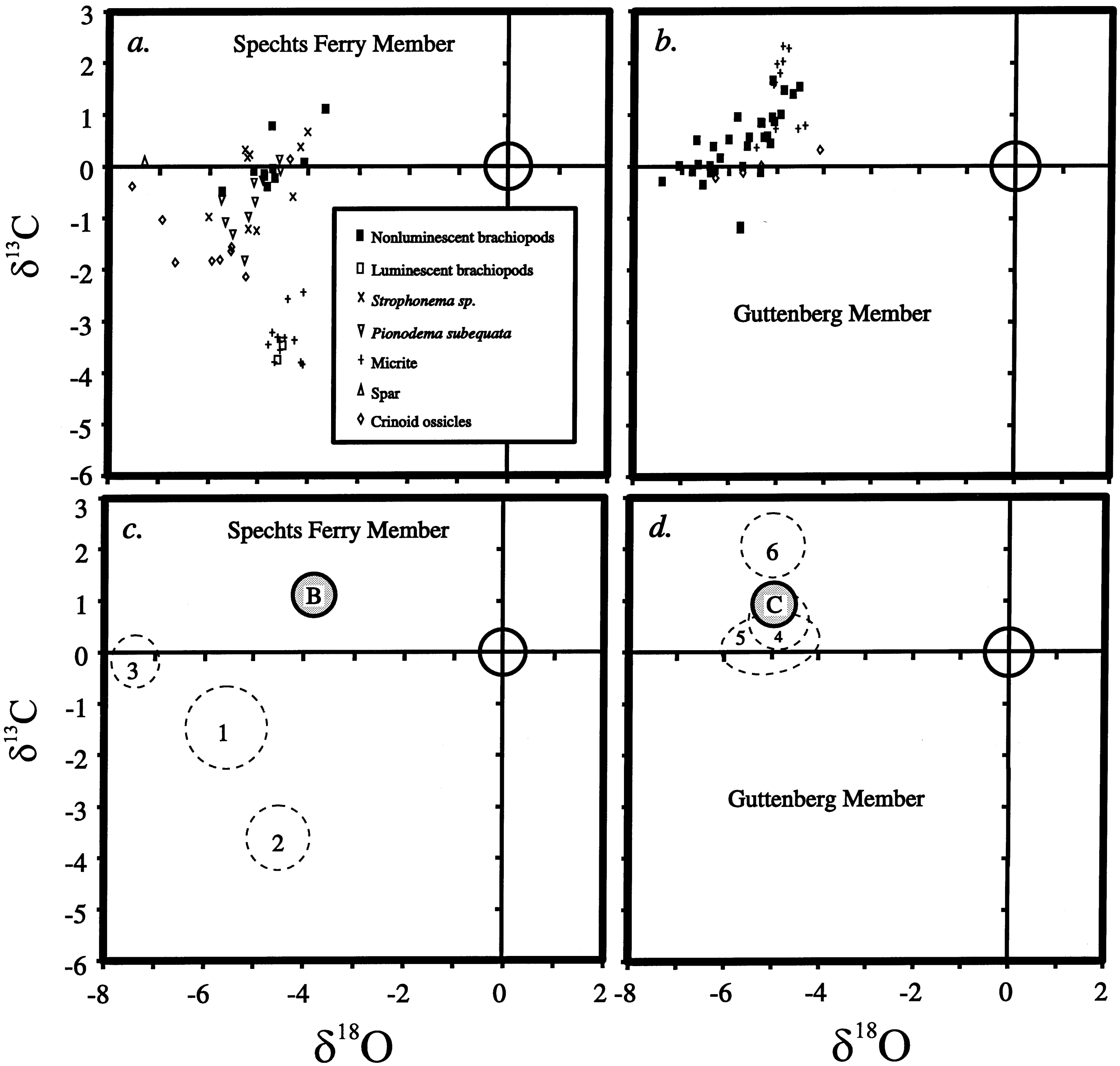

Figure 7. Carbon and oxygen isotope plots of carbonate components in the Decorah Formation. a: Plot of brachiopods, micrite, echinoderms, and calcite spar from the Spechts Ferry Member. b: Plot of brachiopods, micrite, and echinoderms from the Guttenberg Member. c: Compositional fields for carbonate components from the Spechts Ferry Member. d: Compositional fields for carbonate components from the Guttenberg Member. The significance of fields B, C, and 1–6 are discussed in the text. Samples from the Spechts Ferry Member are from the 692.2 ft (211 m) level in the SS-9 core and from specimens of *Pionodema* and *Strophonema* separated from shale outcrops. Samples from the Guttenberg are from the 684.5 ft (208.6 m) and 679.4 ft (207 m) levels in the SS-9 core.

