

# **CALCITE, ARAGONITE, AND BIMINERALIC OIDS IN MISSOURIAN (UPPER PENNSYLVANIAN) STRATA OF KANSAS: STRATIGRAPHIC AND GEOGRAPHIC PATTERNS OF VARIATION**

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## **ABSTRACT**

Ooids from Missourian (Upper Pennsylvanian) strata of Kansas exhibit geographic and stratigraphic patterns of variation in primary mineralogy that reflect secular glacio-eustatic and local environmental controls. Original ooid mineralogy was inferred based on cortical fabric, preservation state, and trace element chemistry. Primary low-Mg calcite ooids exhibit well-preserved radial fabrics and low Mg-low Sr values; high-Mg calcite ooids exhibit microspar replacement of radial fabrics, intracortical dolomite, and high Mg-low Sr values; aragonite ooids exhibit poorly-preserved laminar sparry fabrics, oomoldic porosity, and high Sr-low Mg values.

The primary mineralogies of Missourian ooids exhibit non-random patterns of variation in time and space. Stratigraphically, ooid mineralogy may be correlated to 3rd-order (ca. 1.2-2.0 m.y.) glacio-eustatic cycles, which modulate the amplitude of 4th-order (ca. 400 k.y.) cyclothemic regressions. Within 3rd-order cycles, precipitation of aragonite during relative highstands and calcite during lowstands implicates variation in tropical seawater temperature rather than in aqueous CO<sub>2</sub> or salinity as the primary control on secular mineralogic variation. Geographically, two horizons exhibit mineralogic gradients in response to local environmental controls: Mound Valley ooids change from aragonite to low-Mg calcite and Tyro/Benedict Bed ooids change from high-Mg calcite to aragonite along an outer- to inner-shelf transect. This pattern probably reflects a secular shift from a positive to a negative water balance in restricted inner-shelf areas, consistent with evidence of increasing aridity in midcontinent North America during the Late Pennsylvanian.

Bimineralic ooids mostly consist of a calcitic inner and an aragonitic outer cortex with a characteristic transition diameter ranging from 0.2 to 0.7 mm in different oolitic units. Intracortical transitions in mineralogy may reflect changes in kinetic factors that favor a calcite-to-aragonite transition with increasing fluid shear, but thermodynamic factors ultimately control the degree of seawater carbonate saturation and, hence, the fluid shear threshold at which a mineralogic transition may occur. Deterministic patterns of primary ooid mineralogy have predictive value in locating oomoldic limestones with potential as hydrocarbon reservoirs.

## **INTRODUCTION**

As chemical precipitates, abiotic marine carbonates (AMCs) provide records of ambient paleo-atmospheric and -oceanic conditions. Secular variation in the primary mineralogy of AMCs (i.e., marine ooids and synsedimentary cements) was first reported by Sandberg (1975), and subsequent studies documented a pattern of alternation between epochs dominated by calcitic AMCs and those in which both aragonite and calcite were abundant or, more rarely, in which aragonite was dominant (Sandberg, 1983, 1985; Wilkinson et al., 1985; Wilkinson and Given, 1986). Sandberg identified epochs of aragonite dominance during the Early Cambrian(?), mid-Carboniferous-Triassic, and Early Cenozoic-Recent (Fig. 1A), whereas Wilkinson and colleagues, using a larger dataset, constrained these epochs to the Middle Cambrian-Early Ordovician, mid-Mississippian-Middle Triassic, and mid-Cenozoic-Recent (Fig. 1B-C). Alternating epochs of aragonite and calcite dominance appear to have existed since at least the Middle Proterozoic (e.g., Tucker, 1984, 1985; Singh, 1987; Zempolich et al., 1988; Kidder and Hall, 1993).

Long-term shifts in AMC mineralogy have been linked to 1st-order (10<sup>8</sup>-10<sup>9</sup> yr) geotectonic cycles reflecting variable rates of mantle convection or plume flux (Mackenzie and Pigott, 1981; Wilkinson et al., 1985; Mackenzie and Morse, 1992). In this model, intensification of mantle processes causes faster mid-ocean ridge spreading and elevated atmospheric and oceanic CO<sub>2</sub> levels owing to greater CO<sub>2</sub> outgassing at subduction zones. Elevated CO<sub>2</sub> reduces seawater carbonate saturation, favoring the precipitation of calcite over aragonite. Because aragonite exhibits a more restricted latitude-depth range of saturation than calcite, its precipitation may be severely restricted under conditions of low global seawater carbonate saturation, resulting in "calcite seas." The converse situation, i.e., weak mantle processes and reduced atmospheric and oceanic CO<sub>2</sub> levels, results in expanded ranges of saturation in seawater for both calcite and aragonite, which favors precipitation of the latter owing to kinetic factors, yielding "aragonite seas." Long-term changes in eustatic elevation are commonly used as a proxy for variation in intensity of mantle processes (Fig. 1D).

Although long-term changes in AMC mineralogy are well-documented, short-term changes have received little

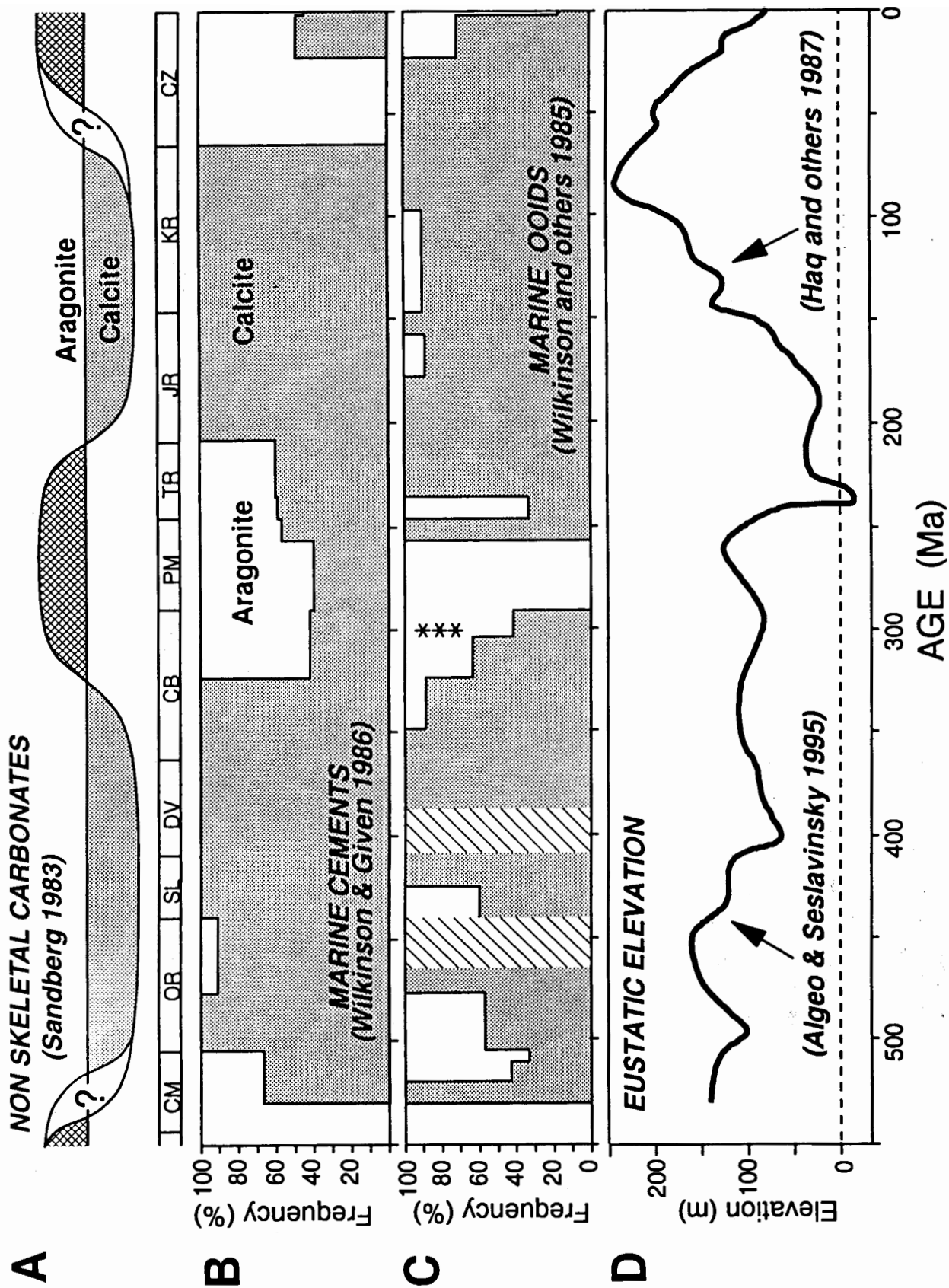


FIGURE 1. Secular Phanerozoic trends in (A) mineralogy of non-skeletal carbonates (Sandberg, 1983), (B) marine cements (Wilkinson and Given, 1986), and (C) marine ooids (Wilkinson et al., 1985). Asterisks indicate age of Missourian Stage ooids of this study. (D) Phanerozoic eustatic elevations based on Paleozoic analysis of Algeo and Seslavinsky (1995) and Mesozoic-Cenozoic analysis of Haq et al., (1987).



attention. However, high-frequency variation in AMC mineralogy may be useful in determining: 1) the character of transition intervals between epochs of aragonite and calcite seas, and 2) differences in primary controls on AMC mineralogy at different timescales. These problems potentially may be addressed through study of units containing bimineralic ooids or stratigraphically interbedded calcite and aragonite ooids (e.g., Land et al., 1979; Moore and Druckman, 1981; Popp and Wilkinson, 1983; Wilkinson et al., 1984; Tucker, 1984; Moore et al., 1986; Singh, 1987; Chow and James, 1987; Swirydczuk, 1988; Weaver, 1992; Kidder and Hall, 1993; Heydari et al., 1993; Heydari and Moore, 1994). Although the petrographic and geochemical characteristics of these oolitic units have been exhaustively studied, there has been comparatively little investigation of patterns of stratigraphic or geographic variation that would assist in understanding primary controls on AMC mineralogy and transition events between calcite and aragonite seas.

This study was initially motivated by the desire to investigate one such transitional interval. A documented occurrence of bimineralic ooids in the Missourian Stage of Kansas (Wilkinson et al., 1984) provided a starting point for investigation of both long-term secular trends and potential relationships with Carboniferous glacio-eustatic cycles. Preliminary examination of thin sections at the Kansas Geological Survey in 1993 resulted in identification of oolitic units of probable primary aragonitic and calcitic mineralogy, as well as some intervals of mixed or bimineralic composition. In order to further examine patterns of spatio-temporal variation in ooid mineralogy, we collected samples both from cores at the survey and from outcrops at locales throughout southeast and east-central Kansas. The goals of the present study are: 1) to document patterns of stratigraphic and geographic variation in primary ooid mineralogy within the Missourian Stage of eastern Kansas, 2) to draw inferences regarding the primary controls on ooid mineralogy, and 3) to develop an integrated sedimentologic, paleoceanographic, and paleoclimatic model to account for the observed patterns of variation.

## PALEOGEOGRAPHIC AND PALEOCLIMATIC SETTING

During Missourian time, the southern Midcontinent region was a shallow-marine platform. To the north and west, the platform extended for hundreds of kilometers, interrupted only by the low-relief Central Kansas Uplift that separated the East and West Kansas shelves (Watney, 1985; Watney et al., 1989). To the south, the platform was bordered by the rapidly subsiding Anadarko and

Arkoma foreland basins, into which voluminous clastics were shed from the Ouachita-Arbuckle uplifts, episodically building out over the Kansas Shelf margin (Houseknecht and Kacena, 1983; Rascoe and Adler, 1983). The shelf margin trended approximately east-west through south-central Kansas, changing to a somewhat northeasterly orientation in southeastern Kansas during early Missourian time.

On a regional scale, ooid shoals are most common along the southern margin of the Kansas Shelf both east and west of the Central Kansas Uplift (Watney, 1985; Feldman and Franseen, 1991). Localization of ooid buildups here may be attributed to: 1) comparatively rapid subsidence close to the hinge line separating the carbonate shelf from the northern Anadarko Basin, 2) focusing of wave and current energy along the break in slope formed by the shelf margin, and 3) pre-existing topographic highs, i.e., phylloid algal mounds, that provided nucleation sites (Heckel, 1979; Watney, 1985). In western Kansas, lobe-shaped oolitic grainstone bodies extend miles shelfward of the hinge line and may represent spillover lobes, indicating onshore transport of oolitic sands (Watney, 1985).

Climatically, the southern Midcontinent region was located slightly north of the equator during Missourian time (ca. 5-10° N; Heckel, 1977; Scotese and Golonka, 1993). Eastern Kansas was positioned near the northern margin of the humid equatorial zone as evidenced by extensive coal development in more shale-rich sequences in Oklahoma and Missouri (Heckel, 1977). However, the northern and western parts of the Midcontinent shelf were located within the arid tropical belt at 10-25° N latitude. Northward drift progressively moved North America into higher latitudes during the Permo-Carboniferous Appalachian-Ouachita Orogeny (Scotese and Golonka, 1993).