were best understood as the record of a long-term monotonic increase of 3.5 per mil in the $\delta^{18}O$ of marine carbonate over the 25 m.y. interval spanning the early Llanvirnian to mid-Caradocian (Fig. 8). Paleogeographic maps for the Middle Ordovician of North America (Witzke, 1990) and the Late Ordovician of the world (Ashgillian; Scotese and McKerrow, 1990) show that all of the deposits included in the synthesis of Figure 8 were located within 30° of their respective paleoequators, so that differences in paleolatitude are probably not a significant factor in the temporal changes shown. More recently, detailed studies of brachiopod geochemistry from a number of Ordovician units in North America have supported this general conclusion regarding secular changes in the isotopic compositions of marine carbonate (Qing and Veizer, 1994).

What do the differences in the brachiopod $\delta^{18}O$ compositions in the Guttenberg and Spechts Ferry Members mean (Fig. 5), and what do the different slopes of the covariant brachiopod $\delta^{13}C$ and $\delta^{18}O$ trends between the Guttenberg and Spechts Ferry Members signify? Differing $\delta^{18}O$ compositions could reflect short-term microenvironmental changes in benthic habitats, including changes in water temperature or salinity, resulting from changes in depth-related seaway stratification or changes in seaway circulation (Railsback et al., 1989, 1990). However, changes in the slopes of covariant brachiopod $\delta^{13}C$ and $\delta^{18}O$ trends are not so easily explained. Carpenter and Lohmann (1990, 1995) showed that the $\delta^{13}C$ and $\delta^{18}O$ values of modern brachiopod shells have positive covariant trends ranging over several per mil, the ^{18}O- and ^{13}C-enriched end members representing isotopic equilibrium values specific to the environments in which the organisms were collected. Carpenter and Lohmann (1990, 1995) attributed varying slopes of covariant $\delta^{13}C$ and $\delta^{18}O$ trends for different brachiopod species to interspecific vital effects. Brachiopod species were not identified from the skeletal components sampled from the Cominco Millbrook Farms SS-9 core, but Willman and Kolata (1978) noted that brachiopod faunas are notably different between the Spechts Ferry and Guttenberg, *Pionodema subequata* dominating in the Spechts Ferry, and *Sowerbyella punctostriata* and *Rafinesquina trentonensis* dominating in the Guttenberg. The apparent differences between brachiopod isotopic compositional fields B and C (Fig. 5), and the different slopes of covariant $\delta^{13}C$ and $\delta^{18}O$ trends for brachiopods sampled from the

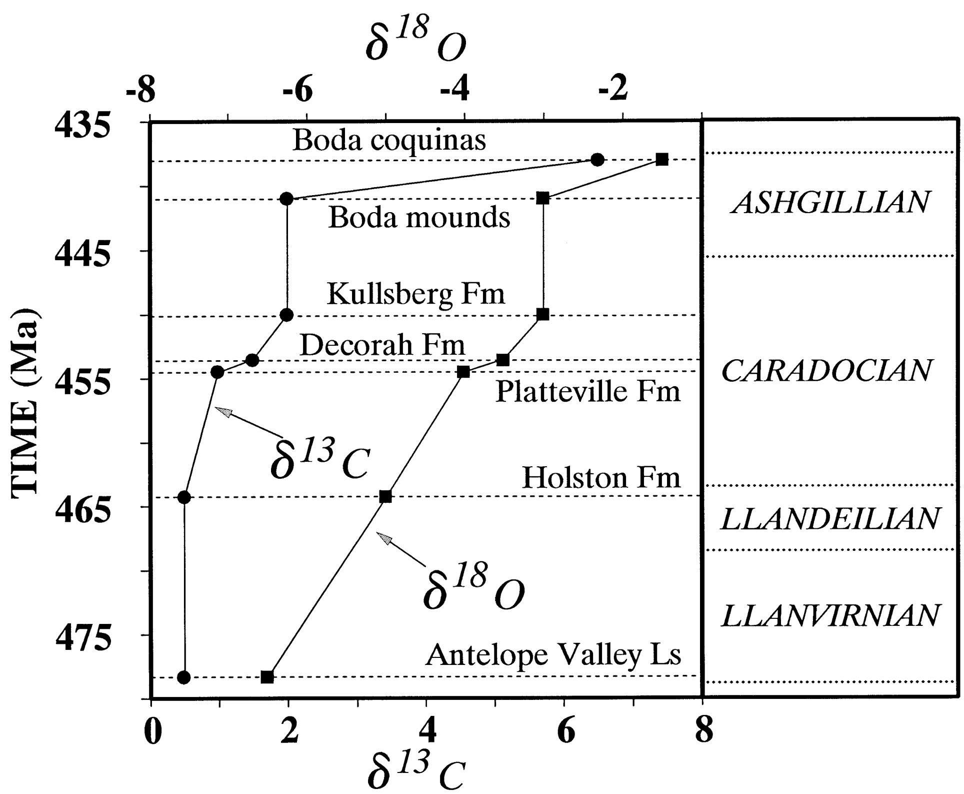

Figure 8. Secular variation in the carbon and oxygen isotopic composition of Middle-Late Ordovician marine carbonate, from Ludvigson et al. (1990b). Estimates of marine carbonate compositions are from the following data sources: Antelope Valley Limestone of Nevada (Ross et al., 1975); Holston Formation of Tennessee (Steinhauff et al., 1989); Platteville Formation of Wisconsin (Hall and Friedman, 1969); Decorah Formation of Iowa (Ludvigson et al., 1990b, and this study); Kullsberg Formation of Sweden (Marshall and Middleton, 1990); and Boda Formation of Sweden (Marshall and Middleton, 1990). The Ordovician time scale used is that of Sloan (1987).

Spechts Ferry and Guttenberg Members might simply reflect differences in interspecific vital effects. Alternatively, if the ^{18}O- and ^{13}C-depleted end members of the brachiopod covariant $\delta^{13}C$ and $\delta^{18}O$ trends actually do record the composition of diagenetic calcites, as suggested by Ludvigson et al. (1990a, 1990b), the covariant trends might result from differences in the early diagenetic histories of the Spechts Ferry and Guttenberg Members.

Diagenetic components. Diagenetic carbonate components in the Spechts Ferry show greater carbon and oxygen isotopic depletions relative to original brachiopod compositions (cf. fields 1, 2, and 3 with field B in Fig. 7c) than those of the Guttenberg (cf. fields 4, 5, and 6 with field C in Fig. 7d). This indicates that the two units had different diagenetic histories; diagenetic alteration of the Spechts Ferry occurred in a more fluid-dominated setting than the Guttenberg, which was diagenetically stabilized in a more rock-dominated setting. Moreover, this indicates that the carbonate stable isotopic chemostratigraphy of the Decorah Formation does not record a purely primary environmental signal, but also includes a secondary diagenetic overprint.

The ^{18}O depletions of diagenetic components in the Spechts Ferry (fields 1 and 3, Fig. 7c) are a noteworthy feature of the data. This isotopic depletion can be explained either by early diagenetic water-rock interaction with a fluid of lower $\delta^{18}O$ than coeval seawater, or by later diagenetic recrystallization at higher temperatures (by several tens of degrees Centigrade), probably in burial environments. One possible source of diagenetic fluids with lighter $\delta^{18}O$ values is meteoric water that could conceivably have infiltrated Spechts Ferry strata as a consequence of offshore intrusion of fresh ground water from a recharge area on the Transcontinental Arch (Fig. 3; also see Ludvigson et al., 1994, for discussion of this process). The overall importance of burial diagenetic processes on the stable isotopic systematics of the Galena Group carbonates remains poorly studied. As will be discussed below, carbonate components from samples in the upper part of the Guttenberg also show a trend toward significant carbon and oxygen isotopic depletion believed to be related to diagenetic overprinting. Further studies are needed.