## STRATIGRAPHY

In eastern Kansas, the Missourian Stage comprises, in ascending order, the Pleasanton, Kansas City, and Lansing groups (Fig. 2). The Kansas City Group is further subdivided into the Bronson, Linn, and Zarah subgroups. Whereas the Pleasanton Group mainly consists of shale and sandstone, the Kansas City and Lansing groups contain numerous limestone units, many of which are oolitic. Upper Pennsylvanian strata of the Midcontinent are characterized by a repetitive succession of rock types known as "cyclothems," which are individually thin (ca. 1 to 15 m) but laterally extensive (commonly 100's of km). Differences in lithology and internal stratigraphy of coeval rock successions in the Midcontinent and Illinois Basin resulted in definition of "Kansas-type" and "Illinois-type"

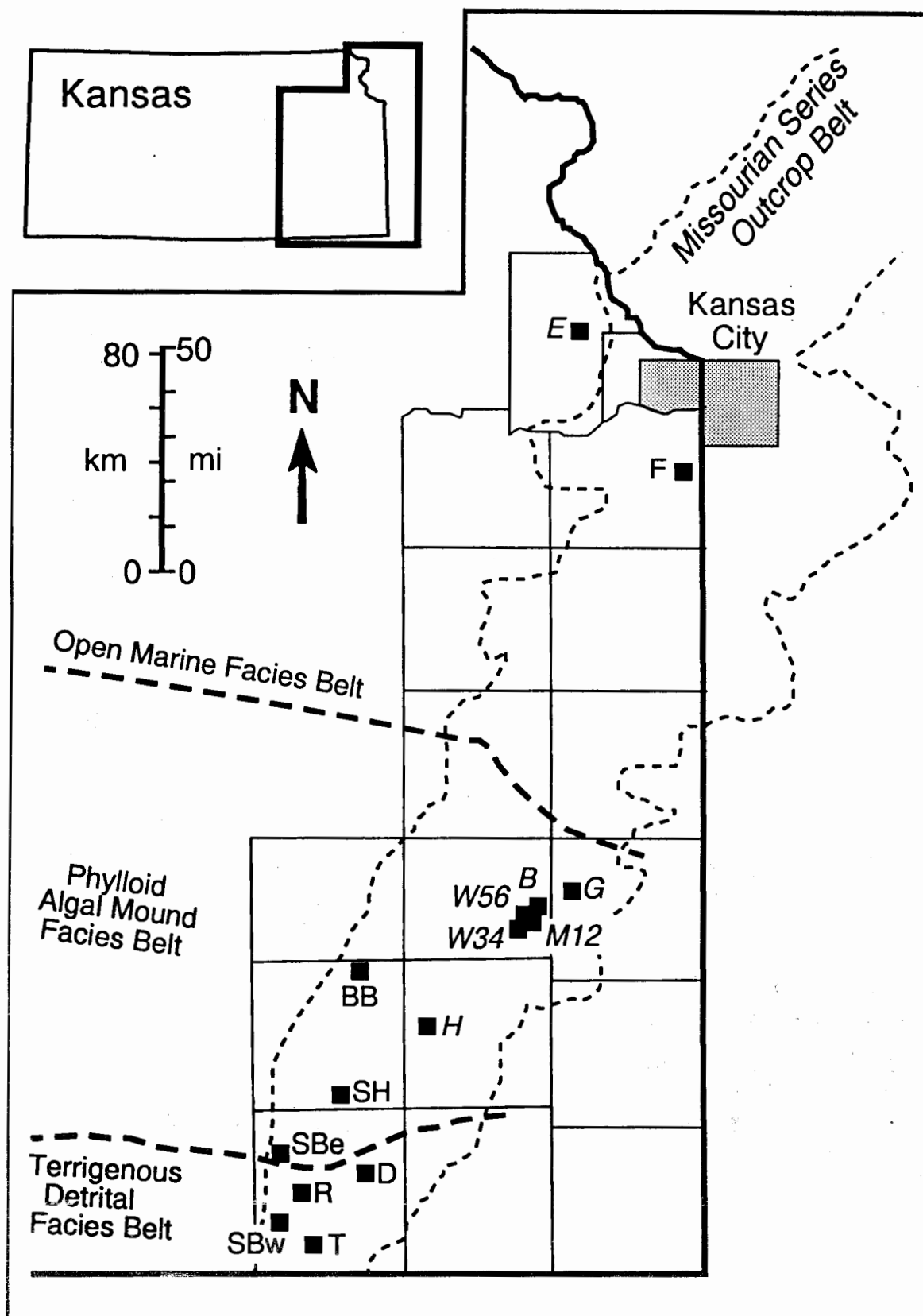


FIGURE 3. Location map of study locales in eastern Kansas (see Table 1 for location and formation data). Missouriian Stage outcrop (light dashed lines) and facies belts (heavy dashed lines; based on facies development in upper parts of regressive limestones) from Heckel (1975); thin lines are Kansas counties. Additional information and outcrop descriptions are available in Heckel (1975, 1978, 1979), and Feldman and Franseen (1991).

TABLE 1. Locations of Study Cores and Outcrops

Abbrv.*	Core/Outcrop	County	Twp./Range/Sct.	Formations
<i>E</i>	Edmonds #1	Leavenworth	9S/22E/35	Bethany Falls
<i>F</i>	Roadcut, I-435 SW of Kansas City	Johnson	N/A	Farley
<i>G</i>	Green Acres #1	Bourbon	24S/22E/26	Bethany Falls, Mound Valley
<i>B</i>	Barnett #1	Bourbon	25S/21E/7	Winterset
<i>W56</i>	Woodward #5, #6	Bourbon	25S/21E/12	Bethany Falls, Mound Valley
<i>W34</i>	Woodward #3, #4	Bourbon	25S/21E/13	Bethany Falls, Mound Valley
<i>M12</i>	Mitchellson #1, #2	Bourbon	25S/21E/18	Bethany Falls, Winterset
<i>BB</i>	Wilson Lake spillway	Wilson	27S/16E/NA	Benedict Bed
<i>H</i>	Heilman #1	Neosho	28S/18E/36	Mound Valley
<i>SH</i>	Roadcut, Hwy 96 W of Neodesha	Wilson	30S/15E/NA	Spring Hill
<i>SBe</i>	Roadcut, W of Elk City Lake	Montgomery	32S/15E/7	South Bend
<i>D</i>	Rivercut, E of Independence	Montgomery	32S/16E/NA	Drum Oolite
<i>R</i>	Farm quarry, S of Timber Hill	Montgomery	32S/14E/2	Rutland Bed
<i>SBw</i>	Roadcut, Hwy 75 SW of Wayside	Montgomery	34S/14E/4	South Bend
<i>T</i>	Wilson's Quarry, N of Tyro	Montgomery	34S/15E/30	Tyro Oolite

\*Cores in italics.

cyclothems (Heckel, 1977). These differences relate primarily to the greater abundance of siliciclastics and coal, representing dominance of paralic environments, in Illinois compared with the carbonate-dominated marine platform of Kansas.

The major components of a "Kansas-type" cyclothem are: 1) outside/nearshore shale, 2) middle/transgressive limestone, 3) core/offshore shale, and 4) upper/regressive limestone (Heckel, 1977, 1988). Each component has characteristic diagnostic features. Outside shales consist of thick prodeltaic sandy shales and thin blocky mudstones (commonly paleosols) deposited in terrestrial or paralic environments during sea-level lowstands (Watney 1980, Schutter, 1983). Middle limestones are thin, fine-grained skeletal wackestones deposited during marine transgressions. Core shales are commonly thin, black, non-fossiliferous, phosphatic units deposited under oxygen-deficient and sediment-starved conditions during periods of maximum shelf inundation. Upper limestones consist of thick units of skeletal wackestone/grainstone containing an abundant, diverse open-marine biota capped by cross-bedded oolitic grainstones that were deposited during sea-level regressions. The tops of upper limestones often exhibit evidence of subaerial exposure, including solution tubes, caliche crusts, erosional surfaces, dissolution of metastable mineral phases (i.e., aragonite), and depleted carbonate  $\delta^{13}\text{C}$  values. Although variations on this facies sequence exist, lithologic and stratigraphic patterns are sufficiently regular to permit correlation of individual cyclothems and component members over wide areas

(Heckel, 1975, 1986; Watney et al., 1989).

Permo-Carboniferous cyclothems are generally regarded as having a glacio-eustatic origin (Wanless and Shepard, 1936; Heckel, 1986, 1994), consistent with their wide correlatability (Ross and Ross, 1985; Connolly and Stanton, 1992) and with known large coeval fluctuations in continental ice mass (Crowley and Baum, 1991). Transgressive-regressive cycles of the East Kansas Shelf exhibit both 3rd-order (1-10 m.y.) and 4th-order (0.1-1 m.y.) cyclicity. Fourth-order cycles are represented by cyclothems at a characteristic timescale of ca. 400 ky (Heckel 1986), but the existence of 3rd-order cycles in the Upper Pennsylvanian Series of the Midcontinent is less well-established. However, 3rd-order cycles having a characteristic timescale of ca. 1.2-2.0 m.y are reflected in: 1) shifting facies belts (e.g., Heckel, 1986; Boardman and Heckel, 1989), 2) overall progradation and backstepping of the East Kansas shelf margin (Watney et al., 1989), and 3) intensified subaerial erosion and early meteoric diagenesis relative to cyclothem tops (Watney, 1985; Prather, 1985). Greater  $^{13}\text{C}$  depletion of meteoric precipitates at 3rd-order cycle tops provides a quantifiable measure of variation in exposure intensity at this stratigraphic level (W.L. Watney, unpubl. data; Watson and Algeo, manuscript in preparation).

## STUDY UNITS

This study investigates ten oolitic limestone units in the

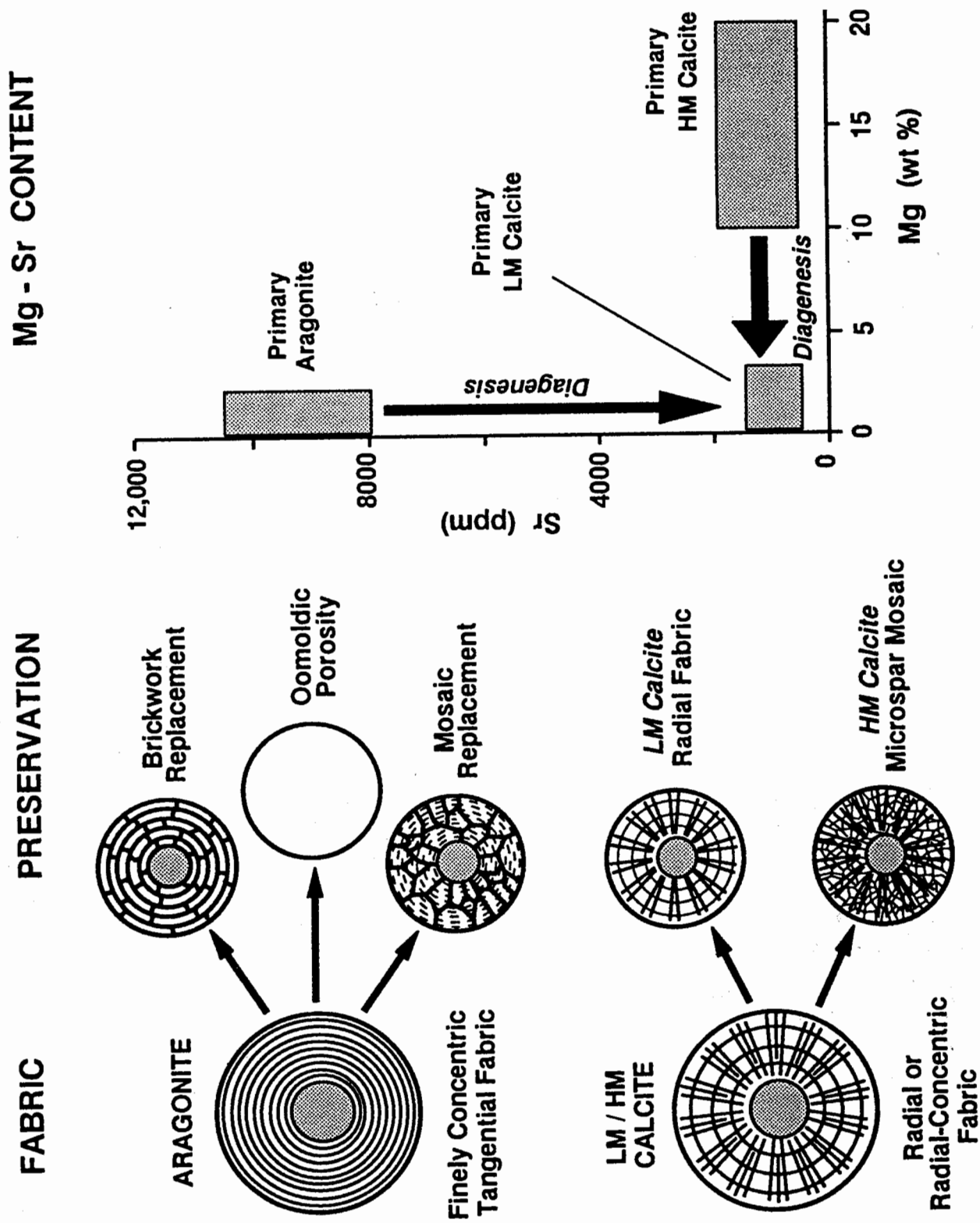


FIGURE 4. Criteria used in identification of primary ooid mineralogy. See text for discussion of diagnostic aspects of fabric, preservation, and Mg-Sr content data.