Micrites. The $\delta^{18}O$ values of micrites from the Decorah Formation shown in Figure 7 (compositional fields 2, 4, and 6), are similar to those of the ^{18}O-enriched end members of the linear covariant carbon and oxygen isotope trends detected in coexisiting brachiopods (compare to fields B and C in Figs. 5 and 7, c and d), which are interpreted as the isotopic compositions of marine calcite in the Decorah Formation. The ^{13}C depletion of Spechts Ferry micrites (field 2, Fig. 7c) by 3.5 to 5 per mil relative to field B in Figure 7c, however, is indicative of precipitation in an environment different than that recorded by brachiopods of the shelly benthos. The geochemical relations discussed above suggest that Spechts Ferry micrites are at least in part microcrystalline calcite cements that formed in modified marine phreatic environments (used here in the sense of Carpenter et al., 1988; Ludvigson et al., 1994). Depletion of ^{13}C in these environments results from incorporation of dissolved CO_2 produced by bacterial oxidation of particulate organic carbon ($\sim\delta^{13}C = -29‰$, see Fig. 1) in marine pore fluids that diffused below the sea floor. This interpretation is further supported by data showing that Spechts Ferry micrites have the lowest Mg contents of the carbonate components sampled from the Decorah Formation (Fig. 6), suggesting diagenetic Mg depletion through water-rock interaction. Modified marine phreatic carbonates from mudrock concretions can produce $\delta^{13}C$ values of less than –20‰ (Ludvigson et al., 1994), while the $\delta^{13}C$ composition of nodular micites in the Spechts Ferry is closer to that of marine carbonate than that of indigenous kerogen. These compositions suggest that either some portion of the micrite originated as a primary marine sediment, or that respired CO_2 composed only a minor portion of the dissolved carbonate in the modified marine phreatic pore-fluid system.

The carbon and oxygen isotopic compositions of micritic components from the Guttenberg (see fields 4 and 6 in Fig. 7d) are more closely similar to marine calcite compositions of the shelly benthos (field C, Fig. 7d) than in the underlying Spechts Ferry. At the 684.5 ft (208.6 m) level, below the peak of the positive $\delta^{13}C$ excursion in the Guttenberg, micrites have $\delta^{13}C$ values just below those of coexisiting brachiopods (cf. fields C and 4, Fig. 7d). At the peak of the positive $\delta^{13}C$ excursion at the 679.4 ft (207 m) level, micrites have $\delta^{13}C$ values *above* those of coexisting brachiopods.

Is this micrite $\delta^{13}C$ "overshoot" of open-marine carbonate values a primary signal residing in detrital carbonate muds, or a secondary diagenetic signal of nodular microcrystalline cement precipitation? Even though the $\delta^{13}C$ of organic matter is up to 4 per mil heavier at the peak of the positive $\delta^{13}C$ excursion, this change in the composition of the source of bacterially produced dissolved CO_2 cannot explain the "overshoot." No mixture of dissolved marine carbonate ($\delta^{13}C = +1‰$) and dissolved carbonate produced from bacterial oxidation of organic matter ($\delta^{13}C = -29$ to -23; Fig. 1) will yield diagenetic fluids with dissolved carbonate $\delta^{13}C$ compositions that range outside these end-member compositions (i.e., up to +2.5‰). Arguments can be advanced in favor of a diagenetic origin for ^{13}C-enriched micrites, however, through marine phreatic bacterial methanogenesis in organic-rich sediments (Gautier and Claypool, 1984).

Alternatively, if the ^{13}C-enriched micrites are primary sedimentary components, they must have formed in a different environment than the brachiopods of the shelly benthos. Berger and Vincent (1986) discussed how "photic pumping," the physical settling of particulate organic carbon in ^{13}C-depleted phytoplankton during geologic episodes of high primary productivity, can enrich dissolved organic and carbonate $\delta^{13}C$ compositions of the sea surface layer, where most photosynthetic primary production takes place. This process is stratigraphically recorded by coeval positive $\delta^{13}C$ excursions in organic and calcareous planktic components in Mesozoic and Cenozoic pelagic deposits (Berger and Vincent, 1986). Such an interpretation for ^{13}C-

enriched micrites in the Guttenberg is not necessarily precluded by a lack of known calcareous planktonic microrganisms in Paleozoic carbonates. Arguments for abiotic carbonate mud formation near the sea surface are well known in the carbonate literature (Shinn et al., 1989). Moreover, coeval positive $\delta^{13}C$ excursions in the organic and inorganically precipitated calcite components of lacustrine marls are known to be associated with episodes of high photosynthetic productivity in modern lakes (Hollander et al., 1992), providing a potential analogy for the positive $\delta^{13}C$ excursion in the Guttenberg.

Additional comparative studies of Decorah Formation micrite petrography and geochemistry, at the micron scale, are recommended to address the current uncertainties about the origin(s) of this critical component.

Echinoderms. Original skeletal carbonates of echinoderms form as a porous microstructure of high magnesium calcite that is subject to fabric-retentive replacement by diagenetic low magnesium calcite during the diagenesis of ancient limestones (Bathurst, 1975). As discussed by Meyers and Lohmann (1985), the probabilistic microsampling of echinoderm grains in diagenetically stabilized limestones yields $\delta^{13}C$ and $\delta^{18}O$ values that range between original marine compositions and those of early diagenetic cements. Thus, the carbon and oxygen isotopic compositions of crinoid grains, when compared with other components (brachiopods) that retain a better "memory" of original marine compositions in ancient limestones, can be used as a proxy indicator for the compositions of early diagenetic cements. Application of this general principle to Decorah carbonates is further supported by CL petrographic observations that early-stage calcite cement zones rimming the echinoderm grains also fill the stereome pore network within the grains.

Comparisons between echinoderm grain compositions and brachiopod-derived estimates of marine calcite compositions for the Spechts Ferry and Guttenberg Members clearly show differences in the diagenetic histories of these two units. In the Spechts Ferry, crinoids (fields 1 and 3; Fig. 7c) have stable isotopic values that are depleted by several per mil relative to marine carbonate values (field B, Fig. 7c), whereas in the Guttenberg, crinoids (field 5, Fig. 7d) have stable isotopic values that partially overlap with and are much less depleted than marine carbonate values (field C, Fig. 7d).

In contrast to the preceding discussions regarding alternatives for the origin of micritic components, the biotic origin of crinoid skeletal grains in benthic environments is well known, so differences between their $\delta^{13}C$ and $\delta^{18}O$ compositions in the Spechts Ferry and Guttenberg record differences in the early diagenetic fate of high magnesium calcite in two rock units that underwent differing extents of water-rock interaction.

Brachiopod grain alteration. The isotopic compositions of diagenetically altered brachiopod shells provide additional insights into the secondary processes that operated on the carbonate geochemistry of Decorah strata. Luminescent brachiopod shell material sampled from a concretionary carbonate interbed at the 692.2 ft (211 m) level in the SS-9 core plot within field 2 of Figure 7c, indicating grain alteration by the same early modified marine phreatic fluids from which enclosing microcrystalline calcite cements were precipitated.

Brachiopod calcite from the shells of *Strophonema* sp. and *Pionodema subequata* that were separated from outcrops of Spechts Ferry shale have isotopic values that plot along the linear covariant brachiopod trend discussed earlier from Figure 5, although results from *Strophonema* generally plot closer to the ^{13}C- and ^{18}O-enriched end member, while results from *Pionodema* plot closer to the depleted end member in area 1 of Figure 7c. The coincidence of *Pionodema* calcite isotopic values with those of diagenetically altered crinoid ossicles in compositional field 1 (see Fig. 7, a and c) could suggest that these brachiopod shells may be hosts to greater proportions of diagenetic intraskeletal calcite than *Strophonema*. These specimens were recovered from shell lag beds in plastic shale outcrops, and their petrography shows that all underwent varying degrees of compactive deformation, as grain fracturing both cross cutting and parallel to the laminar shell microstructure. These fractures are filled by a uniformly bright luminescent calcite cement. Given the volumetric abundance of this diagenetic phase in the shells separated from Spechts Ferry shales (often ≥ 50%), this luminescent calcite can be inferred to have an isotopic composition that plots in field 1 of Figure 7c. This implies that diagenetic phases plotting in fields 1 and 3 (Fig. 7c) were coeval with later shale compaction in the Spechts Ferry, and also indicates a later diagenetic origin for ^{18}O-depleted components in the unit.