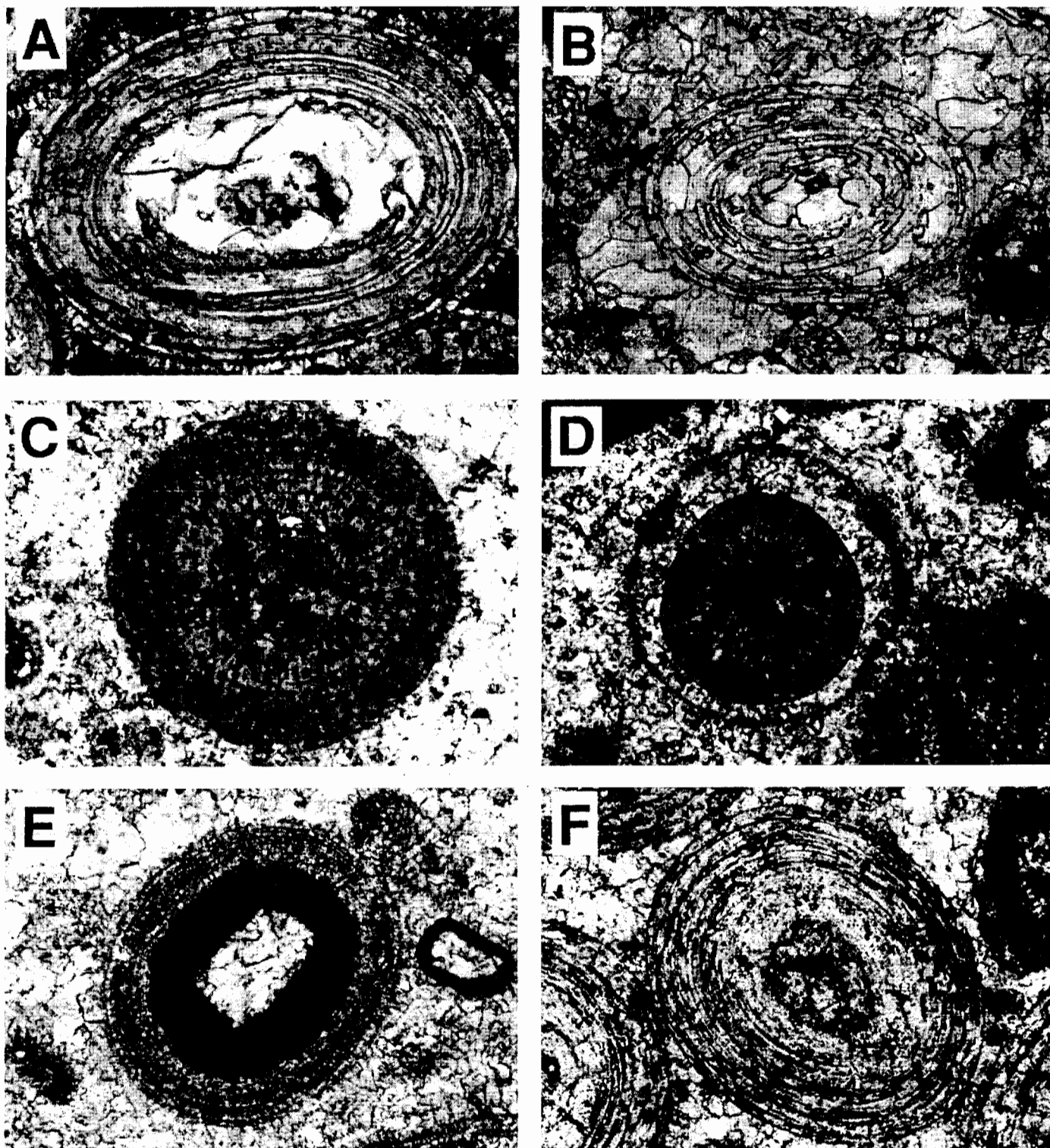


FIGURE 5. Photomicrographs of lower Missourian Stage ooids. *Bethany Falls*: (A) sparry laminar aragonite ooid exhibiting mosaic replacement (type 6, Mitchellson #2), (B) sparry laminar aragonite ooid exhibiting mosaic/ brickwork replacement (type 6, Mitchellson #2). *Mound Valley*: (C) radial calcite ooid (type 1, Woodward #6), (D) bimineralic ooid with well-preserved radial inner and dissolved outer cortex (type 4, Woodward #4; note dropped nucleus), (E) bimineralic ooid with radial inner cortex exhibiting micromoldic porosity and sparry laminar outer cortex exhibiting brickwork/micromosaic replacement (type 4, Woodward #3), (F) finely-concentric sparry laminar aragonite ooid (type 6, Heilman #1). Ooid types are keyed to Figure 11.



Kansas City and Lansing groups of the Missourian Stage of eastern Kansas (Fig. 3; Table 1). Three of these (Tyro, Benedict Bed, and South Bend) comprise transgressive members and six (Bethany Falls, Winterset, Drum, Farley, Spring Hill, and Rutland) regressive members of major cyclothems, while the Mound Valley represents a minor transgression at the top a 3rd-order cycle. Transgressive limestones rarely contain ooids, and coverage of this cyclothem member was limited by availability of material. In contrast, most regressive limestones contain ooids, and material was collected from this member in 6 of 9 major cyclothems of the study interval.

The regressive limestones differ somewhat in regard to depositional setting. In the Bethany Falls, Winterset, and Drum limestones, 1-5-m thick cross-bedded oolitic grainstones were deposited in marine shoals. The Spring Hill contains local oolitic grainstone lenses but tends to be shalier than other regressive limestones owing to a nearby clastic source (Heckel, 1988). In the Rutland Bed (Stoner Limestone), ooids are mostly superficially coated and represent a minor component of fossil grainstones that may have been deposited in tidal channels (Heckel, 1979). In the Mound Valley Limestone, fossil wackestone/packstones grade upward into 0.1-2-m thick oolitic grainstones that exhibit extensive evidence of subaerial exposure, including meteoric porosity, depleted  $\delta^{13}\text{C}$  values, and overlying soil development (e.g., Galesburg Shale; Heckel, 1988; W.L. Watney, unpubl. isotopic data).

The study units are located within the Missourian outcrop belt of eastern Kansas (Fig. 3). In relation to Heckel's (1975) facies belts, most study locales are located in the phylloid algal mound and terrigenous detrital belts, i.e., on the outer shelf or upper slope of the Midcontinent platform. Samples used in this study were collected from outcrops in southeastern Kansas and from drillcores at the Kansas Geological Survey. Study units were chosen to maximize stratigraphic and geographic coverage of Missourian Stage ooids.

### PRIMARY MINERALOGY OF ABIOTIC CARBONATES

Regardless of their primary mineralogy, all ooids in Missourian strata of Kansas (and in most other ancient limestones) now consist of low-Mg calcite. However, those originally composed of aragonite or high-Mg calcite may be recognized based on a combination of: 1) primary cortical fabric, 2) degree of preservation, and 3) Mg-Sr content (Fig. 4). Whereas identifications of the primary mineralogy based on fabric alone are uncertain, this combination of criteria has been shown to yield reliable

results for many oolitic units (e.g., Tucker, 1985; Singh, 1987; Zempolich et al., 1988; Kidder and Hall, 1993; Heydari and Moore, 1994). For general synopses of the characteristics of ooids, see Bathurst (1975) and Richter (1983).

#### *Primary Cortical Fabric*

Aragonite and calcite ooids formed in modern open-marine environments exhibit distinctly different fabrics, and these have provided the principal basis for evaluation of the primary mineralogy of ancient ooids (e.g., Simone, 1981; Medwedeff and Wilkinson, 1983). Aragonite marine ooids have a thinly-laminated, tangential fabric in which micron-sized crystallites are oriented parallel to the ooid surface (Loreau and Purser, 1973). In contrast, calcite marine ooids generally develop a radial fabric, in which blocky, 50- to 500- $\mu$ -long crystals form arrays radiating outward from the ooid nucleus (Marshall and Davies, 1975; Milliman and Barretto, 1975). This mineralogic-fabric association also applies to individual laminae of two-phase ooids, such as those forming in Baffin Bay, Texas (Land et al., 1979). However, the relationship is not universal, and aragonite ooids forming in modern restricted marine and non-marine settings commonly develop radial fabrics (Friedman et al., 1973; Loreau and Purser, 1973; Scholle and Kinsman, 1974; Sandberg, 1975; Davies and Martin, 1976). In most cases, this involves fluids of non-marine chemistry (e.g., hypersaline or brackish), but radial aragonite ooids have been reported from waters of normal marine salinity on the northeast Australian shelf (Davies and Martin, 1976).

#### *Degree of Preservation*

Aragonite and high-Mg calcite are generally thermodynamically unstable in the burial environment and either recrystallize to low-Mg calcite or dissolve (Bathurst 1975, Sandberg, 1985). Recrystallization commonly yields a fine to coarse mosaic of replacement spar that cuts across primary fabric features and does not normally preserve original crystallite orientations, whereas dissolution results in moldic porosity or void-filling sparry cements. In contrast, components having a primary low-Mg calcite composition are generally resistant to replacement and dissolution, and cortical fabric details and primary crystallite orientations are commonly preserved. Missourian Stage limestones in Kansas have experienced protracted histories of burial diagenesis (e.g., Wojcik et al., 1994), and, consequently, simple patterns of alteration are not always encountered. For example, in some two-

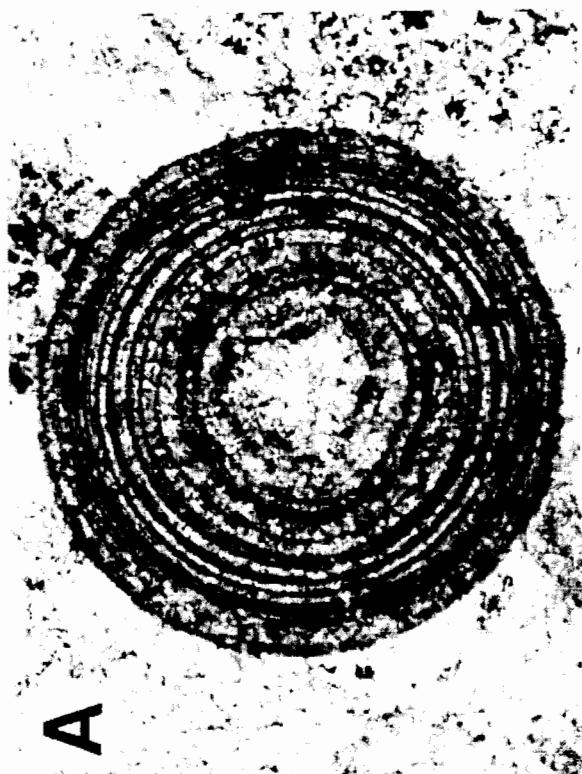


FIGURE 6. Photomicrographs of upper Missourian Stage ooids. *Spring Hill*: (A) sparry laminar aragonite ooid (type 6). *Tyro*: (B) biminerallitic ooid exhibiting poorly-preserved radial-concentric fabric in inner and outer cortex, and thin aragonite laminae (two sparry layers) and replacement dolomite in mid-cortex (originally high-Mg calcite; type 3). *Benedict Bed*: (C) radial aragonite ooid (mineralogic interpretation based on Sr data; type 1A). *Rutland Bed*: (D) radial calcite ooid with thin surficial aragonite layer (type 2). Ooid types are keyed to Figure 11.

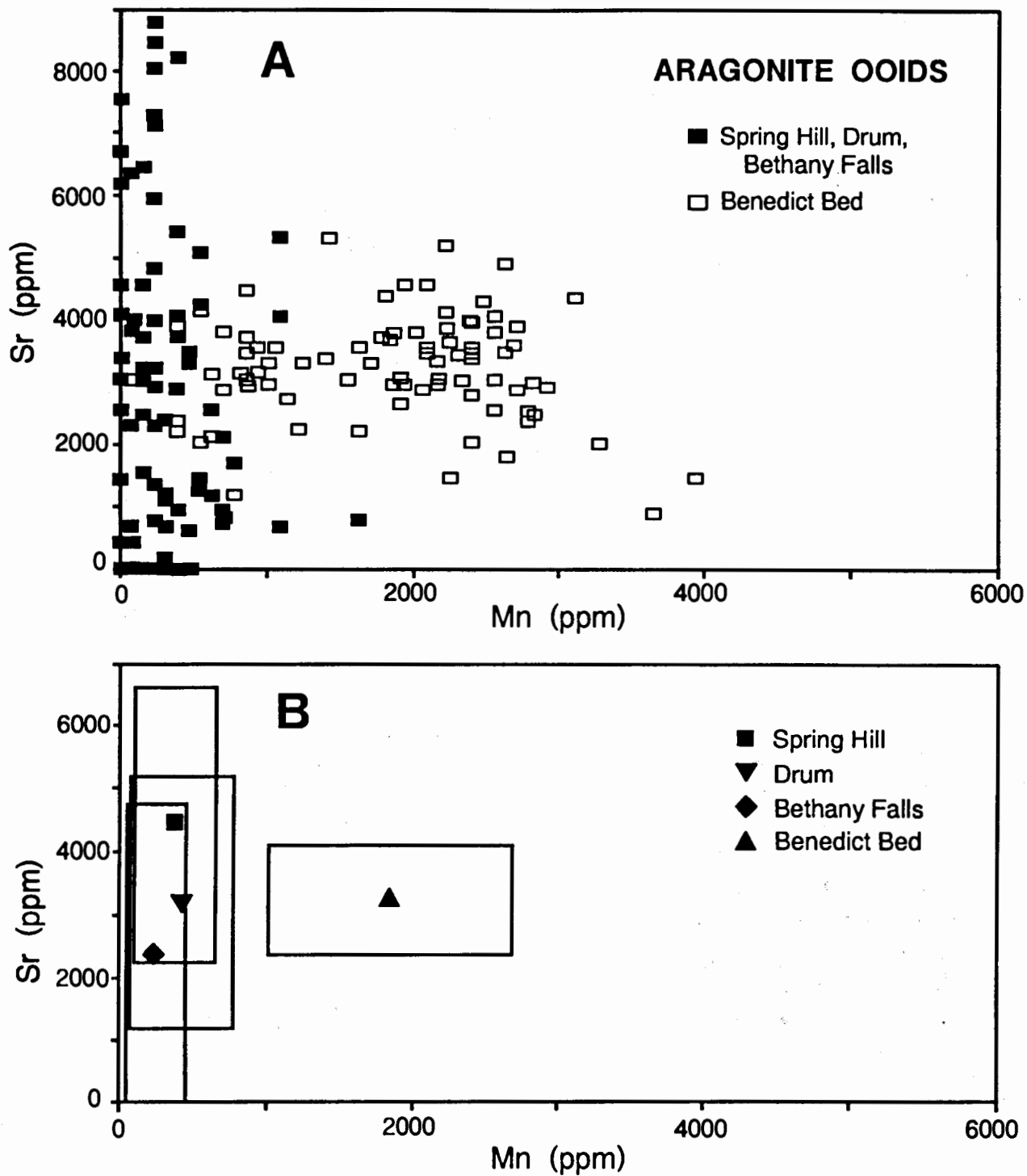


FIGURE 7. Mn-Sr concentrations of ooids of probable aragonitic primary mineralogy. (A) Ooids in the Spring Hill, Drum, and Bethany Falls limestones exhibit sparry laminar cortices and low Mn values; those in the Benedict Bed exhibit radial fabric and high Mn values. (B) Means (symbols) and standard deviation ranges (rectangles) by formation. Number of samples: 156.

phase ooids of the Mound Valley Limestone, aragonite cortical layers recrystallized to a coarse calcite spar at an early diagenetic stage, and finely crystalline calcite cortical layers were subsequently preferentially dissolved by burial fluids (e.g., Fig. 5E). Thus, this criterion can only be applied reliably given an understanding of the diagenetic history of an oolitic unit and in conjunction with information on primary cortical fabric and Mg-Sr content.