CARBONATE COMPONENT CHEMOSTRATIGRAPHY OF THE DECORAH FORMATION

Carbon and oxygen isotope curves for individual carbonate components provide additional insights into the whole-rock carbonate $\delta^{13}C$ curve shown in Figure 9. Brachiopod-derived estimates of marine carbonate $\delta^{13}C$ compositions (dashed heavy line) change less than one per mil through the Spechts Ferry-Guttenberg interval, while micrite $\delta^{13}C$ compositions (curve shown by screened pattern) change by 4 to 6 per mil. This unambiguously shows that the whole-rock carbonate carbon isotope excursion in the Decorah Formation is exclusively carried by micritic components. Moreover, the essentially invariant marine carbonate $\delta^{13}C$ compositions through the interval suggest that this geochemical event in the Decorah Formation does not record a perturbation of the global ocean-atmosphere carbon cycle, as has been proposed for some other carbon isotope excursions in the marine chemostratigraphic record (Arthur et al., 1988; Hollander et al, 1993). Global disturbances in the ocean-atmosphere carbon cycle are stratigraphically recorded by coeval $\delta^{13}C$ excursions in marine organic and carbonate carbon, with changes in the magnitude of $\delta^{13}C_{carbonate}$-$\delta^{13}C_{organic}$ considered to follow changes in global atmospheric P_{CO_2} (Arthur et al., 1988). Moreover, the decoupling of marine carbonate and organic carbon signals indicates that the processes responsible for this positive organic

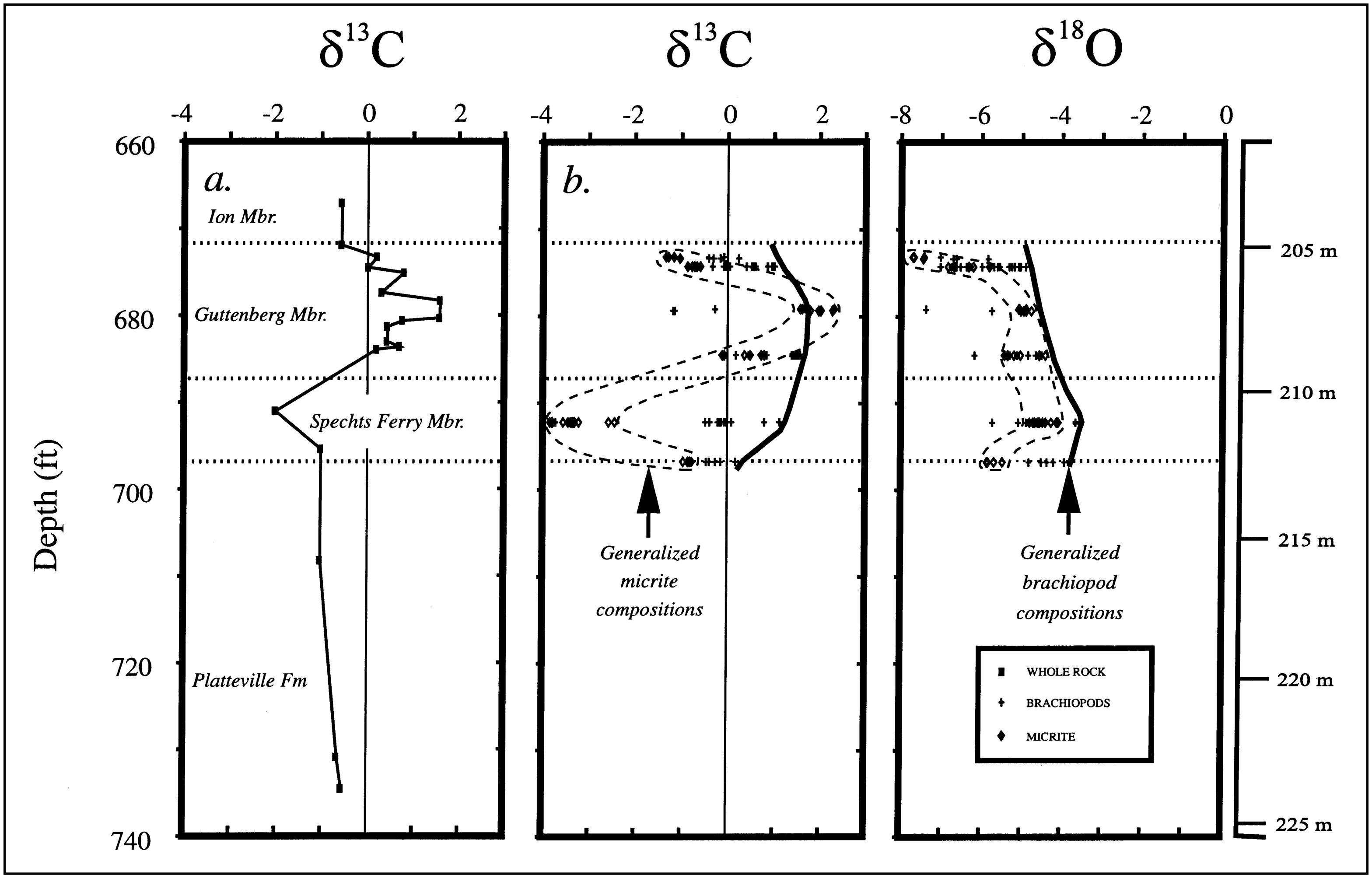

Figure 9. Carbon and oxygen isotope stratigraphy of whole-rock carbonate (a) and carbonate components (b) in the Cominco Millbrook Farms SS-9 core. Note that shifts in whole-rock carbonate $\delta^{13}C$ (solid line connecting filled rectangles) are carried by the $\delta^{13}C$ signal of micritic components (curve shown by dashed lines). Brachiopod-derived estimates of marine carbonate compositions (generalized heavy line) do not follow the $\delta^{13}C$ shifts shown in whole-rock carbonate and micritic components.

carbon $\delta^{13}C$ excursion were not operant in the benthic water mass where the brachiopods lived. This indicates that seaway stratification was an important environmental requirement for the origin of the positive carbon isotope excursion in the Decorah, and supports the "photic pumping" hypothesis of Berger and Vincent (1986) for the origin of this event.

Despite differences in stratigraphic sampling positions and density, comparison between the organic (Fig. 1) and carbonate (Fig. 9) $\delta^{13}C$ curves shows that the positions of the peak negative inflections in the Spechts Ferry are not coincident. The negative $\delta^{13}C_{organic}$ excursion undoubtedly was at least in part responsible for the negative $\delta^{13}C_{carbonate}$ excursion as a diagenetic feedback, in that sedimentary organic matter served as the source of bacterially respired dissolved CO_2 in early diagenetic fluids. Nevertheless, carbonate geochemical data in this study show that early diagenetic processes unique to the Spechts Ferry depositional cycle were responsible for the negative $\delta^{13}C_{carbonate}$ excursion in the unit. Likewise, the trends toward depleted carbon *and* oxygen isotopic compositions in micrites in the two uppermost stratigraphic sampling positions (674.3 ft [205.5 m] and 673.4 ft [205.3 m] levels) in the Guttenberg of the SS-9 core demonstrates that the negative $\delta^{13}C_{carbonate}$ shift in the upper Guttenberg is a diagenetic overprint on a stratigraphic interval characterized by the same marine carbonate $\delta^{13}C$ composition as in underlying strata.

Although the stratigraphic sampling positions of our carbonate component geochemical data are too widely dispersed to test this hypothesis with rigor, data may suggest that both the Spechts Ferry (cycle 4A of Witzke and Bunker, this volume) and Guttenberg-Ion (cycle 4B of Witzke and Bunker, this volume) shallowing-upward depositional cycles are internally characterized by micrites with upward trends in $\delta^{13}C$ depletion that result from systematic changes in the water/rock ratios of early modified-marine phreatic diagenetic environments. Specifically, the lower portions of the cycles may be characterized by rock-dominated diagenetic environments, while upper portions of the cycles are characterized by more fluid-dominated environments. While this observation parallels conclusions that have been applied to shallowing-upward carbonate cycles capped by subaerial exposure surfaces that received recharging meteoric fluids (Allan and Matthews, 1982; Plocher et al., 1992; Algeo, this volume), the shallowing-upward cycles of the Decorah Formation were wholly deposited and lithified in subtidal marine settings. If this conclusion were verified by more detailed studies of Ion strata and overlying units, sequence stratigraphic interpretations of thick subtidal carbonate successions like the Galena Group could be independently tested through stable isotopic chemostratigraphic investigations.

INTERPRETATION OF DEPOSITIONAL PROCESSES

As suggested by Ludvigson et al. (1992a, 1992b), the decoupling of coeval $\delta^{13}C$ signals from the shelly benthos and micritic components in the Guttenberg can be explained by deposition in a stratified seaway, and the positive $\delta^{13}C$ excursion in the Guttenberg apparently results from an increase in photosynthetic productivity near the sea surface during deposition of the unit. These environmental requirements are both satisfied by deposition of the Guttenberg during a period of quasiestuarine circulation (Witzke, 1987) in the epeiric sea.