### Mg-Sr Content

Aragonitic AMCs have a much higher Sr content than calcitic AMCs owing to the larger distribution coefficient of Sr in aragonite than in calcite. Kinsman and Holland's (1969) estimate for  $DSr_a$  of  $1.12 \pm 0.04$  at  $25^\circ\text{C}$  is still valid, but their estimate for  $DSr_c$  of  $0.14 \pm 0.02$  has subsequently been shown not to account for the influence of factors such as precipitation rate, fluid  $\text{Sr}^{2+}/\text{Ca}^{2+}$ , and the presence of other cations (e.g.,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ ) (Lorens, 1981; Pingitore and Eastman, 1986; Morse and Bender 1990). Recent studies yielded  $DSr_c$  values of 0.04-0.07 in seawater at equilibrium (i.e., slow) precipitation rates. However,  $DSr_c$  increases to at least 0.20 in dilute waters with low  $\text{Sr}^{2+}/\text{Ca}^{2+}$  and at high precipitation rates (Lorens, 1981; Pingitore and Eastman, 1986).  $DSr_c$  also increases with increasing precipitate  $\text{Mg}^{2+}$  content up to values of 0.3-0.4 at 10-15 mol% Mg, and, consequently, high-Mg calcite contains considerably more Sr than low-Mg calcite (Mucci and Morse, 1983; Morse and Bender, 1990). Predicted Sr concentrations for aragonite precipitated in thermodynamic equilibrium with tropical seawater are 7,200-10,600 ppm (Bathurst, 1975), and this range encompasses the Sr values of most modern marine aragonite ooids (Kahle, 1965; Milliman, 1967; Loreau and Purser, 1973; Land et al., 1979; Brand and Veizer, 1983; Major et al., 1988). In contrast, predicted Sr values for calcite in equilibrium with seawater are 400-2000 ppm, which agree well with observed mean values of 400-500 ppm for low-Mg calcite and 1000-2000 ppm for high-Mg calcite (Land et al., 1979; Major et al., 1988; Major and Wilber, 1991).

Calcite exhibits a continuous distribution of Mg concentrations from ca. 0 to 30 mol%  $\text{MgCO}_3$ , although values above 18-20 mol% are rare (Tucker and Wright, 1990). High-Mg calcite is usually defined as containing  $>4$  mol%  $\text{MgCO}_3$ . The distribution coefficient of magnesium in calcite ( $DMg_c$ ) ranges from 0.01 to 0.08 (Tucker and Wright, 1990) and is strongly influenced by temperature (Morse, 1985; Burton and Walter, 1987) and, possibly, saturation state (Given and Wilkinson, 1985). Diagenetic recrystallization of high-Mg calcite under closed-system conditions commonly yields low-Mg calcite

containing (micro-)dolomitic inclusions (e.g., Lohmann and Meyers 1977). The distribution coefficient of magnesium in aragonite ( $DMg_a$ ) is 0.00016 (Oomori et al., 1987), and aragonite rarely contains more than 1.5 mol%  $\text{MgCO}_3$  (Bathurst, 1975; Major et al. 1988).

Diagenesis commonly alters the concentrations of Sr, Mg, and other trace elements in primary components as a result of solution-precipitation reactions (e.g., Brand and Veizer, 1980; Veizer, 1983; Popp et al., 1986; Veizer et al., 1986). These studies have shown that, in general, concentrations of Sr, Mg, and Na decrease and those of Mn and Fe increase with increasing diagenetic alteration. The effect of transformation of aragonite to low-Mg calcite on Sr content (or of high-Mg calcite to low-Mg calcite on Mg content) depends on the degree of openness of the diagenetic system (Tucker and Wright, 1990; Banner and Hanson, 1990). In open diagenetic systems (in which precipitate volume is small relative to that of pore fluids), the compositions of porefluids and precipitates remain constant. In closed diagenetic systems (in which precipitate volume is large relative to that of pore fluids), the compositions of porefluids and precipitates evolve, and later precipitates become progressively enriched (depleted) in trace elements with distribution coefficients less (greater) than unity.

With regard to Sr in primary aragonite undergoing recrystallization, an open diagenetic system with porefluids of marine or meteoric origin would yield precipitates containing  $<2000$  ppm, whereas a completely closed system would yield precipitates with Sr values that progressively converge on those of the components undergoing dissolution, regardless of the mineralogy of the secondary precipitates (Tucker and Wright, 1990). Dissolution-precipitation of aragonite on a local scale with minimal introduction of external porefluid would thus yield secondary calcites exhibiting elevated Sr concentrations. Most ancient limestones have Sr values of  $<1000$  ppm (Bathurst, 1975), indicating a primary calcitic mineralogy, open diagenetic conditions, or both. In contrast, ancient ooids of inferred primary aragonitic mineralogy commonly yield Sr concentrations of ca. 2000-5000 ppm (e.g., Tucker 1985; Singh, 1987; Swirydczuk, 1988; Heydari et al., 1993; Kidder and Hall, 1993). Systematic enrichment of Sr in diagenetic precipitates above ca. 2000 ppm may be accepted as *prima facie* evidence of both the former presence of aragonite and at least semi-closed diagenetic conditions. The same considerations apply to recrystallization of primary high-Mg calcite components. However, because Mg in diagenetic fluids may derived from other sources as well (e.g., clay minerals), high concentrations of Mg in secondary precipitates must be

interpreted cautiously as evidence of a high-Mg calcite precursor.

## ANALYTICAL METHODS

About 150 samples were collected from outcrops and cores at stratigraphic intervals of 0.2-1.0 m. All samples were thin-sectioned for petrographic analysis, and most thin sections were polished to a final thickness of 20 microns in order to better clarify crystallographic detail. Thin sections were stained using Alizarin Red-S to detect the presence of calcite. Petrographic analysis was carried out using a Nikon Optiphot2-Pol Microscope equipped with a UFX-DX 35 top-mount SLR camera. Each sample was characterized using the Dunham classification, and abundances of grains, matrix, cement, and porosity were estimated by inspection. For oolitic limestones, detailed information was recorded regarding ooid size and sorting, nucleus size and type, cortical fabric and thickness, lamina thickness, and preservation state.

Major and trace element chemistry was determined through microprobe analysis. About 20 thin sections were washed with acetone, polished using 1 $\mu$  and 0.5 $\mu$  alumina powder, rewashed in an ultrasonic bath to remove polishing compound, and vacuum-coated with carbon. Analyses were conducted at the University of Kentucky Electron Microprobe Laboratory using an ARL model SEMQ Electron Microprobe with wavelength- and energy-dispersive spectrometric capabilities (recently refurbished by Advanced Microbeam Services). Samples were analyzed for Ca, Al, Si, K, Mg, Mn, Fe, and Sr, and data were processed on-line with PROBE software (versions 1.7 and 2.53). Smithsonian Institute standards were used in microprobe calibration: USNM-R10065 Strontianite (Sr), USNM-R2460 Siderite (Mn), and USNM-10057 Dolomite (Mg). Machine precision was evaluated by multiple paired analyses of standards without repositioning of the electron beam: 66.86 $\pm$ 1.2 wt% (Sr), 2.90 $\pm$ 0.02 wt% (Mn), and 22.73 $\pm$ 0.1 wt% (Mg). Detection limits for each element varied between runs; average values are 733 ppm (Sr), 524 ppm (Mn), and 506 ppm (Mg). A total of about 528 samples were probed, including 431 ooid cortices, 55 interparticle cements, and 42 other components; only the ooid data are reported here.

Owing to the complex history of fluid migration within Pennsylvanian units of the Midcontinent area (e.g., Wojcik et al., 1994), it was necessary to undertake a thorough analysis of the diagenetic history of each study unit. Petrographic study was combined with trace element and stable isotope data to fully characterize the various secondary phases and their relationships to multiple

episodes of rock-fluid interaction and diagenetic alteration (Watson and Algeo, manuscript in preparation).

## IDENTIFICATION OF PRIMARY OOID MINERALOGY

### *Petrofabrics*

Missourian ooids exhibit two principal fabric types with several variations on each. Most cortical fabrics are easily classified petrographically as either "sparry laminar" (e.g., Fig. 5A,B) or radial (e.g., Fig. 5C, 6C). In ooids with a sparry laminar fabric, cortices exhibit strongly developed, finely concentric laminae and lack any hint of radial structure. Diagenetic alteration of these ooids resulted in mosaic replacement, in which secondary crystal boundaries discordantly cut across primary laminae (Fig. 5A), brickwork replacement, in which secondary crystal boundaries are concordant with primary laminae (Fig. 5F), or a combination of both (Fig. 5B). Comparison with modern ooid fabrics suggests that sparry laminar ooids once contained tangentially oriented crystallites that have been lost through diagenetic alteration. Wholesale dissolution of ooid cortices, resulting in oomoldic porosity or secondary void-filling cements (e.g., Fig. 5D), is found mostly in association with sparry laminar ooids. In ooids with a radial fabric, cortices consist of fine radially-oriented crystallites and exhibit only weakly developed concentric laminar structure (Fig. 5C, 6C). Rarely, radial fabrics are partially obscured by development of micromoldic porosity (Fig. 5E) or replacement by a microspar mosaic (Fig. 6B). Strong fabric contrasts are present in ooids inferred to have had two primary mineralogies (e.g., Fig. 5D,E).

### *Trace Element Data*

**Sr Content.**--Systematic differences in Sr concentrations between Missourian ooids exhibiting sparry laminar versus radial cortices support mineralogic identifications based on fabric and preservation criteria. In ooids having sparry laminar cortices and exhibiting poor preservation, Sr values are generally high (Fig. 7). Approximately 75% of measured Sr values exceed 2000 ppm, a rough upper limit for primary marine calcite, and a few exceed 8000 ppm, which is equivalent to Sr concentrations in unaltered marine aragonite. Approximately uniform distribution of Sr values over the range 0-9000 ppm is consistent with alteration of aragonite ooids in diagenetic systems ranging from open to closed. Although some Sr might be derived from other marine aragonitic components undergoing dissolution (e.g., green

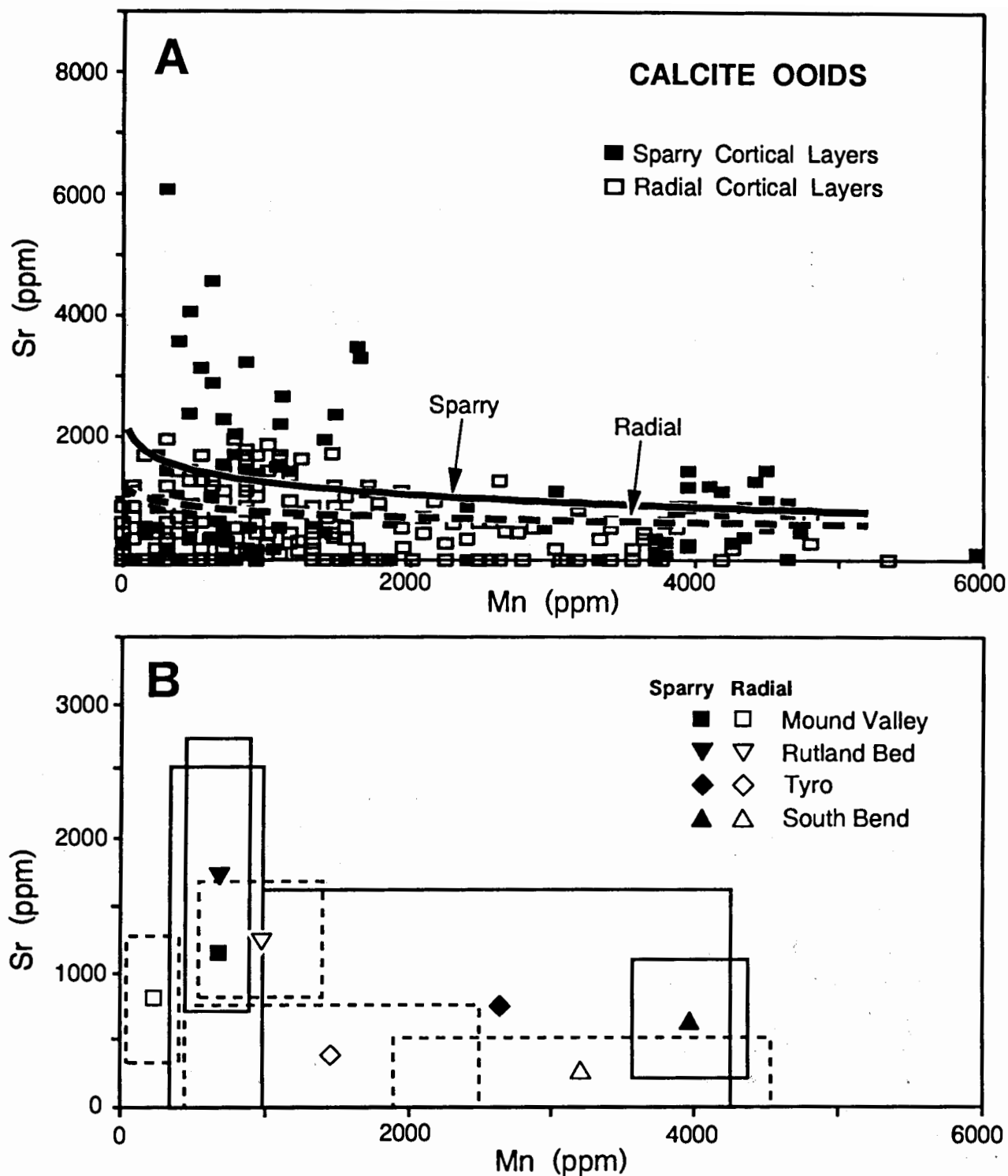


FIGURE 8. Mn-Sr concentrations of ooids of probable calcitic primary mineralogy. Data plotted separately for radial (open symbols, dashed rectangles) and sparry cortical layers (solid symbols and rectangles). Sparry cortical layers (primary aragonite; solid curve) yield higher Sr values at all Mn concentrations than radial cortical layers (primary calcite; dashed curve); curves are least-squares logarithmic fits. Note change in vertical scale in B. Number of samples: 180 (radial layers), 95 (sparry layers).



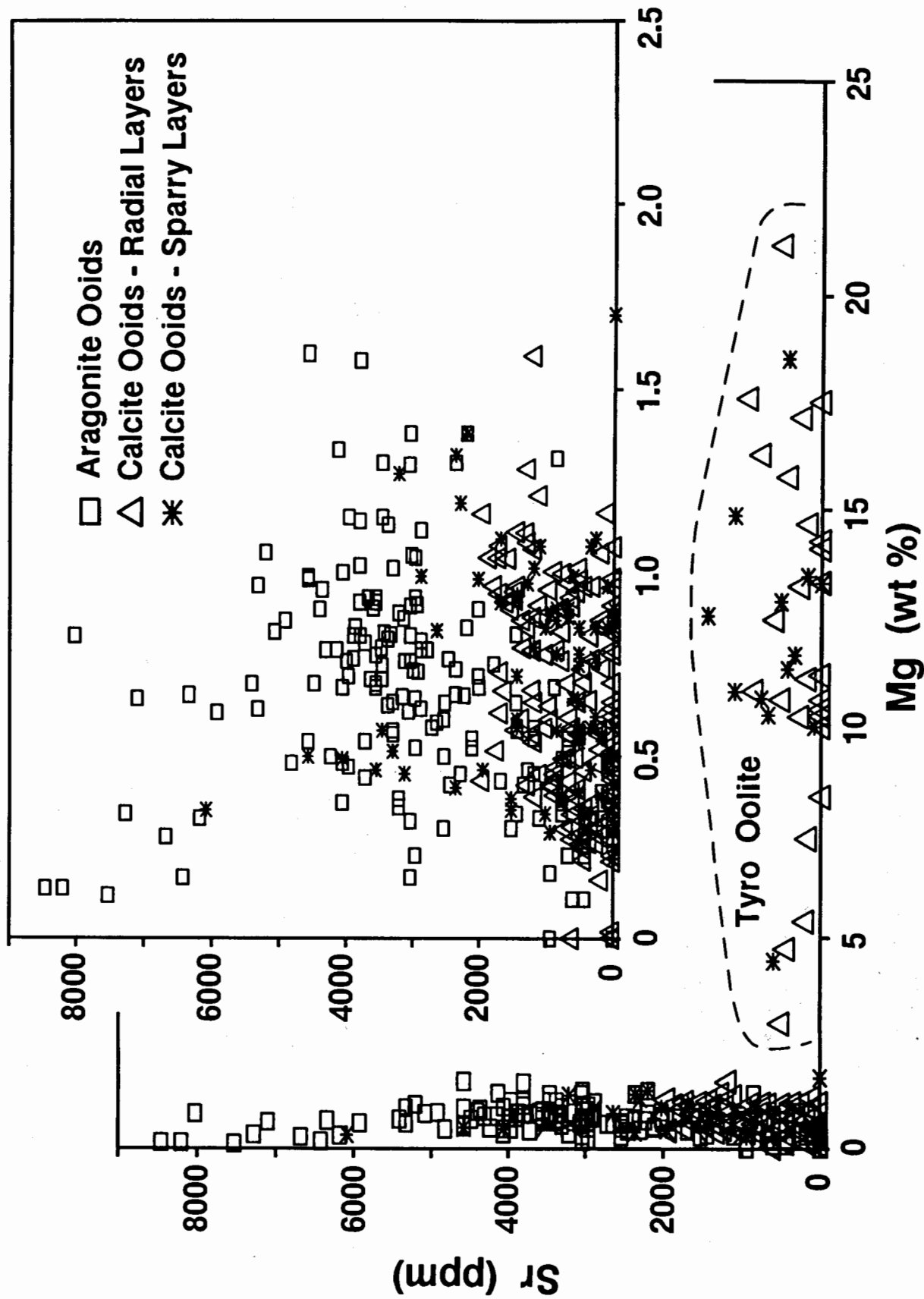


FIGURE 9. Mg-Sr concentrations for probable aragonite ooids (squares) and for radial (triangles) and sparry layers (asterisks) of probable calcite ooids. Inset expands resolution of ordinal axis at low Mg values. Tyro ooids exhibit MgO values of 3-21%, suggesting a primary high-Mg calcite mineralogy, whereas ooids from other units exhibit low MgO values (<2 wt%), consistent with low-Mg calcite or aragonite mineralogies. Note that ordinal values are wt% MgO, not wt% Mg as shown.

algae, micrite), the consistent relationship between cortical fabric and high Sr content supports local derivation of Sr in these ooids.

In ooids with well-preserved radial fabrics, Sr concentrations are mostly <2000 ppm, and all Sr values that exceed 2000 ppm are associated with sparry cortical laminae (Fig. 8). At all Mn values (and, hence, degrees of diagenetic alteration), sparry cortical layers are enriched in Sr over radial layers by a factor of 1.5-2.0. The lesser degree of Sr enrichment of thin aragonitic laminae in largely calcitic ooids relative to ooids composed entirely of aragonite probably reflects fluid exchange and elemental mixing between layers of differing mineralogy within two-phase ooids. For comparison, reported Sr concentrations for other ancient ooids of inferred primary aragonitic mineralogy are mostly 1000-5000 ppm, whereas coexisting ooids of inferred calcitic mineralogy generally contain <1000 ppm Sr (e.g., Tucker, 1985; Singh, 1987; Swirydczuk, 1988; Heydari et al., 1993; Kidder and Hall, 1993).

Differences between sparry laminar and radial ooids with respect to fabric, preservation state, and Sr content are consistent with inferred primary aragonite and calcite mineralogies, respectively. Owing to the strong relationship among these variables, primary ooid mineralogies will be regarded as unequivocally identified and referred to as "calcitic" or "aragonitic" henceforth. The only exception to the fabric-Sr content relationship discussed above is the Benedict Bed. In this unit, most samples exhibit sparry laminar fabrics, but large well-preserved ooids from the lowermost stratigraphic level yielded radial fabrics (Fig. 6C) in combination with elevated Sr values (2000-5000 ppm; Fig. 7). Owing to similar Sr concentrations in radial and sparry laminar ooids and to a gradational vertical transition in cortical fabric without evidence of two coexisting primary mineralogies, all of these ooids are inferred to have had a primary aragonitic composition. Benedict Bed ooids are also unusual with regard to their facies association. Whereas many Missourian oolitic units were deposited as thick, cross-bedded grainstone shoals near shelf margins, Benedict Bed ooids accumulated between columnar stromatolites in a transgressive shoreline setting (Heckel 1975), suggesting deposition under possibly hypersaline conditions. Aragonite ooids have been reported to form radial fabrics under hypersaline conditions in a number of modern restricted marine and lacustrine settings (e.g., Friedman et al., 1973; Loreau and Purser, 1973; Sandberg, 1975).

**Mn Content.**--Because little  $Mn^{2+}$  is present in (oxic) marine waters, elevated Mn concentrations in marine

carbonates are generally considered to be an indication of diagenetic alteration in a reducing environment (e.g., Brand and Veizer, 1980; Veizer, 1983). In the Missourian Stage, the most salient trend with regard to Mn is the markedly greater enrichment of calcite ooids, as a group, compared to aragonite ooids (Fig. 7, 8), suggesting that the former experienced systematically greater alteration in such a reducing environment. Petrographic and stratigraphic evidence indicates that differences in Mn concentrations may be due to a combination of: 1) mineralogy-dependent differences in timing of diagenesis, and 2) stratigraphic differences in burial fluid chemistry (Watson and Algeo, manuscript in preparation).

**Mg Content.**--Trace element data may help to distinguish primary high-Mg calcite from low-Mg calcite, although positive identification of the former in diagenetically altered ancient carbonates is difficult. All Missourian oolitic units of both primary calcitic and aragonitic mineralogy exhibit low Mg concentrations except for the Tyro Oolite, in which the majority of samples contain between 3 and 21 wt% MgO (average 12 wt%; Fig. 9). Equivalent  $MgCO_3$  concentrations for the Tyro are 7 to 48 mol% (average 28 mol%). These values are too high to reflect derivation of Mg solely from a high-Mg calcite precursor, but Tyro ooids exhibit two other features consistent with such a primary mineralogy and not observed elsewhere in the Missourian Stage: 1) replacement of a primary radial fabric by a microspar mosaic, and 2) intracortical growth of coarsely crystalline dolomite (note that microprobe analyses were targeted at non-dolomitic cortical areas). These observations suggest that, whereas most non-aragonitic ooids had a low-Mg calcite precursor, those in the Tyro Oolite may have been composed of high-Mg calcite. In the latter case, recrystallization of a metastable high-Mg primary phase resulted in overgrowth of a primary radial fabric by a microspar mosaic and in localized intracortical dolomite formation (probably with some introduction of Mg from porefluids).

## PATTERNS OF OOID MINERALOGIC VARIATION

### *Primary Mineralogy of Individual Units*

With regard to primary mineralogic composition, Missourian oolitic limestones fall into three groups: 1) units originally composed exclusively of aragonite ooids, 2) units in which ooids were composed dominantly of calcite but commonly contained one or more thin aragonite cortical layers, and 3) units that contained mixtures of

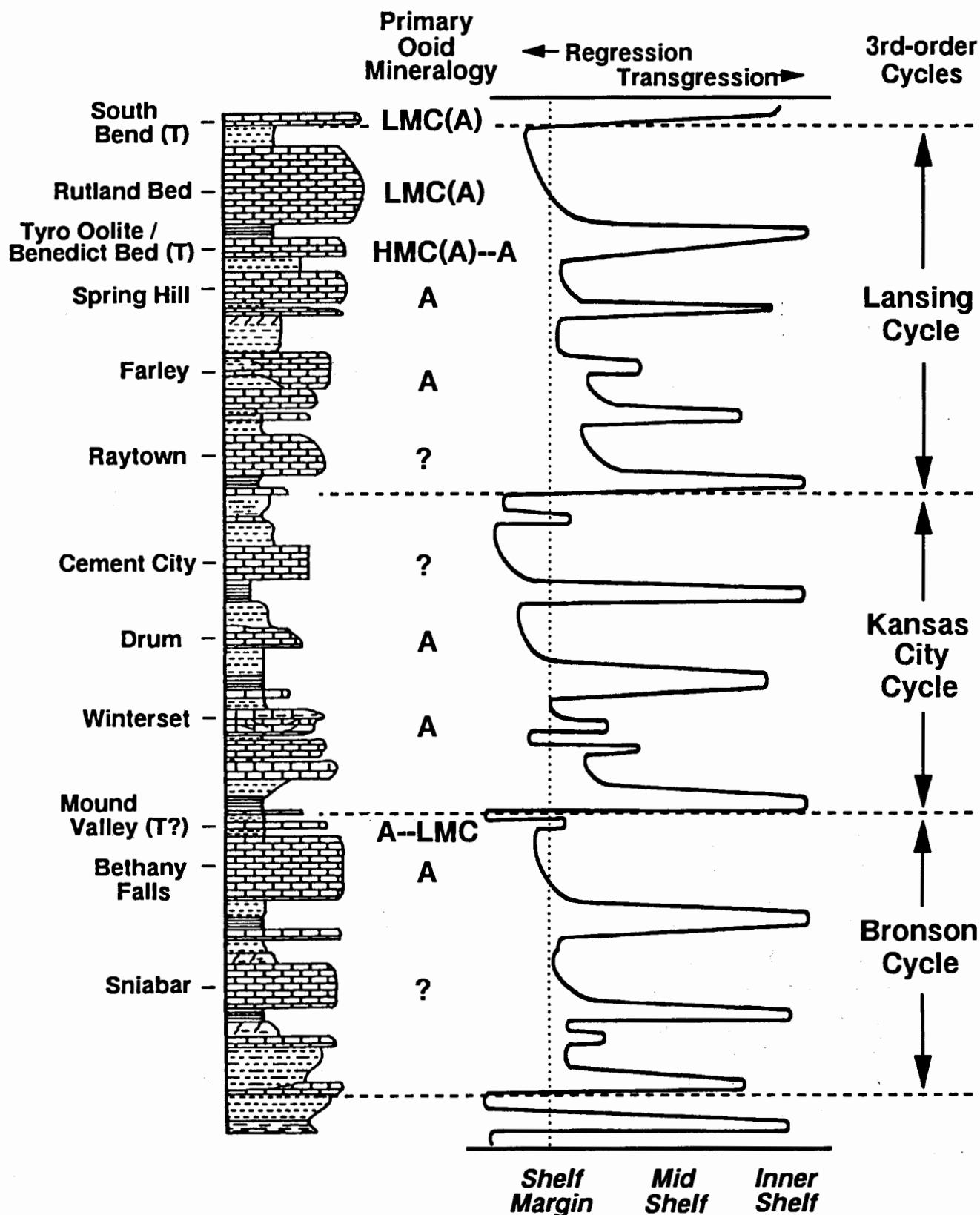


FIGURE 10. Stratigraphic trends in primary ooid mineralogy. Identified formations include regressive limestones of all 4th-order cyclothems and transgressive limestones that contain oolites (T). Primary ooid mineralogies: A = aragonite, LMC = low-Mg calcite, HMC = high-Mg calcite, C(A) indicates the dominant (subordinate) components of a biminerale unit, and C--A represents an outer-to inner-shelf mineralogic gradient. Sea-level curve redrawn from Boardman and Heckel (1989) with adjusted vertical scale. Note that no oolitic samples were available from the Sniabar, Cement City, and Raytown limestones, and that the 3rd-order megacycles identified here do not coincide exactly with groups of the same name (Fig. 2; e.g., Heckel, 1978).