Sea-level rise attending Guttenberg deposition gave rise to periodic benthic dysoxia-anoxia, indicating expansion of an oceanic oxygen minimum zone into the North American epicontinental seaway. Freshwater runoff from clastic source areas on the Transcontinental Arch (Fig. 3) is proposed to have established a positive runoff/evaporation balance in the seaway, giving rise to offshore surface currents and establishment of a density-stratified water column with a brackish surface layer. Onshore bottom currents are suggested to have been vertically diverted toward the sea surface as they impinged on the shelf slope of the Decorah clastic wedge (Fig. 4). The mixing between upwelling marine bottom waters and brackish surface waters fed by fluvial runoff provided limiting nutrients required for photosynthetic activity, leading to an episode of high surface productivity and increased particulate rainout of ^{13}C-depleted organic material to the sea floor. Quasiestuarine circulation thus explains how Guttenberg components derived from the surface layer (organic matter; mud-sized inorganically precipitated detrital carbonate) carry the positive $\delta^{13}C$ excursion, while Guttenberg components derived from the bottom layer (brachiopods) do not.

The decoupling of carbon isotopic chemostratigraphic signals detected from coeval benthic brachiopods and organic matter in the Decorah Formation also has important implications for the paleoecology and phyletic affinity of *G. prisca*, the organic-walled microfossil that composes nearly all of the organic carbon in the unit (Jacobson et al., 1988). This decoupling is incompatible with the suggestions of some authors that *G. prisca* inhabited benthic environments (Reed et al., 1986; Foster et al., 1990; Stasiuk et al., 1993), because shifting dissolved carbon $\delta^{13}C$ compositions in the benthic water mass should also have been sensed by brachiopods in the Decorah. Because the processes responsible for the positive $\delta^{13}C$ excursion apparently were not operant on the sea floor, origination in a photic surface layer provides a simple logical alternative. These relationships suggest a phytoplanktic origin for the extinct organic-walled microfossil *G. prisca*.

CONCLUSIONS

The stratal geometry and tempestite proximality trends of the Decorah Formation of eastern Iowa indicate that the unit was deposited on an open-marine subtidal shelf near maximum storm wave base, and maximum transgression is represented in the organic-rich strata of the Guttenberg Member. Brachiopod-derived marine carbonate isotopic compositions from the Spechts Ferry Member are $\delta^{13}C = +1‰$ and $\delta^{18}O = -3.5‰$; whereas in the Guttenberg Member they are: $\delta^{13}C = +1‰$ and $\delta^{18}O = -5‰$. This short-term change is superimposed on a recently recognized long-term secular increase in the $\delta^{18}O$ of

Middle Ordovician marine carbonates. Decorah carbonates lithified in early diagenetic modified-marine phreatic environments, during which a characteristic wavy to nodular bedding style formed in organic-rich strata of the Guttenberg Member. Isotopic data from diagenetic components show that the Spechts Ferry Member lithified in a more fluid-dominated system than the immediately overlying Guttenberg Member, which was characterized by a rock-dominated system.

Whole-rock carbonate $\delta^{13}C$ shifts in the Decorah Formation are carried by micritic components. A positive shift in the Guttenberg Member to micrites with $\delta^{13}C$ values up to +2.5‰ indicates either that some of the micrite signal is primary and not of benthic origin, and/or that early diagenetic marine phreatic fluids in the organic-rich Guttenberg were affected by bacterial methanogenesis. Carbonate component chemostratigraphy suggests that subtidal shallowing-upward depositional cycles in the Decorah Formation (the Carimona-Spechts Ferry cycle and the Guttenberg-Ion cycle) are each internally characterized by micrites with stratigraphically upward trends toward ^{13}C-depletion as a consequence of progressively increasing marine phreatic water/rock ratios. The decoupling between the invariant open-marine carbonate $\delta^{13}C$ signal carried by the shelly benthos and the $\delta^{13}C$ shifts carried by coeval organic carbon and micrite indicate that the positive $\delta^{13}C$ excursion in the Guttenberg resulted from an episode of increased photosynthetic productivity near the sea surface. This event was a consequence of quasiestuarine circulation attending marine transgression in the Guttenberg Member. Relationships described in this chapter suggest that the extinct organic-walled microfossil *Gloeocapsomorpha prisca* was a phytoplanktic organism.

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