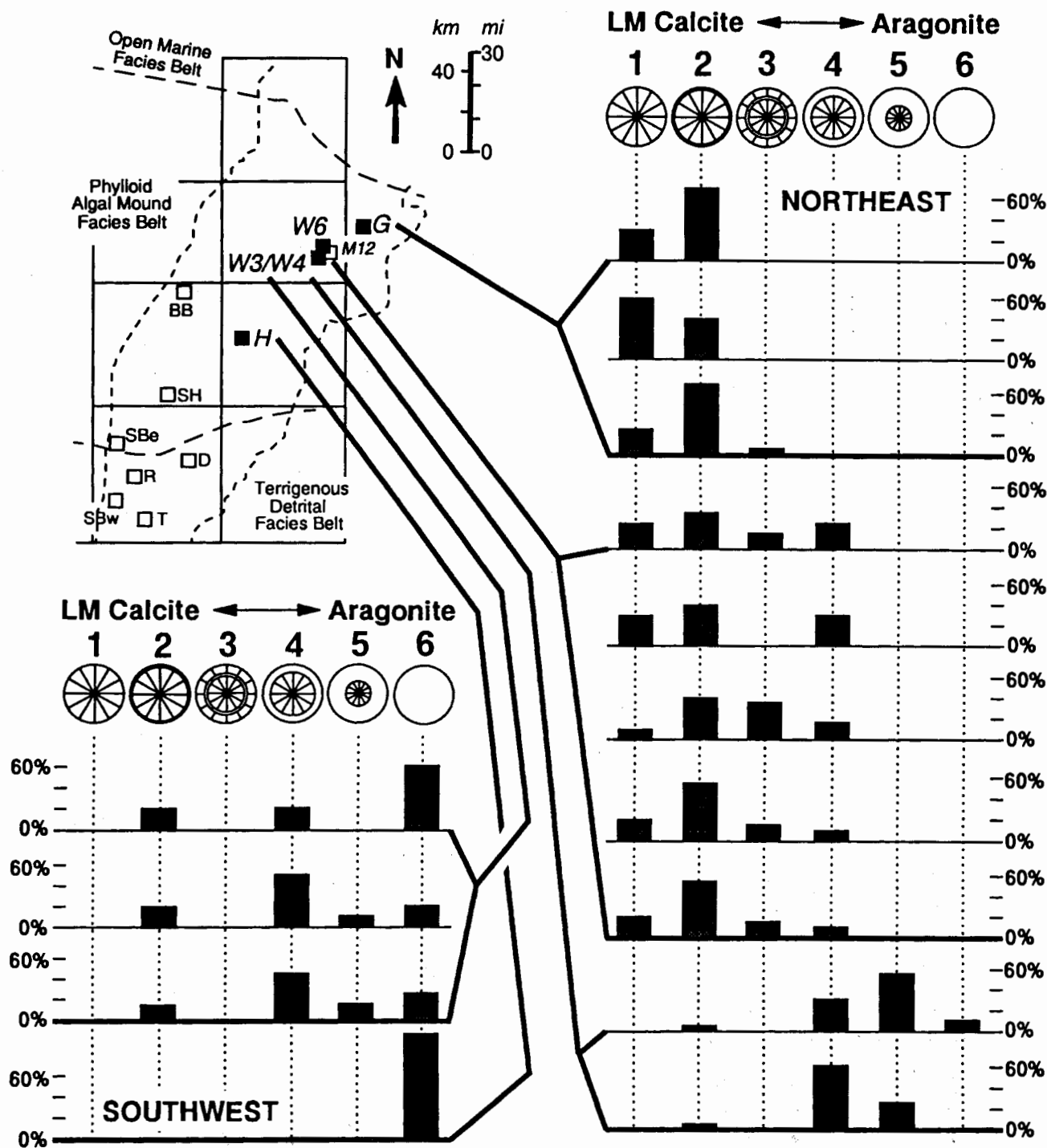


FIGURE 11. Geographic trends in fabric and primary mineralogy of Mound Valley ooids. Bar graphs illustrate absolute frequencies of six ooid cortical types: 1) radial, 2) radial with thin surficial sparry lamina, 3) radial with one or more thin internal sparry laminae, 4) inner radial and outer sparry layers of subequal thickness, 5) thin inner radial and thick outer sparry layers, and 6) sparry laminar (nuclei not shown in schematic illustrations of cortices). Radial and sparry laminar fabrics correlate with primary low-Mg calcite and aragonite mineralogies throughout unit. Cortical-type frequencies are visual estimates based on 1-3 thin sections per horizon with an uncertainty of  $\pm 5\%$  for low and high estimates and  $\pm 10\%$  for mid-range values. Location designations as in Figure 3; multiple bar graphs for single locales represent series of approximately equally-spaced, stratigraphically-ordered samples.



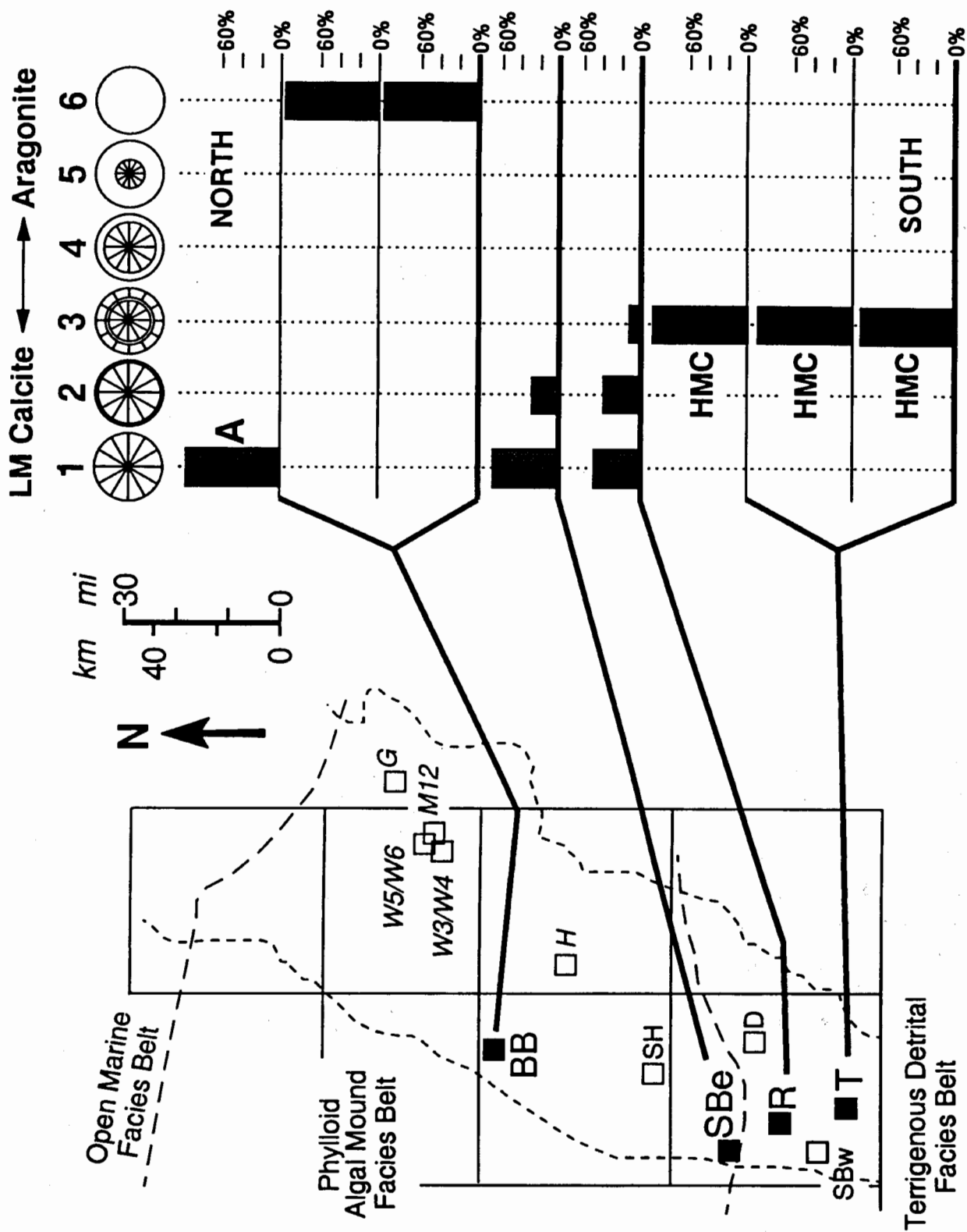


FIGURE 13. Geographic trends in fabric and primary mineralogy of oolitic units in the Stanton and South Bend cyclothem. Bar graphs illustrate absolute frequencies of six ooid cortical types (see Figure 11). Radial and sparry laminar fabrics correlate with primary calcite and aragonite mineralogies, except as noted by A (radial aragonite in upper Benedict Bed) and HMC (radial-concentric high-Mg calcite in Tyro Oolite). Note that not all of these units are stratigraphic equivalents. Other information as in Figure 11.



calcite, aragonite, and two-phase ooids in subequal proportions (Fig. 10). The first group (exclusively aragonite) includes the regressive limestone members of most cyclothems (Bethany Falls, Winterset, Drum, Farley, and Spring Hill limestones) as well as the Benedict Bed. The second group (dominant calcite with subordinate aragonite) includes the Tyro Oolite, Rutland Bed, and South Bend Limestone, all of which are located in the upper part of the Missourian Stage. The third group (mixed mineralogies) is represented only by the Mound Valley Limestone.

### *Stratigraphic Variation in Ooid Mineralogy*

The primary mineralogies of Missourian ooids do not exhibit a simple stratigraphic pattern of progressive change in the proportion of calcite and aragonite upsection that would be consistent with a simple long-term transition in AMC mineralogy (e.g., Fig. 1). Rather, ooid mineralogies vary in a manner suggesting a possible relationship to either 3rd- or 4th-order eustatic cycles. Third-order cycles reflect variation in the extent of sea-level fall within successive 4th-order cyclothems (Fig. 10). During minimal 4th-order regressions (i.e., 3rd-order highstands), eustatic elevations were higher than during maximal 4th-order regressions (i.e., 3rd-order lowstands). In relation to the 3rd-order Bronson, Kansas City, and Lansing "megacycles" (defined herein), ooids in the lower to middle (highstand) part of each megacycle are composed exclusively of aragonite, whereas those in the upper (lowstand) part have calcitic or biminerale compositions (note that information is lacking regarding ooid mineralogy in the upper part of the Kansas City megacycle). Alternatively, ooid mineralogy may vary in relation to position within 4th-order cyclothems, i.e., ooids in transgressive cyclothem members have calcitic or biminerale compositions, whereas those in regressive members exhibit mainly aragonitic compositions (Fig. 10). However, the Rutland Bed, a dominantly calcitic oolitic unit located basinward of the regressive Stoner Limestone (Heckel, 1975), does not conform to this 4th-order pattern.

Dependence of ooid mineralogy on absolute sea-level elevation (high-low) versus the overall direction of sea-level change (transgression-regression) is potentially of significance because underlying controls (e.g., temperature and aqueous  $\text{CO}_2$ ) do not vary in a similar manner in each case. If absolute sea-level elevation may be inferred from the distance of peritidal oolitic deposits from the shelf margin, then the most basinward units (Tyro Oolite, Rutland Bed, South Bend Limestone) indicate that calcite AMC precipitation may have been favored under lowstand

conditions (Fig. 13). On the other hand, predominantly calcitic ooids of the Tyro-Rutland-South Bend succession were deposited during a T-R-T cycle within the same general area, implying that the direction of sea-level change exerted little control on ooid mineralogy (Fig. 10, 13). It should be noted that Missourian oolitic units exhibit no general relationship between absolute sea-level stand and transgressive-regressive character, e.g., transgressive deposits do not systematically coincide with sea-level highstands.

### *Geographic Variation in Ooid Mineralogy*

Geographic variation in primary ooid mineralogy was investigated at several stratigraphic levels, including the Bethany Falls, Mound Valley, and Winterset limestones, and in transgressive members of the Stanton cyclothem (Tyro Oolite and Benedict Bed). The Bethany Falls and Winterset limestones were investigated in 7 cores over a 230-km transect and in 3 cores over a 4-km transect, respectively, and ooids in both formations were uniformly of monomineralic aragonitic composition. In contrast, ooids in the Mound Valley Limestone and basal Stanton cyclothem exhibit mixed mineralogies and spatially complex patterns of compositional variation.

The Mound Valley Limestone exhibits greater mineralogic variation than other study units, containing monomineralic ooids of both calcitic and aragonitic composition as well as biminerale types. Frequency analysis indicates a regular spatial distribution in ooid mineralogies along a southwest-northeast transect. To the southwest at Heilman #1, ooids were composed entirely of aragonite, whereas to the northeast at Green Acres #1, ooids were entirely calcitic or possessed, at most, a thin surficial aragonite lamina; between these locales, ooids had gradational compositions with biminerale species predominating (Fig. 11). However, most of the mineralogic change was constrained to a limited zone between the Woodward #3/#4 and Woodward #6 cores, an area of local stratigraphic thinning and strong soil development in the Bethany Falls-Mound Valley interval suggestive of a paleo-topographic high (Fig. 11, 12). Differences in ooid mineralogy at different stratigraphic levels of a single locale were smaller than those between locales, although a weak trend toward greater proportions of aragonite at higher levels existed at some locales (e.g., Woodward #3, #4, #6).

The transgressive limestone members of the Stanton cyclothem, including the Tyro Oolite and Benedict Bed of the Captain Creek Limestone Member, exhibit lateral

variation in primary ooid mineralogy over a distance of ca. 100 km (Fig. 13). Tyro ooids were mostly bimineralic, having high-Mg calcitic cortices that contained one or a few aragonitic laminae in an inner to mid-cortical position. In the Benedict Bed, both sparry laminar and radial ooids have high Sr contents (2000-5000 ppm), suggesting that ooids exhibiting both fabrics originally had a primary aragonitic mineralogy.

### *Internal Variation in Ooid Mineralogy*

Missourian ooids exhibit regular patterns of internal mineralogic variation, i.e., in the number, location, and sequence of calcitic and aragonitic layers within cortices of bimineralic ooids, that permit inferences regarding controls on AMC precipitation. First, in nearly all bimineralic ooids, the inner cortex originally consisted of calcite and the outer cortex of aragonite (Fig. 5, 6, 11, 13). To underscore the rarity of the converse situation, only a single grain was identified in any unit with an inner aragonite and outer calcite cortex (Mound Valley, Woodward #6). Second, although the mineralogic transition can be found at all fractional cortical diameters in bimineralic ooids, it is much more common to encounter a thick inner calcite and thin surficial aragonite layer than the converse (Fig. 5D, 6D). Third, the mineralogic transition is located at a relatively constant absolute cortical diameter within a given unit, but the transition diameter commonly differs between units. Average transition diameters are  $0.53 \pm 0.13$  mm to  $0.65 \pm 0.14$  mm in the Mound Valley (Woodward #3 and Green Acres #1, respectively),  $0.32 \pm 0.05$  mm in the Tyro,  $0.34 \pm 0.05$  mm in the Rutland, and  $0.21 \pm 0.05$  mm in the South Bend. Ooid size tends to covary with transition diameter. Fourth, when multiple mineralogic transitions occurred within individual bimineralic cortices, primary aragonite layers commonly consisted of single laminae and were invariably thinner than adjacent calcite layers (Fig. 6B). The converse, i.e., thin isolated laminae of calcite within a predominantly aragonitic cortex, is almost never encountered. These observations suggest that during bimineralic ooid growth: 1) conditions favored calcite precipitation initially, 2) calcite precipitation was commonly interrupted by transient changes permitting aragonite growth, and 3) once conditions favoring aragonite precipitation were firmly established, a return to calcite growth conditions was rare. The nearly invariant calcite-to-aragonite growth sequence implies that mineralogic transients generally result from changes in physico-chemical or hydrographic conditions closely linked to increasing ooid size.

Several observations permit inferences regarding

simultaneity, or lack thereof, in the growth of ooids within a given unit. First, in most bimineralic units (Tyro, Rutland Bed, and South Bend limestones), the number and position of cortical aragonite layers was fairly constant within an individual unit but varied substantially between units (Fig. 11, 13). In Rutland Bed and South Bend ooids, aragonitic laminae were present only on the outer cortical surface (Fig. 6D, 13), whereas in Tyro ooids, laminae were present exclusively in an inner to mid-cortical position (Fig. 6B, 13). In Mound Valley ooids, most aragonitic laminae are outer cortical, although intracortical laminae are found occasionally (Fig. 5D, 11). Second, the Tyro Oolite exhibits a well-defined vertical trend with regard to cortical lamina position. In the Tyro, aragonitic layers, which comprise 5-30% of fractional cortical diameter, shift slightly from a mid- to an inner cortex location in moving upsection through the 4-m-thick unit at the Tyro Quarry. Frequent development of surficial aragonitic laminae may be due to size-dependent changes in environmental conditions (as noted above) that are independent of simultaneity, or lack thereof, in the growth of ooids within a given unit. However, constancy in the number and location of inner-cortical laminae, as in Tyro ooids, implies co-formation of ooids throughout the unit, and inward migration of aragonitic laminae upsection implies initiation of precipitation of ooids deposited at the base of the unit slightly earlier than those deposited at the top.

### **CONTROLS ON OOID MINERALOGY**

Numerous factors influence the mineralogy of abiotic marine carbonates (AMCs), and these factors operate at various characteristic temporal and lateral scales. In the following discussion are considered: 1) the effects of changes in temperature,  $\text{CO}_2$  levels, and salinity on seawater carbonate saturation, and the relationship of these factors to glacio- and tectono-eustatic fluctuations, 2) potential control of stratigraphic variation in Missourian ooid mineralogy by these factors, and 3) potential control of geographic variation in Missourian ooid mineralogy by local environmental rather than global factors.

#### *General Controls on AMC Mineralogy*

The bulk mineralogy of AMCs is dependent on: 1) the saturation state of seawater with respect to calcite and aragonite, and 2) kinetic factors that promote or inhibit precipitation of one mineral relative to the other. For thermodynamic reasons, calcite has a broader "saturation range" than aragonite, i.e., the integrated latitudinal-depth range over which seawater is saturated with respect to

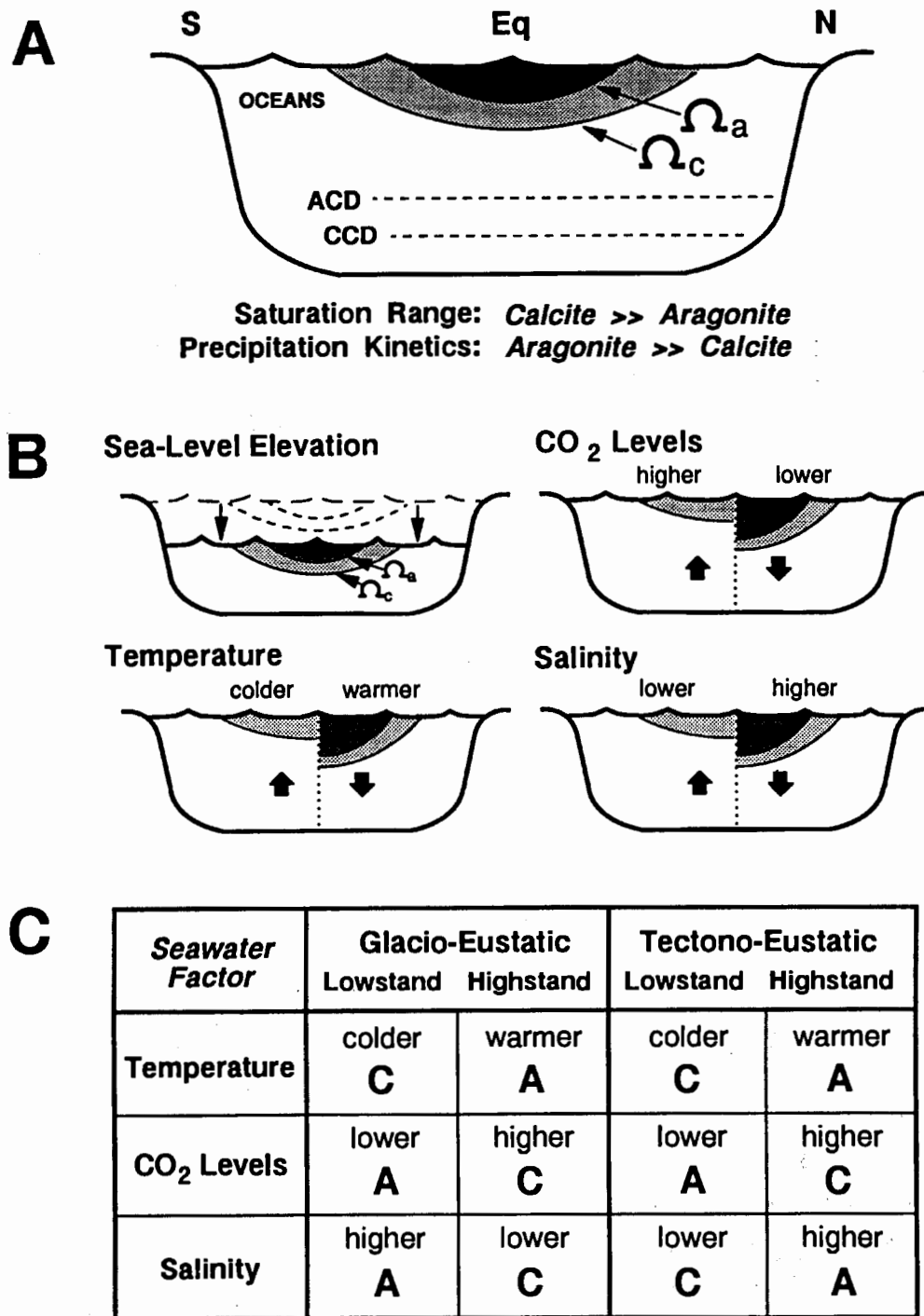


FIGURE 14. Controls on primary carbonate mineralogy. (A) Seawater saturation with respect to  $\text{CaCO}_3$  is limited to shallow depths and low latitudes. Aragonite exhibits a more limited saturation range ( $\Omega_a$ ) than calcite ( $\Omega_c$ ) but may dominate sediments in areas of high carbonate saturation owing to faster precipitation kinetics. (B) Changes in saturation range of aragonite and calcite in response to temperature,  $\text{CO}_2$ , and salinity perturbations. (C) Glacio- and tectono-eustatic fluctuations cause changes of predictable direction in seawater temperature,  $\text{CO}_2$  levels, and salinity; these alter seawater carbonate saturations, favoring either aragonite (A) or calcite (C). Dominance of aragonite at highstands and calcite at lowstands implicates temperature as the primary control on AMC mineralogy within 3rd- to 5th-order ( $10^4$ - $10^7$  yr) glacio-eustatic cycles, whereas dominance of calcite at highstands and aragonite at lowstands implicates aqueous  $\text{pCO}_2$  as the primary control within 1st-order ( $10^8$ - $10^9$  yr) tectono-eustatic cycles.



calcite ( $\Omega_c$ ) is greater than that of aragonite ( $\Omega_a$ ; Fig. 14A). At the margins of the saturation range of calcite, seawater is undersaturated with respect to aragonite and calcite alone will precipitate. Within the saturation range of aragonite, low degrees of supersaturation yield similar precipitation rates for both minerals, but high degrees of supersaturation result in higher relative precipitation rates for aragonite owing to kinetic factors (Burton and Walter, 1987). As a consequence, AMC's tend to be composed of calcite in areas of low seawater carbonate saturation and aragonite in areas of high saturation.

The degree of seawater carbonate saturation is influenced by numerous factors, including temperature,  $\text{CO}_2$  levels, and salinity (Fig. 14B). Increasing temperature and salinity and decreasing  $\text{CO}_2$  levels lead to greater saturation, favoring precipitation of aragonite over calcite, other factors being equal. Seawater temperature,  $\text{CO}_2$  levels, and salinity vary in a predictable manner in response to glacio- and tectono-eustatic fluctuations at timescales of  $10^4$ - $10^7$  yr and  $10^8$ - $10^9$  yr, respectively (Fig. 14C). Within glacio-eustatic cycles, highstands are associated with reduced continental ice mass, elevated  $\text{CO}_2$  levels, warmer sea-surface temperatures, and lower seawater salinity (Barnola et al., 1987; Pichon et al., 1992; Sanyal et al., 1995). Within tectono-eustatic cycles, highstands are associated with accelerated MOR spreading rates, increased  $\text{CO}_2$  outgassing, warmer temperatures, and elevated seawater salinity and  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratios as a result of enhanced MOR hydrothermal circulation and, possibly, increased rates of continental weathering (Mackenzie and Agegian, 1989). Although the magnitude of changes in temperature,  $\text{CO}_2$  levels, and salinity are not well constrained, the directional response of these factors to tectono- and glacio-eustatic cycles is well-established, and, thus, their effect on seawater carbonate saturation and AMC mineralogy can be predicted (Fig. 14C).

In addition to saturation state, bulk AMC mineralogy is influenced by factors related to the reaction kinetics of carbonate precipitation, including  $\text{Mg}^{2+}/\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , and organic matter. High  $\text{Mg}^{2+}/\text{Ca}^{2+}$  levels increase the Mg content of calcite but inhibit its precipitation overall (Berner, 1975; Burton and Walter, 1987). Low  $\text{CO}_3^{2-}$  levels may inhibit aragonite precipitation (Lahann, 1978; Given and Wilkinson, 1985; Morse and Mackenzie, 1990), although Burton and Walter (1987) experimentally demonstrated that temperature exerts a much stronger influence on carbonate mineralogy than  $\text{CO}_3^{2-}$  concentrations. Sulfate, phosphate, and organic compounds (e.g., humic and fulvic acids) suppress carbonate precipitation, although their effects on calcite and aragonite vary (Mucci et al., 1989; Burton and Walter,

1990; Berner et al., 1978). Sulfate, however, has a long residence time in seawater (9 m.y.; Berner and Berner, 1987), making much variation at glacial-interglacial timescales unlikely, and neither phosphate nor organic compounds are present in seawater in sufficient concentrations to have much effect on carbonate precipitation. In general, little is known about secular variation of these dissolved species in relation to glacio- and tectono-eustatic cycles, and, therefore, potential kinetic controls on mineralogic variation in Missourian ooids will not be considered further.

### *Controls on Stratigraphic Variation in Ooid Mineralogy*

Stratigraphic variation in ooid mineralogy can provide important information on secular changes in global or local environmental controls on carbonate precipitation. Within the Missourian Stage as a whole, aragonite was the dominant abiotic carbonate phase: aragonitic oolitic units are generally thicker, more ooid-rich, and more areally extensive than calcitic ones (e.g., Fig. 11; cf. Heckel, 1975, 1979). Dominance of aragonite during Late Pennsylvanian time is broadly consistent with documented secular trends (Fig. 1; Sandberg, 1983; Wilkinson et al., 1985). However, stratigraphic variation in the mineralogy of Missourian ooids does not exhibit a simple secular trend, as might be anticipated if a simple long-term transition were in progress. Rather, ooid mineralogy appears to vary in concert with 3rd- or 4th-order sea-level cycles, suggesting a primary control linked to eustasy (Fig. 10).

Within 3rd-order Missourian eustatic cycles, aragonite precipitation appears to have been favored during highstands and calcite precipitation during lowstands (Fig. 10). The same relationship between ooid mineralogy and sea-level elevation may exist for the Pleistocene-Holocene. Whereas Recent marine ooids are mostly aragonite, relict Pleistocene ooids appear to have had primary calcite compositions (Fig. 15). Radial ooids found at water depths of 80-150 m on the Brazilian Shelf have been radiocarbon-dated at 14-21 ky ( $n = 6$ ) and 38 ky ( $n = 1$ ; Milliman and Barretto, 1975;), and their age-depth relations are in good agreement with estimates of Pleistocene sea-level elevations (Richards et al., 1994). Similar ooids found at depths of 100-120 m on the northeast Australian shelf are undated but probably of late Pleistocene age (Marshall and Davies, 1975). Bimineralic ooids from slightly shallower depths (40 m) on the east Florida shelf yielded slightly younger radiocarbon dates (9.6-13.7 ky; Major et al., 1988). These reports suggest that calcite may have been the dominant AMC precipitate in shallow peritidal

environments during the last glacial maximum, and that a mineralogic transition to aragonite may have occurred in the late Pleistocene or early Holocene. Thus, ooid mineralogy exhibits the same relationship to glacio-eustasy within both 3rd-order (1-10 m.y.) Pennsylvanian and 5th-order (10-100 k.y.) Pleistocene-Holocene cycles, i.e., calcite at lowstands and aragonite at highstands.

The link between eustatic elevation and Missourian ooid mineralogy implies control of AMC mineralogy by factors associated with Gondwanan glaciation or glacio-eustasy. Among the major controls on seawater carbonate saturation, only temperature varies in a manner consistent with aragonite precipitation during highstands and calcite during lowstands (Fig. 14C). In contrast, the inverse relationship between AMC mineralogy and eustatic elevation is observed within 1st-order geotectonic cycles, i.e., calcite precipitation during highstands and aragonite during lowstands (Fig. 1). Among the major controls on seawater carbonate saturation, only atmospheric/oceanic  $p\text{CO}_2$  varies in a manner consistent with this mineralogic pattern.

Apparent differences in the primary controls on AMC mineralogy associated with 1st-order tectono-eustatic processes at a 100-1000 m.y. timescale and 3rd- to 5th-order glacio-eustatic processes at a 0.01-10 m.y. timescale may reflect differences in the relative magnitudes of temperature and atmospheric/oceanic  $\text{CO}_2$  fluctuations. Conceptually, temperature fluctuations may be larger relative to  $\text{CO}_2$  fluctuations during glacial cycles than during geotectonic cycles, resulting in short-term temperature-dependence and long-term  $\text{CO}_2$ -dependence of AMC mineralogy. Proxy records and models of temperature and atmospheric/oceanic  $\text{CO}_2$  variation may support this hypothesis. Changes in tropical seawater temperature during Pleistocene glacial-interglacial cycles are in the range of 3-8°C with a mean of ca. 5°C (Emiliani and Ericson, 1991; Rostek et al., 1993; Anderson and Webb, 1994). Although a matter of some controversy, AMC oxygen isotopic data exhibit a ca. 3 ‰ mid-Paleozoic shift indicating a change in tropical marine temperatures of some 10-15°C (Lohmann and Walker, 1989), a result consistent with estimates based on GCM-derived  $\text{CO}_2$ -temperature relationships (Oglesby and Saltzman, 1990) and atmospheric  $\text{CO}_2$  models (Berner, 1994). In comparison, atmospheric  $\text{CO}_2$  levels vary by a factor of ca. 1.5 during Pleistocene glacial cycles (Barnola et al., 1987) and by a factor of ca. 10-20 at tectonic timescales (Berner, 1994). These estimates may support the hypothesis that temperature fluctuations are relatively larger at glacial timescales and  $\text{CO}_2$  fluctuations relatively larger at geotectonic timescales. This relationship may be

due in part to the fact that temperature- $\text{CO}_2$  co-variance is non-linear: temperature becomes less sensitive to changes in atmospheric  $p\text{CO}_2$  at high  $\text{CO}_2$  levels (Oglesby and Saltzman, 1990), and, hence, large  $\text{CO}_2$  excursions at tectonic timescales may not elicit equally large temperature changes.

### *Controls on Geographic Variation in Ooid Mineralogy*

Geographic variation in ooid mineralogy can provide important clues to environmental gradients and local controls on carbonate precipitation. Modern bimineralic ooids offer the best opportunity to directly evaluate the physico-chemical conditions responsible for such spatial variation. Although Baffin Bay, Texas, a semi-restricted coastal lagoon, experiences large fluctuations in water chemistry and temperature during wet-dry cycles, turbulence levels were identified as the most important control on lateral trends: ooid maturity and the proportion of tangential (aragonitic) laminae increased with greater water agitation (Land et al., 1979). In contrast, the primary control on ooid mineralogy in Pyramid Lake, Nevada, was inferred to be aqueous  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratios in the zone of mixing of spring and lake waters: an increase in dilute Ca-rich spring waters ( $\text{Mg}^{2+}/\text{Ca}^{2+} = 0.01-0.1$ ) favored calcite, whereas an increase in alkaline lake waters ( $\text{Mg}^{2+}/\text{Ca}^{2+} = 5-20$ ) favored aragonite (Popp and Wilkinson, 1983). In this case, water agitation was cited only as a factor contributing to lakewater carbonate saturation and ooid growth.

Lateral mineralogic transitions indicative of environmental gradients have been reported from several ancient oolitic units. In the Upper Mississippian Pitkin Limestone, aragonite ooids formed in a marine shoal and calcite ooids in a backshoal lagoon (Heydari et al., 1993), whereas in the Upper Jurassic Smackover Formation, calcite ooids formed in a shelf-margin shoal and aragonite ooids in a restricted shelf interior (Heydari and Moore, 1994). In the latter case, the mineralogic gradient was interpreted to reflect changes in seawater chemistry associated with strong evaporation of restricted inner-shelf waters adjacent to an arid landmass, i.e., landward decreasing aqueous  $\text{CO}_2$  and increasing  $\text{CO}_3^{2-}$ ,  $\text{Ca}^{2+}$ , and temperature, resulting in increasing seawater carbonate saturation (Heydari and Moore, 1994). Similar controls might be inferred for the Upper Cambrian Port-au-Port Formation, in which calcite ooids formed in subtidal bars and aragonite ooids on intertidal sand flats (Chow and James, 1987).

Lateral trends in Missourian ooid mineralogy differ between the two horizons characterized by such variation:



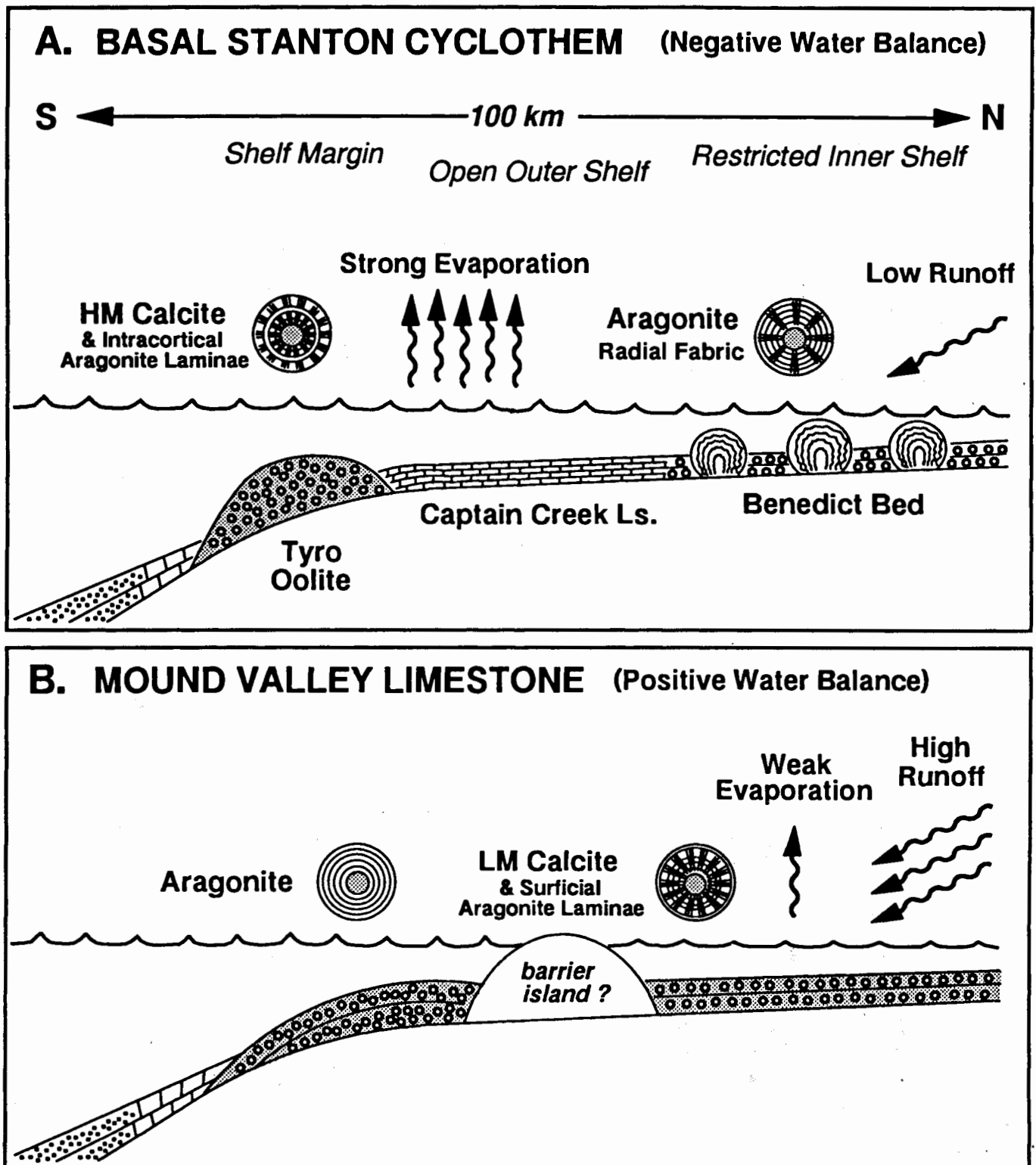


FIGURE 16. Models of controls on geographic variation in ooid mineralogy within the basal Stanton cyclothem (A) and the Mound Valley Limestone (B). The Tyro Oolite is a thick, cross-bedded unit of predominantly high-Mg calcitic mineralogy deposited in an open-marine shoal, whereas the Benedict Bed consists of radial aragonite ooids associated with columnar stromatolites, consistent with deposition in a hypersaline, restricted shoreline setting. This mineralogic gradient reflects greater seawater carbonate saturation in inner-shelf areas, probably as a consequence of arid climatic conditions and a negative water balance. Mound Valley ooids change from aragonite to calcite in a landward direction. This mineralogic gradient reflects lesser seawater carbonate saturation in inner-shelf areas, probably as a consequence of humid climatic conditions and a positive water balance.

the Mound Valley Limestone and the basal Stanton cyclothem. In transgressive members of the Stanton cyclothem, ooids precipitated in shelf-margin shoals (Tyro Oolite) are predominantly high-Mg calcite, whereas those precipitated in restricted inner-shelf areas (Benedict Bed) are aragonite (Fig. 16A), suggesting that carbonate saturation levels increased in a landward direction (cf. Smackover Formation; Heydari and Moore, 1994). In contrast, Mound Valley ooids were precipitated as aragonite in open outer-shelf and as calcite in restricted inner-shelf settings (Fig. 16B), implying that carbonate saturation levels *decreased* in a landward direction. Higher aqueous CO<sub>2</sub> levels are unlikely in a restricted inner-shelf setting, but lower water temperatures or salinities might have resulted from enhanced runoff (cf. Baffin Bay, Texas; Land et al., 1979). Thus, the fundamental difference in controls on Missourian ooid mineralogic gradients may be humidity: a positive water balance during Mound Valley time yielded an aragonite-to-calcite landward gradient, whereas a negative water balance during Stanton time yielded a calcite-to-aragonite landward gradient. This pattern of mineralogic variation is consistent with increasing aridity in the Midcontinent area during the middle to late Pennsylvanian as a result of northward drift of North America out of the intertropical convergence zone (10°S-10°N) into the arid tropical zone (10-25°N; Schutter and Heckel, 1985; Cecil, 1990).

### *Controls on Internal Variation in Ooid Mineralogy*

Mineralogic and fabric variation within ooid cortices may be of importance in understanding short-term changes in the chemical and hydrographic environment in which ooids form. As with Missourian ooids of this study, bimineralic ooids of all ages consist preferentially of a calcitic inner and an aragonitic outer cortex (e.g., Tucker, 1984; Chow and James, 1987; Singh 1987; Major et al., 1988; Kidder and Hall, 1993; Heydari and Moore, 1994) with few exceptions, e.g., Baffin Bay ooids, which do not exhibit any preferred cortical sequence (Land et al., 1979). Mineralogic transitions commonly occur at a characteristic cortical diameter in different units. Among Missourian ooids, transition diameters range from 0.21 mm in the South Bend to 0.65 mm in the Mound Valley; late Pleistocene ooids from the Florida shelf have an intermediate transition diameter of 0.30-0.35 mm (Major et al., 1988). Also common are intracortical fabric transitions in monomineralic calcite ooids, in which a transition from a radial inner to a radial-concentric outer cortex is observed (e.g., Heller et al., 1980; Medwedeff and Wilkinson, 1983; James and Klappa, 1983). In the

Upper Cambrian Warrior Formation, this transition occurred at a cortical diameter of ca. 0.6 mm (Heller et al., 1980).

Intracortical mineralogic transitions have been inferred to result from a physico-chemical threshold related to crystallization kinetics associated with fluid shear, in which low-energy conditions favor slow-growing, small calcite ooids and high-energy conditions favor fast-growing, large aragonite ooids (Major et al., 1987). On the other hand, a physical control has been inferred for intracortical fabric transitions, in which transport style changes with increasing ooid size: frequent suspension of small immature ooids in the water column favors unimpeded radial elongation of cortical crystals, whereas bedload transport of large mature ooids results in frequent abrasion and accretion of thinner laminae having tangential crystallite orientations (Heller et al., 1980). These factors co-vary in many environments, which may account for commonly observed mineralogic-fabric associations. However, the absence of intracortical mineralogic transitions in many oolitic units suggests that factors linked to carbonate saturation must influence AMC mineralogy as well. For example, under conditions of intermediate seawater carbonate saturation, changes in kinetic precipitation factors may favor a calcite-to-aragonite transition at a given level of fluid shear and, hence, a given cortical diameter. In contrast, under conditions of low or high seawater carbonate saturation, calcite or aragonite may be thermodynamically favored regardless of changes in kinetic factors.

### CONCLUSIONS

1) The Missourian Stage of Kansas contains ooids of probable primary low-Mg calcitic, high-Mg calcitic, and aragonitic composition. Primary low-Mg calcite ooids exhibit well-preserved radial fabrics and low Mg and Sr concentrations. Former high-Mg calcite ooids exhibit microspar mosaic replacement of primary radial fabrics, moderate to high Mg and low Sr concentrations, and growth of intracortical dolomite. Former aragonite ooids exhibit poorly-preserved laminar sparry fabrics, frequent development of oomoldic porosity, and moderate to high Sr and low Mg concentrations.

2) The only exception to the fabric-Sr relationship is the Benedict Bed, in which ooids exhibiting both sparry laminar and radial fabrics yield high Sr values (2000-5000 ppm). Benedict Bed ooids, which are associated with columnar stromatolites in a restricted shoreline setting, were probably all composed of primary aragonite. Similar radial aragonite ooids are known from hypersaline paralic

environments in the Red Sea and Persian Gulf.

3) Most regressive limestone members of major cyclothems contained exclusively aragonitic ooids, including the Bethany Falls, Winterset, Drum, Farley, and Spring Hill limestones. The Mound Valley Limestone, representing a minor transgression at the top the Bronson megacycle, contained a mixture of aragonitic, calcitic, and bimineralic ooids. Both transgressive and regressive units at the top of the Lansing megacycle (Tyro, Rutland, and South Bend limestones) contained ooids composed dominantly of calcite with subordinate quantities of aragonite.

4) Stratigraphic variation in the primary mineralogy and abundance of ooids may be related to 3rd-order glacio-eustatic cycles. During highstands, aragonite ooids were deposited in thick cross-bedded shelf-margin shoals, whereas during lowstands, calcite or bimineralic ooids were deposited mainly as thin lenses in lagoonal, tidal channel, or paralic environments. A relationship of ooid mineralogy to 4th-order cyclothems is possible but unproven.

5) The primary control on stratigraphic variation associated with Pennsylvanian and Pleistocene-Holocene glacio-eustatic cycles is probably temperature, whereas the primary control on Phanerozoic AMC mineralogy is probably atmospheric  $p\text{CO}_2$ . The difference in controls associated with 1st-order tectonic and 3rd- to 5th-order glacial processes may indicate that temperature fluctuations are larger relative to  $\text{CO}_2$  fluctuations at glacial timescales ( $10^4$ - $10^7$  yr) than at geotectonic timescales ( $10^8$ - $10^9$ ).

6) Geographic variation in primary ooid mineralogy occurs at two horizons: 1) in the Mound Valley Limestone (lower Missourian), inner-shelf ooids were composed of low-Mg calcite and shelf-margin ooids of aragonite, and 2) in the transgressive members of the Stanton cyclothem (upper Missourian), inner-shelf ooids were composed of aragonite (Benedict Bed) and shelf-margin ooids of high-Mg calcite (Tyro Oolite).

7) The primary control on geographic variation in Missourian ooid mineralogy is probably water balance: in nearshore areas, a positive water balance during Mound Valley time resulted in lower carbonate saturation and precipitation of calcite, whereas a negative water balance during Stanton time resulted in higher carbonate saturation and precipitation of aragonite. This pattern is consistent with increasing aridity in midcontinent North America during the Late Pennsylvanian.

8) Internal variation in bimineralic ooids is mostly manifested as a calcitic inner and an aragonitic outer cortex having a characteristic transition diameter that varies

between 0.2 and 0.7 mm in different units. Intracortical transitions in mineralogy may reflect changes in kinetic factors that favor a calcite-to-aragonite transition with increasing fluid shear, but thermodynamic factors ultimately control the degree of seawater carbonate saturation and, hence, the fluid shear threshold at which a mineralogic transition may occur.

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